X-RAY X ABSORPTION SPECTRA OF SOLID ARGON AND KRYPTON

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of the Ohio State University

By

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X-RAY ABSORPTION SPECTRA OF SOLID ARGON AND KRYPTON

I. INTRODUCTION

1.1 Spectroscopy of the Solid State

When the isolated atoms of a gas agglomerate to produce solid crystalline material, a considerable perturbation of the motions of the electrons of the individual atoms occurs. The presence of the strong electrostatic or magnetic fields of near atoms produces a type of molecular binding spreading throughout the bulk of the crystal and producing its more obvious mechanical and electrical properties. The development of the spectroscopic tools of the last forty years has made it possible to examine transitions between various steady states of such a crystalline system. An attempt can thus be made to gain an understanding of the role of the electrons in the properties of electrical conductors and insulators, magnetic materials, polycrystalline materials and others. Investigations of this type fall into three broad categories, characterized chiefly by the amount of energy involved in the transitions studied; i.e., infrared, visible and near ultraviolet, and far ultraviolet and x-ray.
Infrared investigations have primarily revealed information about the large mass vibrations of whole atoms of the solid and, with a few exceptions, have not contributed materially to knowledge of the electronic behavior of the material. Experiments in the visible and near ultraviolet region have been very fruitful in yielding information of at least a gross nature about the electronic states of solids. Especially clear and interesting are the experiments of R. W. Wood on the reflectivity of metallic mirrors.


However, workers in this area have been handicapped by the difficulties in making accurate quantitative interpretations of the spectra observed. The schematic energy level diagram of Figure 1 shows why this is so. For the isolated atom (a), electronic transitions occur between the outer, or valence, levels giving rise to the well known "optical spectra" characteristic of each element of the Mendeleef table. Also permitted are transitions of the x-ray type (shown in Figure 1) involving a valence level and an inner level of the atom. For the atom combined in a simple diatomic molecule, a slight splitting and rearrangement of the optical levels occurs, and experiments in the visible and near ultraviolet have born this out. The x-ray spectrum is also only slightly different from that of the free atoms, the experimental resolution in this wavelength region being just sufficient to distinguish these effects.

Fig 1

(a) Atom

(b) Molecule

(c) Solid

![Diagrams of energy levels for atom, molecule, and solid.](image-url)
The effect of combining 10 or so atoms into a crystal enormously complicates the spectroscopic picture. Transitions between "bands" of energy levels, or even within a given band, cannot be interpreted in terms of the individual levels involved. For this purpose, the x-ray transition seems ideally suited, involving as it does a transition between a relatively sharp inner level and a continuum of outer levels. The resulting spectra, of course, are not sharp lines but rather broad, structured bands reflecting the density of states available to the valence electrons.

1.2 Theory of Electronic Band Structure

The Schroedinger equation for hydrogen is the only one simple enough to be solved exactly with explicit functions. Even as simple an atom as helium whose Schroedinger equation

\[ (\hat{H} - W) \psi = 0 \]  

has the Hamiltonian operator

\[ \hat{H} = -\frac{\hbar^2}{2m} \left( \nabla_x^2 + \nabla_y^2 + \nabla_z^2 \right) - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{r_{12}} \]  

cannot be solved explicitly for the eigenvalues \( W \) (the stable energies of the atom). In view of this, many approximation methods have been developed for computing the eigenvalues of complex systems; i.e., heavy atoms, molecules, and crystalline solids. One of the earliest of these methods which has had many successful applications is the self consistent field method of Hartree.\(^3\) Hartree's method

---

assumes the electrons move in a static field made up of the effective charge distribution of all the other electrons and the nucleus, but the method ignores coupled motions between electrons which are inherent in energy terms of the type $e^2/r_{ij}$. Slater and Fock later showed that Hartree's method was equivalent to setting

$$\Psi'_{ni} = \psi_i(r_i) \psi_j(r_j)$$

(3)

and minimizing the integral

$$\iint \Psi'_{ni}^{*} H \Psi'_{ni} \, dr_i \, dr_j$$

(4)

Thus no better wave functions can result from the Hartree calculations than those satisfying the condition above. Fock's approach was to form

$$\Psi'_{ni} = \psi_i(r_i) \psi_j(r_j) + \psi_j(r_i) \psi_i(r_i)$$

(5)

and then minimize the integral

$$\iint \Psi'_{ni}^{*} H \Psi'_{ni} \, dr_i \, dr_j$$

(6)

after the manner of Hartree. It is interesting to note that the Hartree calculations have been carried through for Be and the total

binding energy of the atom computed. The disagreement with the observed binding energy is of the order of one half electron volt per electron. Two important types of solution of the Fock equation have been widely used, namely the Heitler-London type and the Hund-Milliken-Bloch type. The workers after whom the two methods are named used one-electron \( \psi \) functions of the type described but not in connection with the Hartree-Fock equations. The Heitler-London


scheme assumes the \( \psi \) functions are large only in the neighborhood of the atoms, whereas the Bloch scheme assumes the \( \psi \) function to extend over the entire system of atoms. The Bloch method has been


very successfully applied to the large periodic configurations of crystals and will be of most concern here.

Thus it is seen that the basis for all solutions of the Schrödinger equation for complex molecules, and especially crystals, lies in the so-called one-electron approximations, in which a single electron is thought to move through a static field made up of contributions from the atomic nuclei and from the other electron.
The effect of interactions between the electrons is treated as a perturbation of the basic wave functions. It is inherent in the type of one-electron approximation which is assumed that errors of the order of one half electron volt per electron will occur when comparing the observed total binding energy to the calculated value. This effectively sets a limit upon the accuracy of calculations of this type.

When the one-electron functions of the type used by Bloch are applied to large crystalline solids, in which the potential energy term, V(r), is periodic, the ψ functions can be expressed as combinations of the simple form

$$\psi_k = \phi_k(r) e^{2\pi i k \cdot r}$$  \hspace{1cm} (7)

in which φ has the periodicity of V, and k is a wave number vector, given by p/ħ. For the free electron moving in the solid, and bound only by forces at the surfaces, φ is constant and the energy of the electrons is given by the simple formula

$$E = \frac{\hbar^2 k^2}{2m}$$  \hspace{1cm} (8)

This is the free electron form calculated by Sommerfeld, which is
applicable in many simple metals. Of more concern here, however, are the cases in which $\phi$ is neither constant, nor localized to a specific atom of the solid (an inner shell electron), but rather behaves somewhat between these two extremes. In such a case, the energy, $E$, has forbidden regions separating regions of continuous values of $E(k)$. If a two dimensional lattice is depicted, for example, and the wave number vector $k$ is plotted in the plane of the lattice, the energy surface for the free electron case is a paraboloid of revolution. (See Figure 2). For the partially bound electrons, on the other hand, the energy surface cannot be described so simply. A plane section through the origin has the form of Figure 2a or, in another direction, Figure 2b. The surfaces at which $E$ is discontinuous are polyhedra called the zone boundaries.

In particular, the Schrödinger equation for lattice type potentials has been solved for several simplified lattices. An early calculation by Kramers for the one dimensional case, and a calculation by Brillouin for the two dimensional case illustrate the general procedure for calculations of this type.

The particular elements of interest in this paper, the noble gases, are composed of closed shell atoms, held together in the solid by interactions of the dipole-dipole, or multipole-multipole
Fig. 2
type. These small attractive forces were first implicitly postulated by Van der Waals in his equation of state. The net force between


atoms of this type is attractive only at fairly large interatomic distance (~5Å), so it follows that the localized electron methods of Heitler-London may be conveniently applied to crystals of this type. In Section V the detailed calculations applicable to such condensed noble gases will be described.

1.3 Excited Electronic States of Solids in the Band Scheme

The x-ray spectrum of a solid of the type depicted in Figure 1c is composed of two complementary spectra obtained from emission and from absorption processes. In the former case an outer electron falls into an empty inner shell and a quantum of radiation leaves the crystal. In the second case an incident quantum raises an inner electron to one of the available states in the bands. Since the electron must be raised to an empty state lying, in general, among a continuum of empty states, the electron becomes a conduction electron. This result is true even if the solid is an insulator, since this designation implies only that all the electronic states within any given band are either completely full, or completely empty. Any photoionization process which will excite an electron into an empty band will make the crystal photoconductive, the conductivity remaining until the exciton energy is radiated away and the electron returns to the filled band. A few solids, known as
semi-conductors, have an energy gap between filled and empty bands which is small enough to permit thermal excitation of electrons into the empty, or conduction, band.

The absorption spectrum of a solid such as that described is depicted schematically in Figure 3(b). Although three absorption peaks are clearly depicted it does not follow that the conduction bands can be described directly from this curve. The energy gap between conduction bands is a function of the direction of the wave vector k of the excited electron as it moves through the lattice. For this reason, there exists a finite probability of an absorption process of all energies greater than the critical energy, E_c.

Figure 3(a) shows the corresponding emission spectrum of the solid. Most of the emitted radiation is concentrated in intense sharp lines corresponding to transitions involving the unperturbed inner electrons of the atoms. However, at the high energy limit of the emission spectrum structure is observed corresponding to transitions from the filled band into the inner empty level. Structure at the high frequency edge of the emission spectrum can be interpreted in terms of the density of states in the filled band.

1.4 Experimental Verification of Band Theory

As early as 1920, Kossel 16,17 had predicted a fine structure


Fig. 3

State X-ray Spectrum: (a) Emission; (b) Absorption
in the x-ray absorption limit of isolated atoms, based on his theory of the origin of x-ray spectra. An extensive series of experiments by Hanawalt\textsuperscript{18} revealed some structure in Zn and Xe, all of which could be interpreted by Kossel's ideas. However, further experiments by Hanawalt\textsuperscript{19} and by Coster and Veldkamp\textsuperscript{20} revealed an additional kind of structure extending many volts from the main absorption edge and peculiar to polyatomic gases and crystalline materials. Kronig, using the results of the wave mechanical treatment discussed in Section 1.2, proposed a theory to explain the extended structure. Bloch and others had shown that not all possible kinetic energies are permitted to an electron traversing a periodic lattice. Kronig calculated the higher forbidden energy zones and found they approximately followed the form

\[ E(n) = \frac{n^2 \hbar^2}{8md^2} \]  

where \(d\) is the interatomic distance. Since the actual photo electrons have no preferred direction in the crystal, \(d\) is not clearly defined. Kronig\textsuperscript{21} was able to show in a later paper that

\[ 21. \text{Kronig, R., Zeit. f. Phys. 75, 191 (1932)} \]
even when all possible directions are available to the photo-electrons, there remains an irregularity in the absorption curve. Many experiments have been carried out in attempts to prove the Kronig theory. Lindsay investigated a number of elements and

22. Kievit, B. and Lindsay, G. A., Phys. Rev. 36, 648 (1930)

found absorption structure too far from the absorption edge to be atomic structure of the type suggested by Kossel. Later Coster and Veldkamp were able to show the dependence on lattice constant predicted by equation (9) above in the K edge structure of Cu, and the L edge structure of Pt and Au. More recently, Stephenson and co-workers have attempted to observe the Kronig


fine structure as a function of direction in the crystal lattice by using a polarized x-ray beam.

An extensive study of silver was undertaken by Parratt in


1936. The complete L emission spectrum and the three \( \left( 2s_{\frac{1}{2}}, 2p_{\frac{3}{2}}, 2p_{\frac{1}{2}} \right) \) L absorption edges were observed. Fine structure was observed in the absorption spectrum, both near (less than the cadmium ionization potential) to the absorption limit and far from it. Therefore no separation of resonance lines into Kossel and Kronig type structures
was made. No structure corresponding to conduction band electrons was observed at the high energy limit of the emission spectrum.

A later work on the absorption edge structure of metallic potassium was undertaken by Platt.\textsuperscript{25} His results were in all respects similar to those obtained for silver.

A large number of elements, mostly metals, have been studied at short wave lengths,\textsuperscript{26, 27, 28} using K x-rays. A comparison of


\textsuperscript{26} Barnes, A. H., \textit{Phys. Rev.} 44, 141 (1933)

\textsuperscript{27} Ross, R. A., \textit{Phys. Rev.} 44, 977 (1933)

\textsuperscript{28} Zinn, W. H., \textit{Phys. Rev.} 46, 659 (1934)

Foss's\textsuperscript{27} data for the K absorption edge of silver and the L edge data of Parratt\textsuperscript{22} reveals a major shortcoming in the higher energy experiments. The width of the inner K level of silver is so great as to obscure all but the gross features of the absorption edge structure. Two faint maxima can be seen in Ross's silver transmission data, compared to nine or more in the L edge data taken by Parratt. This result is uniformly observed in all the high energy x-ray work reported.

Beeman and Friedman\textsuperscript{29} reported in 1929 on K absorption edge

\textsuperscript{29} Beeman, W.W. and Friedman, H., \textit{Phys. Rev.} 56, 392 (1939)
structure in seven elements (26Fe to 32Ge) and the L_{111} absorption structure of platinum. In each case the Kβ2 or Kβ3 emission lines were also shown to correlate the position of the Fermi level in the lowest occupied band. The copper data were shown to be in good agreement with calculations by Krutter\textsuperscript{30} and by Slater\textsuperscript{31} for the density of electronic states in the conduction band. The data obtained by Beaman and Friedman do not extend beyond about 40 volts from the absorption edge and therefore offer no test of the free-electron theory of Kronig. However, in 1948, Coster and Kiestra\textsuperscript{32} confirmed the work of Beeman and Friedman of Fe, Mn and Cr, and extended the data to higher energies, observing some Kronig type structure. It is interesting to compare their observations with the earlier results of Veldkamp\textsuperscript{33,34} of the same laboratory which offer the most satisfactory agreement with the structure predicted by Kronig. In the energy region (0-70 volts) where the data of

\textsuperscript{30} Krutter, H., Phys. Rev. 48, 664 (1935)

\textsuperscript{31} Slater, J. C., Phys. Rev. 49, 537 (1936)

\textsuperscript{32} Coster, D. J., and Kiestra, S., Physica 14, 175 (1948)

\textsuperscript{33} Veldkamp, J., Zeit f. Phys. 77, 250 (1932)

\textsuperscript{34} Veldkamp, J., Zeit f. Phys. 82, 776 (1932)
the two experiments overlap, there is no agreement in the position or intensity of the structure observed.

In an attempt to increase the experimental resolution in x-ray studies of solids, many observers have used the very soft x-ray transitions from 50 - 500 Å. In this wavelength region the inner level of the atom is much sharper, since it has a longer life before undergoing a radiative transition. The preparation of absorbers for use in this wavelength region is very difficult, however, and most of the data reported has been on emission spectra. Skinner\(^3\), in a notable paper to the Royal Society of London,

\(^3\) Skinner, H. W. B., *Trans. of the Royal Soc. Lon.*, 239, 95 (1940)

reported long wavelength x-ray emission curves for lithium, beryllium, sodium, magnesium, aluminum, carbon, boron, silicon, phosphorous and sulfur. The density of states predicted by electron band theory was clearly in evidence. A sharp edge, representing the Fermi level in the conduction band appeared in each metallic spectrum. In the non-conductors studied, the edges were observed to be much less sharp than in the metallic cases. In addition, Skinner’s work included the temperature dependence of the edge structure, and showed conclusively the applicability of the Fermi formula

\[ N(E) = N_0 (E_m) \left[ 1 + \exp \left( \frac{E - E_m}{kT} \right) \right]^{-1} \]  

(10)

where \( E_m \) is the energy of the emission edge and \( N_0(E) \) is the value of the density of states function, \( N(E) \) at the absolute zero of temperature.
Soft x-ray absorption work has been undertaken by several observers, a recent experiment by Tombaulian and Pell:


being especially interesting. The L$_{2,3}$ absorption edge of metallic aluminum was investigated, for absorbers of several thicknesses. The strong effect of absorber thickness on structure in the region of the absorption edge was thought to be due to penetration of the aluminum into the substrate lattice with resulting confusion of the absorption data. Fine structure observed on the short wavelength side of the absorption edge was in good agreement with that observed at the K edge of aluminum by Munier, Bearden and Shaw. The structure, which extended some 75 volts from the edge, was not analyzed into Kronig components.

From the preceding discussion, it is apparent that abundant spectroscopic evidence exists to confirm the band theory of solids. However, fine structure in the x-ray emission and absorption spectra obtained is not yet well understood. The calculations of Kronig
on the scattering of free electrons in a crystalline lattice
appear to explain much of the fine structure observed in x-ray
absorption experiments; but they cannot be successfully applied
close to the absorption edge, where the electrons are not free.
In addition to the above difficulties, the question has recently
been raised concerning the effect of the x-ray ionized atom on

the band structure of the solid. The suggestion is advanced here
that the ionized atom behaves in the lattice like an impurity atom
of effective nuclear charge \((Z+1)\) giving rise to bound or exciton
levels lying, for a metal, just beneath the filled band. For an
insulator, the exciton levels are formed beneath the empty conduction
band and the absorption spectrum would be expected to be atomic
in nature, consisting of a series of discrete lines leading to a
series limit in the empty conduction band.

Considerable data have been obtained supporting the exciton
theory in insulators, although all the insulators studied to date
have been ionic crystals. For KCl, Trischka has observed

absorption peaks in the K edge structure of both the potassium and
the chlorine which might be explained as transitions to exciton levels. The peak spacing is four volts at the K edge but L edge data of a similar nature gives peaks only two volts apart. A possible explanation is that the change in $Z_{\text{eff}}$ is less than one for an atom with an ionized L shell, thus reducing the gap between the exciton level and the conduction band.

1.5 Spectroscopy of Monatomic Gases

In Kossel's paper\textsuperscript{42,43} of 1920 appeared a summary of information on x-ray emission and absorption phenomena and a proposed general qualitative scheme of energy levels. On this basis Kossel described the line spectra observed and the absorption edges to be expected. In particular, he pointed out that the absorption spectrum of an isolated atom should consist of sharp lines approaching a series limit similar to that observed in optical spectra. Frick\textsuperscript{44} failed to observe any such structure at the Argon K edge but shortly after a paper by Lepape and Dauvillier\textsuperscript{45} reported some Kossel type fine structure.

\textsuperscript{42} Kossel, W., Zeit. f. Phys. 1, 119 (1920)

\textsuperscript{43} Kossel, W., Zeit. f. Phys. 2, 470 (1920)

\textsuperscript{44} Frick, H., Phys. Rev. 16, 202 (1920)

\textsuperscript{45} Lepape, A. and Dauvillier, Comptes Rendus 177, 37 (1923)
structure in the $L_2$ absorption of Xenon. However, the line was too diffuse and too broad (13 volts) to permit a comparison with optical results.

In 1926, Coster and Van der Tuuk\textsuperscript{46} reported on a series of absorption experiments on chlorine, calcium and argon. They attempted to correlate the observed energy differences between features of the absorption spectrum with known data on the optical levels. Limited resolving power and experimental uncertainties in the photographic technique made the actual agreement between theory and experiment mostly hypothetical.

Hanawalt,\textsuperscript{47} in 1930, investigated a number of elements as the

\textsuperscript{47} Hanawalt, J. D., Phys. Rev. \textbf{37}, 715 (1931)

pure vapor, crystalline solid, and in molecular combination, reporting no fine structure for Kr or Hg vapor. A line was observed in the Xenon $L_2$ and $L_3$ edge structures but not in the $L_1$ edge. Hanawalt suggested that selection rules might deny transitions from the 28 level ($L_1$) to the orbital levels but in view of the results of Coster and Van der Tuuk for argon this seems unlikely. The Argon $L_{23}$ absorption edge at 50 A was obtained by Prins\textsuperscript{48} in 1934

\textsuperscript{48} Prins, J. A., Physica \textbf{1}, 1174 (1934)
but the data reported were not resolved into Kossel components. Ciofari\textsuperscript{49} in 1937, reported the results of investigations of bromine and iodine absorption edges, using the pure gases and also various compounds. His results were significant mainly because many of the absorbers were obtained in solid and liquid, as well as gaseous, form. A faint evidence of Kronig type structure appeared in the solid data for iodine and for K Br. A similar experiment was performed by Drynski and Smoluchowski\textsuperscript{50} using Ge Cl\textsubscript{4} as gas, liquid and solid absorber, and with similar results. The effect of electron scattering within the molecule is evident in the absorption edge structure of these polyatomic gases.

The most significant experiment on monatomic gases, which finally demonstrated conclusively the predictions of Kossel, was the K absorption edge structure of Argon obtained by Parratt in 1938. The relatively narrow ls level, .58 ev as measured by Parratt\textsuperscript{51}, and the high resolution, two crystal spectrometer technique developed during the 1930's made possible the resolution of absorption structure

\textsuperscript{49} Ciofari, B., Phys. Rev. 31, 630 (1939)

\textsuperscript{50} Drynski and Smoluchowski, R., Physica 6, 929 (1939)

\textsuperscript{51} Parratt, L., Phys. Rev. 56 296 (1939)
into discrete optical type transitions. Lindh and Nilsson\textsuperscript{52},


using a single crystal photographic instrument confirmed Parratt's results in detail, resolving the first 3 optical p lines clearly. The transition of the inner 1s electron into the 4p, 5p and 6p optical levels was clearly evident. Calculation of energy differences was in excellent agreement with the term values of potassium (Z=1), known from optical data. (This experiment and a similar one on krypton were repeated in the course of the work reported in this paper and so will be discussed in more detail in a later section.) Shaw\textsuperscript{53}, also using a two crystal spectrometer, invested the K edge structure of Kr but the wide inner level corresponding to this wavelength (.87A), and the relatively close spacing of the optical levels in the heavier atom prevented any resolution of Kossel structure.


A rather ingenious technique was employed by Brogren\textsuperscript{54} recently to observe resonance transitions in argon, krypton and xenon. The gas being studied was introduced into a Geiger counter. In such

a case a rise in absorption in the gas causes an increase in recorded x-ray intensity. Brogren's data clearly shows resonance absorption in the neon and argon K edges, and in the krypton and xenon L edges, but the method is inherently incapable of giving accurate relative intensities. On the basis of his results, and interpolating results for other elements, Brogren suggests an inner level width of about one volt for argon.

1.6 Program of Experiments on Argon and Krypton

In an attempt to obtain direct energy correlation between the electronic states of an isolated atom and those of the solid crystal, the present investigations were undertaken. To avoid the complicating effect of electron scattering within the gaseous molecule, monatomic gases were required. Although certain of the metals can be obtained as monatomic gases, the noble gases offer experimental simplification and were selected for this reason. In addition, no experimental work had been done on the band structure or exciton levels of molecular solids. High resolving power in the spectrometer was considered essential to work of this type; also, the inner level of the atom chosen must be sharp. Argon was therefore chosen as an ideal gas, having as it does a K absorption edge in the medium soft x-ray region (3.86 Å). The inner level width of .58 eV measured by Parratt was felt to be more than adequate to resolve the expected solid structure. Following the successful experiment with argon, an additional series of observations were made using the krypton K absorption edge at 0.87 Å. In this case the Kossel structure of the isolated gas
atom could not be resolved, in agreement with Shaw's experience, but structure was observed in the solid.
II. APPARATUS AND EQUIPMENT

2.1 The Two-Crystal Vacuum Spectrometer

An earlier paper from this laboratory\textsuperscript{55} described the construction of the vacuum spectrometer in detail, including design of the crystal axes, the steel vacuum bell and the vacuum plumbing and pumps. Since that time certain modifications of the instrument have been made. The magnetically focussed x-ray tube\textsuperscript{56} has been abandoned, permitting the cathode and target assemblies to be mounted completely within the steel bell. Figure 4 is a view of the interior of the bell, showing the mounting of the x-ray tube components.

The electron gun cathode in the new model is a one fifth scale version of the model used in the earlier tube\textsuperscript{57} and is capable of delivering 60 mA into a 2 mm diameter focal spot. Figure 5 is a section view of the cathode mounting block drawn to 4 times scale.

\textsuperscript{55} Shaw, C. H., Spielberg, N. and Soules, J. A., Report No. 8, Contract N6 ONR - 22521 NR 017606, Columbus, Ohio State University Research Foundation, May 1951

\textsuperscript{56} Soules, J. A., Thesis M S, Ohio State University, 1950

Figure 4. Interior of Spectrometer Bell; X-ray Tube Components
56 Drill thru O-80 Tap
3 holes equally spaced, as shown
on .830 B.C.

56 Drill thru
O-80 Tap 2
as shown

42 Drill 6
holes equally spaced
as shown. Drill on radius

42 Drill 3 holes, equally spaced as shown, on .830 B.C.

- 1/2
- 1/4
- 1/4
- 1/2
- .670
- .165
- .830 B.C.
- .005
- .050
- .070
- .090
- .115
- .115
- .115
- .115
**DETAIL #2**
Lavite ring, full scale

- #49 drill thru 2 holes, on 1238 BC

*Note:* See Detail

**SECTION A-A**

- #48 drill thru on 15° angle
- 2-56 NF-2 Tap

**DETAIL #3**
Lavite ring, full scale

- #49 drill thru 2 holes, equally spaced on 1238 BC

- Groove 3/8 wide, 3/16 deep
- 100 drill thru 2 holes, equally spaced on 1/2 BC

*Note:* 3/16 counterebore 2 holes from top, 2 from bottom, as shown.

**SECTION A-A**

- End detail of rod
- 3/16 wide, 3/16 deep
- Tongue to fit groove, Detail #3
- Cut on 15° angle

---

**OHIO STATE UNIVERSITY**
Parts for Cathode Mount

*Project No.: 27; Dwg. No.: 5*

*Scale:* As shown; *No. Req.: 1 each*

*Date:* 5-22-53

*Mat'l:* As shown

*Inst's:*
nickel disk at the top. Figure 6a is a sketch of the assembled electron gun structure. Electrical connections are spot welded to the cathode and heater and supported on bead insulators as shown. The electron gun assembly is mounted on an insulating ring of lavite which is in turn mounted on a brass arm in such a way that the cathode can be adjusted to any position relative to the target. Figure 6b is a photograph of the cathode mounting structure.

The x-ray target is shown in Figure 7. A thin wall copper tube supports the solid copper anode surface in the vacuum chamber. Cooling water is forced against the back of the target surface, permitting, for typical domestic water pressures, a maximum power loading of at least 500 watts. The entire target structure is centered in a \( \frac{1}{2} \) inch glass insulating plate and bolted to the spectrometer lid. Figure 8 shows details of the target insulator and mounting parts. For the production of an intense continuous spectrum of medium wavelength (3-4 A) the copper target face was heavily gold plated. Since the water cooled x-ray target operates at potentials as high as 12 kilovolts above ground, the hoses carrying cooling water to the target were made long. Two lengths of vinyl hose, each fifty feet long, carry inlet and exhaust water to and from the target. The coiled hoses are mounted in a large rack suspended from the ceiling. Leakage current in the water is approximately 0.5 ma at 10 kV; no deterioration due to products of electrolysis has been observed.

For wavelength calibration purposes, a similar target was used
5 OD to fit 1/16 smoothly into part, Detail #3

1 1/8 ID O-ring groove 0.160 wide x 0.100 deep

3/4 bore x 1/16 deep

1/4 drill thru. 3/32 counterbore x 3/16 deep

#9 drill thru. 6 holes equally spaced on 2 1/2
Fig. 8

Spectrometer Arrangement, Schematic
having a removable anode plate. This plate, a 1/8 inch thick disk of copper, plated with silver, was bolted to the target body, and vacuum sealed using 50 mil indium gaskets. The silver radiating surface was prepared by amalgamating mercury to the copper disk and then rubbing powdered silver into the mercury. After the mercury-silver amalgam had set, the disk was silver plated, silver sticking only to the prepared area, however.

For the short wavelength radiation used in the krypton experiments, the internal x-ray tube was not used. A conventional tungsten target Machlett X-2 diffraction tube was mounted on the outside of the bell, sealed in place with an O-ring.

Operation of the x-ray tube required a very high vacuum in the spectrometer tank, much higher than was required to reduce air absorption at 3.86 Å. Accordingly all measurements were made at pressures below 1 x 10⁻⁶ mm and most were made at half that pressure. It was observed that the x-ray target surface remained free of deposited carbon only at powers of 300 watts or more. A liquid air trap, shown in Figure 4, assisted in maintaining a high vacuum at the x-ray tube position.

2.2 Ten Kilovolt Power Supply; A: Design

The 10 KV high current regulated power supply for the x-ray tube is patterned after an original circuit by Pepinsky and Jarmotz.⁵⁸

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It is described in detail in an earlier paper from this laboratory\textsuperscript{59}.

\textsuperscript{59} Slusher, W. E., \textit{Thesis} M S, Ohio State University, 1950

The unit incorporates two separate voltage sources, one adjustable for voltages up to 10 KV to provide the accelerating potential for the x-ray target, and the second adjustable up to 3 KV to provide the electron gun nozzle potential. Two major modifications of the original circuit have been made. The electron gun x-ray tube as it is presently used requires a grounded cathode rather than a grounded nozzle circuit. Accordingly the two supplies have been reconnected, tying the negative lead of each supply to the cathode at ground potential. With this arrangement, none of the series type interaction mentioned in Slusher's thesis has been observed. In addition, a type 845 triode tube has been substituted for the type 100 TH used in the original design, with a considerable improvement in performance.

Figure 9 is a simplified schematic diagram of the power supplies as they are presently connected, showing sampling circuits, metering circuits, etc. The D. C. amplifiers and RF rectifier-filter circuits are the same as reported by Slusher. Since the modification mentioned above, the performance equations derived by Slusher are no longer applicable.

Referring to the diagram, Figure 10, the stabilization parameters can be calculated for the modified circuit. The high voltage bleeder resistors are $R_3$, $R_4$ with the target voltage sampled across $R_3$, the resulting error signal amplified $A$ times in the D. C.
FIG. 9
Simplified Schematic, 10kV Power Supply
amplifier, and applied to the grid of the voltage control tube $T_v$.

Similarly for the current regulator: The error signal picked up across $R_2$ and amplified $B$ times in the D.C. amplifier $B$ is fed to the grid of the current control tube $T_C$. The current control tube controls the nozzle potential $E_n$ by adjusting the voltage drop across $R_1$. Parameters of the control tubes are represented in conventional notation by $g_{m_c}, \mu_c, r_{pc}$ and $g_{m_v}, \mu_v, r_{pv}$.

It is convenient to define a parameter $\alpha$, the sampling ratio, by

$$\alpha = \frac{R_1}{R_2 + R_v} \quad (11)$$

Analysis of the loop equations then gives the voltage feedback equation

$$\Delta E_v \left[ \alpha \mu_v A - \alpha \frac{g_{m_v}}{R_v} - 1 \right] = \Delta i_{c} \left[ \frac{r_{pv}}{R_v} + R_2 \right] \Delta E_v \quad (12)$$

The corresponding current feedback equation is

$$\Delta E_c = R_1 \Delta i_N - R_1 \Delta i_c \left[ \frac{\mu_c B R_v}{r_{pc}} + 1 \left( \frac{1}{r_{pv}} + \frac{1}{r_{pc}} \right) \right] \quad (13)$$

where

$$g_{m_c} = \left( \frac{\Delta i_{c}}{\Delta E_N} \right) \left| E_n \right| \quad (14)$$

The emission current of the electron gun is space charge limited and experience has demonstrated that the formula

$$i_N + i_c = \Phi E_n^{3/2} \quad (15)$$

is valid in this case. Experience has further shown that $i_N$, to a first approximation, is constant for all $E_n$ above 200 volts provided
that \( R_t \) is larger than \((R_n + 1000)\). This condition is always met in practice. As \( R_n \) becomes large, \( i_n \) is observed to fall slightly giving a negative resistance nozzle and effectively improving the current stabilization. From formulas (14) and (15) above, the parameter \( g_{\text{MK}} \) is calculated to be

\[
g_{\text{MK}} = \frac{3}{2} \times R_n^{\frac{1}{2}}
\]

With these approximations the feedback equations (12) and (13), become

\[
\Delta E_T \left[ \alpha \mu_x A - \frac{\alpha \tau R_v}{R_z} - 1 \right] + \Delta E_v \\
+ \left( R_v + R_z \right) \left[ \frac{\mu_c R_t R_z B}{r_{pc}} + \frac{R E_n^{-\mu_x}}{3 R} \left( 1 + \frac{R_z}{r_{pc}} \right) \right] \Delta E_c = 0
\]

and

\[
\Delta i_T = - \left[ \frac{\mu_c R_t R_z B}{r_{pc}} + \frac{2 E_n^{-\mu_x}}{3 R} \left( 1 + \frac{R_z}{r_{pc}} \right) \right] \Delta E_c
\]

Thus no interaction between the current and voltage stabilizers can occur, at least to a first approximation. In the event that \( \Delta i_n \) is not zero, the interaction term \( R_i \Delta i_n \) in equation (13) above will be of much greater importance than the possible interaction effect of \( g_{\text{MK}} \). As the supplies are used the target cooling water offers a parallel resistance from target to cathode of the order of 2 megohms. Since the total current, cathode rays plus water leakage, is regulated, an interaction term of the form

\[
\Delta i_T = - \frac{\Delta E_T}{R_w}
\]

occurs directly. It remains to evaluate the performance of the
stabilizers for particular values of the parameters and to demonstrate the stability against oscillation in the presence of the feedback terms. Since the x-ray tube was operated at 8 KV and 43 ma total current (of which 4 ma was water current) for most of the experiments reported here, these values will be used for the calculations which follow.

2.3 Ten Kilovolt Power Supply: B4 Performance

The performance equations of the ten kilovolt supply were shown in Section 2.2 to have the form

\[ M_{11} \Delta i_T + M_{12} \Delta E_T + M_{13} \Delta E_c + M_{14} \Delta E_v = 0 \]  
\[ M_{21} \Delta i_T + M_{22} \Delta E_T + M_{23} \Delta E_c + M_{24} \Delta E_v = 0 \]

where the parameters \( M_{ij} \) are expressed as

\[ M_{11} = -\frac{r_{hv}}{R_2} \]  
\[ M_{12} = \alpha M_v A - \alpha \frac{r_{hv}}{R_3} - 1 - \frac{r_{hv}}{R_w} - \frac{R_2}{R_w} \]  
\[ M_{13} = 0 \]  
\[ M_{14} = 1 \]  
\[ M_{21} = \frac{M_c B R_1 R_2}{r_{pc}} + \frac{1}{g_m x} \left( 1 + \frac{R_1}{r_{pc}} \right) \]  
\[ M_{22} = \frac{M_c B R_1 R_2}{r_{pc} R_w} + \frac{L}{g_m x R_w} \left( 1 + \frac{R_1}{r_{pc}} \right) - R_1 \frac{\partial i_N}{\partial E_T} \]  
\[ M_{23} = 1 - R_1 \frac{\partial i_N}{\partial E_c} \]  
\[ M_{24} = 0 \]
All of the circuit parameters appearing in the $M_{ij}$ may be easily estimated except the terms $g_{mx}$ and $\frac{\partial i_N}{\partial E_r}, \frac{\partial i_N}{\partial E_c}$. To avoid complicating the solution unduly, it will be assumed that

$$\left|\frac{\partial i_N}{\partial E_r}\right| < 5 \times 10^{-10} \text{ mhos} \tag{23}$$

$$\left|\frac{\partial i_N}{\partial E_c}\right| < 10^{-5} \text{ mhos} \tag{24}$$

a condition which is fulfilled in practice. It is seen that the actual values of these two parameters depend upon the fringing field between the electron gun nozzle and the target and can therefore be obtained only by experiment. The term $g_{mx}$ can be obtained from equation (14) of Section 2.2. The value of the emission constant, $k$, of the electron gun may become a function of $E_n$ in time as the cathode surface ages and the space charge limited condition is no longer applicable. However, for the case considered here, it may be assumed to be constant. Slight differences in $k$ may also occur for different electron guns, depending on alignment and construction.

With these considerations in mind, the calculation of the performance parameters may be undertaken. Table I lists the circuit constants and their values at the 8 KV, 40 ma settings of the regulated supply. The $M_{ij}$ listed below were calculated from the values in Table I; terms in parenthesis are one or more orders of magnitude smaller than the principal terms and so may be neglected.
### TABLE I

**Operating Parameters of 10K V Power Supply**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{PV}$</td>
<td>Effective plate resistance of two 450TL triodes in parallel</td>
</tr>
<tr>
<td>$r_{PC}$</td>
<td>Plate resistance of 845 triode</td>
</tr>
<tr>
<td>$M_v$</td>
<td>Amplification factor of 450 TL triodes</td>
</tr>
<tr>
<td>$M_o$</td>
<td>Amplification factor of 845 triode</td>
</tr>
<tr>
<td>$R_1$</td>
<td>100 TH Plate load resistor</td>
</tr>
<tr>
<td>$R_2$</td>
<td>Current pickup resistance in 40 mA position</td>
</tr>
<tr>
<td>$R_3$</td>
<td>Voltage sampling resistance in 8 KV position</td>
</tr>
<tr>
<td>$R_4$</td>
<td>High voltage bleeder resistor</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$R_2/R_3 + R_4$</td>
</tr>
<tr>
<td>$A$</td>
<td>Gain of voltage D. C. amplifier</td>
</tr>
<tr>
<td>$B$</td>
<td>Gain of current D. C. amplifier</td>
</tr>
<tr>
<td>$1/\xi_{\infty}$</td>
<td>$3/2k R_0^{1/3}$ where $E \approx 800$ volts at these settings. $k \approx 1/565$</td>
</tr>
</tbody>
</table>

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* Slusher, W. E., Thesis, M. S., Ohio State University, 1950

** RCA Tube Handbook**

*** Himac Tube Data ***
\[ M_{11} = -1400 - 65 = -1465 \, \text{ohms} \]
\[ M_{12} = -159 - (1.5 \times 10^{-4}) - (1) - (7.5 \times 10^{-4}) - (32 \times 10^{-5}) = -159 \]
\[ M_{13} = 0 \]
\[ M_{14} = 1 \]
\[ M_{21} = -10.6 \times 10^6 + (207) = -10.6 \, \text{megohms} \]
\[ M_{22} = -5.3 + (1.0 \times 10^{-4}) - (1.25 \times 10^{-5}) = -5.3 \]
\[ M_{23} = 1 - .25 = .75 \]
\[ M_{24} = 0 \]

Clearly the feedback terms are negligible. Any tendency toward low frequency hunting would be quickly damped out. The most uncertain of these parameters is \( M_{23} \) which contains an important contribution from \( \frac{\partial i_N}{\partial E_c} \). With these considerations the equations (20) and (21) then become

\[-1465 \Delta i_T - 159 \Delta E_T + \Delta E_V = 0 \] (25)

\[-10.6 \times 10^6 \Delta i_T - 5.3 \Delta E_T + .75 \Delta E_c = 0 \] (26)

The quantities \( \Delta E_V \) and \( \Delta E_c \) may be varied independently by adjustment of the respective control variacs but a more interesting case in actual practice is that of line voltage changes where

\[ \Delta E_c = \frac{E_c}{E_V} \Delta E_V \] (27)

For the case considered here,

\[ \Delta E_c = .125 \Delta E_V \] (28)

Under these conditions the equations (27) and (28) are solvable to give

\[ \Delta i_T = +2.1 \times 10^{-8} \Delta E_V \] (29)

\[ \Delta E_T = 16.3 \times 10^{-3} \Delta E_V \] (30)
\[ \Delta i_T = 2.1 \times 10^{-6} \Delta E_V \]  
\[ \Delta E_T = 6.3 \times 10^{-3} \Delta E_V \]  

The preceding discussion does not give a complete description of the effectiveness of the power supply stabilization. In particular the very high speed of response of the regulator circuits has not been mentioned. No attempt has been made to calculate conventionally used parameters such as "effective internal impedance", stabilization ratio, etc. The reason for this is that a quantity such as the effective internal impedance is less important in describing the action of a current and voltage regulator of this type than the complete performance equations which include the two independent input voltages. Of equal importance to the performance of the regulator are the small variations in the parameters of Table I which produce drift in the operating point of the supply.

60. The effective internal impedance, \( \left( \frac{\Delta E_T}{\Delta i_T} \right)_{E_V} \), is 9.2 ohms for the example calculated.


are two important effects omitted from this discussion. From the equations (29) and (30) it is seen that the current regulator is much more sensitive than the voltage regulator. An improvement in the supply could be brought about by increasing the reference
voltage of the D.C. Amplifier, thus increasing the sampling ratio, \( a \). An increase of five times here would be possible and useful. No further design improvements would be practical short of temperature control of critical reference circuits.

2.4 Forty Kilovolt Power Supply

For the short wavelength experiments the 40 KV, 50 ma supply was built by James Collenge of this laboratory was used. Figure 11 is a simplified schematic diagram of the stabilizer circuits. The method of voltage stabilization is identical to that used in the 10 KV supply. The current stabilizer is designed to operate with a Machlett K2 Diffraction X-Ray Tube by Controlling the filament current. The D.C. Amplifier used is a rather unique design using the cutoff point of the input tube as a reference potential. The error signal is amplified and applied to the grids of the 2A3 control tubes. The dynamic plate resistance of the 2A3's is reflected in series with the x-ray filament through transformer, T. Since the temperature response of typical x-ray tube filaments is fairly slow, a low pass filter of 5 cps cutoff is used in the input circuit.
of the D. C. amplifier. No detailed analysis of this power supply will be presented here.

During all experiments in which the 40 KV supply was used, the voltage and current to the x-ray tube were monitored using Sensitive Research Instrument Co. meters. Voltage fluctuations were never visible, although a slight long time warmup drift appeared. Current fluctuations of the order of 0.5 ma at 16 ma were common. An attempt was made to hold the average current constant in the face of small, short period fluctuations. It is believed that power supply stability offered a serious limitation to the expected accuracy of the short wavelength experiments. However, the short term (1 minute) stability was probably as good as 2 percent, and the long term stability much better.

2.5 Geometry of the Two-Crystal Spectrometer

In the spectrometer as originally designed, a given wavelength region was scanned by rotating the first crystal using a precision micrometer and lever arrangement. However, investigations into the geometry of the two crystal spectrometer revealed that "walking" of the x-ray beam on the crystal faces could be a serious problem, limiting the wavelength region which could be scanned at any one
setting of the crystals. It was found that the walking problem

was considerably greater for rotation of the first crystal than for rotation of the second. Accordingly, modifications were undertaken to permit rotation of the second crystal. Figure 12 shows the main lever arm clamped in place on the second axis table and held firmly against the precision linkage by a spring. A steel ball in the main lever bears on a hardened pad set in the linkage to assure a repeatable calibration for the system. Figure 13 shows the correction curve for the rotation of the second axis as a function of the position of the external micrometer screw. Dispersion of this arrangement is $2/3$ second of arc per thousandth of a millimeter displacement. Settings are repeatable within less than $\pm 2$ seconds of arc.

To prepare the spectrometer for observations in the spectral region of a wavelength $\lambda$, the Bragg angle $\Theta(\lambda)$ is calculated according to the formula

$$\Theta = \arcsin \frac{\lambda}{2d}$$

where $d$ is the lattice spacing of the particular crystals used.

The first axis is then rotated to an angle ($\Theta$) with the index line of the spectrometer (line of centers of the axes). The second axis
Figure 12. View of Spectrometer Base Plate
is rotated to an angle \((-\Theta)\) and the x-ray tube and detector are set at angles \((+2\Theta)\) and \((-2\Theta)\), respectively. The detector mounting pivots about the second axis while the x-ray tube is adjusted by rotation of the spectrometer bell.

It has been shown that the walking of the x-ray beam on the crystals is a function only of the Bragg angle. For a Bragg angle of \(40^\circ\), approximately corresponding to the reflection of the wavelength of the argon K absorption edge from calcite crystals, the walking of the x-ray beam as a function of wavelength is given in Table II. Table III records the walking at \(8^\circ\), corresponding to reflection of the krypton K absorption edge wavelength from calcites.

\(D_1\) is the displacement of the x-ray beam on the first crystal, \(D_2\) is the displacement on the second crystal and \(D_3\) is the displacement on the detector window for a target 12 inches from the first crystal, 8 inches distance between axes, and 4 inches distance from the second crystal to the detector. These are the dimensions of the Ohio State University spectrometer. It is seen that for limited wavelength regions the beam moves only slightly on the crystals at \(40^\circ\), somewhat more at \(8^\circ\). To assure reliable data, it is essential that the x-ray reflectivity remain uniform over the surface of the crystal used.

2.6 Preparation of Crystals

The first crystals used to resolve the argon structure at 3.86 Å were quartz plates, approximately 3 × 4 cm, loaned by Professor
<table>
<thead>
<tr>
<th>$\Delta \lambda$</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 mu</td>
<td>.10 in</td>
<td>.17 in</td>
<td>.04 in</td>
</tr>
<tr>
<td>50</td>
<td>.20</td>
<td>.33</td>
<td>.07</td>
</tr>
<tr>
<td>100</td>
<td>.39</td>
<td>.65</td>
<td>.14</td>
</tr>
<tr>
<td>150</td>
<td>.58</td>
<td>.91</td>
<td>.21</td>
</tr>
</tbody>
</table>
TABLE III

Walking of X-Ray Beam at $\Theta = 8^\circ$ (calcite crystals)

<table>
<thead>
<tr>
<th>$\Delta \lambda$</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>$D_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 nm</td>
<td>.35 in</td>
<td>.58 in</td>
<td>.04 in</td>
</tr>
<tr>
<td>50</td>
<td>.68</td>
<td>1.15</td>
<td>.07</td>
</tr>
<tr>
<td>100</td>
<td>1.29</td>
<td>2.15</td>
<td>.14</td>
</tr>
<tr>
<td>150</td>
<td>1.83</td>
<td>3.05</td>
<td>.21</td>
</tr>
</tbody>
</table>
Parratt of Cornell. The plates were accurately ground and polished parallel to the 110 faces and had been tested by taking a large number of (1, -1) rocking curves for wavelengths from 0.56 Å to 4.59 Å. The spectrometer was aligned after the manner outlined by Parratt. An optical flat was substituted for each crystal and each flat was then adjusted to be parallel to its axis within 10 seconds of arc as measured by a distant Gauss telescope. The second axis mount was then tilted toward the first axis by approximately 5 minutes of arc to compensate for the bending of the spectrometer base plate under vacuum. After the axes had been adjusted, it was possible to monitor their motions as the spectrometer was evacuated by sighting through a glass plate over the x-ray target mounting port. Table IV records the observed deflections of the axes parallel and perpendicular to the index line of the spectrometer. After accurately aligning the axes and crystal mounts by means of the optical flats, the calibration of the spectrometer was determined.

It was found that with the optical flats accurately parallel to the index line of the instrument the scale readings of the crystal tables and detector mounting were as given in Table V. The x-ray tube position was determined by a steel tape measure fastened to the rim of the spectrometer base plate to measure arc length around the rim from the index point.

A number of rocking curves in the 2,+2 position were taken with
<table>
<thead>
<tr>
<th></th>
<th>First Axis</th>
<th>Second Axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel to Index Line</td>
<td>20 - 30 sec</td>
<td>5 min</td>
</tr>
<tr>
<td>Perpendicular to Index Line</td>
<td>10 sec</td>
<td>20 sec</td>
</tr>
</tbody>
</table>

TABLE IV

Deflections of Crystal Axes Under Vacuum
### Table V

**Zero Positions of Crystal Axes**

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Axis</td>
<td>$48.85 \pm 0.05$</td>
</tr>
<tr>
<td>Second Axis</td>
<td>$-0.05 \pm 0.05$</td>
</tr>
<tr>
<td>Detector</td>
<td>$-3.5 \pm 0.1$</td>
</tr>
<tr>
<td>X-Ray Tube</td>
<td>$-0.5\text{mm} \pm 0.1\text{mm}$</td>
</tr>
</tbody>
</table>
the quartz crystals using iron $\text{K}\alpha_2$ radiation. The second crystal was tilted at various angles to compensate for the tilt in the axis, since all the data were taken at atmospheric pressure. The minimum width of the iron line was 227 seconds at a tilt of $5 \pm 1$ minutes confirming the earlier measurement of axis tilt. Furthermore, this was taken as proof that the crystal planes were parallel to the physical faces of the crystals within one minute of arc.

Preliminary experiments on the argon absorption edge proved the quartz crystals to be inadequate for the problem. The advantage of the high resolving power of the quartz was more than offset by its low reflectivity. Intensities were too weak for any but very crude measurements and so after some beginning tests (see Section III) the quartz crystals were removed and replaced with calcites.

A number of calcite crystals were prepared by cleaving from good quality rough calcites of unknown origin. None of the calcite used was of so-called optical quality but an attempt was made to select transparent crystals with a minimum number of visible flaws. Following the suggestions of Manning the crystals were cleaved into slabs approximately $1 \times 2 \times 3$ cm and then ground on plate glass using titanium dioxide abrasive. They were washed in ether and in alcohol, and etched for 6-8 seconds in 0.70 normal hydrochloric acid. A number of rocking curves of the iron $\text{K}\alpha_2$ lines in the $(l, -1)$ position were taken, using various combinations of crystals and

68. Manning, K. V., Rev. Sci. Inst. 5, 316 (1934)
angles of tilt. In no case could rocking curve widths less than 18 seconds be obtained with polished crystals. In one instance, a newly cleaved pair gave a rocking curve width of 15 seconds which became 21 seconds after polishing. Following this experience, a new pair of crystals were carefully cleaved from the block, using a milling saw. The calcite block was mortared into a metal holder with Plaster of Paris to allow it to be held firmly in the milling machine without introducing internal stresses. The first pair of cleavage surfaces produced in this way were good enough to be considered class 1 without grinding and etching. Actually, tests were made only on the Fe Kα lines in the (1, -1), (1, 1), and (2, +2) positions so the behavior of the crystals with wavelength has not been determined. However, as shown in Table VI, they are apparently "perfect" crystals at this wavelength. Since an excellent (2, +2) rocking curve had been obtained at a Bragg angle of 39.6° (Fe Kα, in 2nd order), no further adjustment of the crystals was made before beginning the argon absorption experiment. Later experience with the krypton absorber at a Bragg angle of 8° indicated that the crystals were not equally good at all points on their faces, since the reflected intensity was not constant for all positions of the beam. This was not thought to be a serious handicap to the krypton experiment since high resolving power was not necessary for the krypton spectrum.
**TABLE VI**

Rcking Curve Width at Half Maximum: Calcite Crystals

in Various Positions, Fe Kα$_2$ Radiation

<table>
<thead>
<tr>
<th>Crystals</th>
<th>(1, -1) Width (secs)</th>
<th>(1, 1) Width (secs)</th>
<th>(2, 2) Width (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>* Bearden and Shaw</td>
<td>12.6</td>
<td>68.4</td>
<td>(140)</td>
</tr>
<tr>
<td>** Parratt</td>
<td></td>
<td>73.5</td>
<td></td>
</tr>
<tr>
<td>*** Allison</td>
<td></td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>This report</td>
<td>13 ± 1</td>
<td>66 ± 2</td>
<td>145 ± 3</td>
</tr>
</tbody>
</table>

(Value in parenthesis is interpolated)


** Parratt, L. G. *Phys. Rev.* 44, 695 (1933)

2.7 Proportional Counter X-Ray Detector

The spectrometer is constructed to be used with a variety of x-ray detecting devices including photomultipliers, geiger and proportional counters. Photographic recording is not possible with the two crystal design. The proportional counter type of radiation detector is eminently suited for use with an x-ray crystal spectrometer since it permits discriminating against short wavelength radiation which is Bragg reflected from the crystals in high orders.

Two proportional counters of identical construction were used in the course of the experiments on argon and krypton. For the long wavelength work the counter was filled with 13.7 cm pressure of xenon gas and 1.8 cm of methane. The counter used for the shorter wavelength measurements was filled to 66 cm xenon pressure, and 4 cm of methane. The counters were of the side window type similar to a design prepared at the Oak Ridge National Laboratory by Dr. R. W. Knowles. Figure 14a describes the counter construction and assembly. After machining, the inside of the cylindrical shell was carefully sandpapered before soldering. All points were soldered using pure tin to prevent possible contamination by radioactive lead. The thin beryllium windows of the counters were sealed to the shells
The Beavellium Sheet is clamped around counter and sealed with glyptal.

Solder to core.

Stainless steel disc.

1/16" section.

Stupanoff #95-2024.

100 stainless steel tube, 1/8" wall.

4003 wire stem center wire.

All assembly joints soldered with tin.

Proportional Counter (A)
**Cascode Preamplifier**

- **6AK5**
- **100μfd**
- **2 MΩ**
- **20 MΩ**
- **680 Ω**
- **Hi volts**

- **6J6**
- **5k**
- **3.3k**
- **0.1**
- **220**
- **270 0.5 0.25**
- **30 1.5k 0.1**

**Inputs:**
- **SIG OUT**
- **FIL**

**Outputs:**
- **B+**
- **Pilot**

**Components:**
- **Counter Center Wire**
with glyptal and clamped firmly in place. The low pressure counter used a 3 mil window while the high pressure counter used a 5 mil window.

A 100 micro-micro-farad "Ceramicon" condenser mounted directly adjacent to the counter signal lead carried the counter pulses to the preamplifier grid. This condenser, rated at 10 KV, adequately blocked the high voltage direct current of the counter center wire without introducing spurious counts due to insulator leakage. Figure 15 is a general view of the counter and preamplifier. Because of its inherent low noise characteristic, the cascode amplifier circuit developed by Wallman \(^1\) was selected for use with the proportional counter. Figure 14b is a schematic diagram of the circuit arrangement used. Because of the need for a minimum input capacitance, the first stage (6AK5, triode connected) of the preamplifier was located directly on the detector mounting frame. In this arrangement the total load capacity receiving the pulse of charge is probably of the order of 20 micro-micro-farads. Due to the low output impedance of the first stage, however, a high capacitance coupling arrangement could be used between it and the following stage. In this circuit, a two foot length of No. 20 wire carried the signal to the cathode of the 6J6 amplifier which was located outside of the spectrometer. Noise output of the preamplifier was of the order of 10 microvolts rms.

Figure 15. Proportional Counter Mounting
Even with the spectrometer bell raised, pulses as small as 300 microvolts could be counted above the hum pickup. Figure 16 is a view of the underside of the spectrometer base plate showing the external preamplifier unit.

The cathode follower output stage of the preamplifier was used to drive an Atomic Instrument Company Linear Amplifier, Model 204 B. For all the measurements reported here the Linear Amplifier was set for positive pulses of 0.2 micro-second rise time. An Atomic Instrument Company Pulse Height Analyzer, Model 510, was used to select appropriate pulses and the output fed into an Atomic Instrument Company Decade Scaler, Model 105. The scaler unit incorporates a 3000 volt regulated power supply which proved to be adequately stable for use with the proportional counters. The low pressure counter was operated at 1100 volts and the high pressure counter at 1900 volts, giving in each case a mean pulse height of the order of 30 - 40 volts with the amplifier at maximum gain.

Figure 17 is a typical pulse height distribution curve obtained from continuous spectrum x-rays reflected from calcite crystals at 39.6. The first and second order reflections are apparent. With the Pulse Height Analyzer set to reject large pulses, the second order pulses can be practically eliminated. An advantage of this technique is that it permits the x-ray tube to be operated at much higher voltages without recording the resulting high energy photons.
Figure 16. Preamplifier Mounting
2.8 Absorption Cell and Cryostat

The mass absorption coefficients of argon on the high and low energy sides of the absorption edge at 3.86 A are 1460 and 148 respectively. By differentiating the absorption equation

\[ I = I_0 e^{-\mu x} \]  

one can obtain an equation for the thickness of absorber which gives the maximum contrast between two wavelengths whose absorption coefficients are \( \mu_1 \) and \( \mu_2 \). (See Section 5.1) For this optimum thickness,

\[ \rho x = \frac{\ln \mu_1/\mu_2}{\mu_1 - \mu_2} \]  

where \( \rho \) is the density in gm/cm\(^3\), \( x \) is the thickness in cm and \( \mu \) is measured in cm\(^2\)/gm. For argon, the result \( \rho x = 1.74 \text{ mg/cm}^2 \) is obtained. If a density of solid argon of 1.4 gm/cm\(^3\) is assumed

\[ x \]  

1.25 x 10\(^{-3}\) cm, the optimum thickness of the solid absorber. Since no method was available to prepare a crystal of argon this thin, it was decided to prepare the solid argon absorber by spraying...
the gas against a cold window directly in the spectrometer vacuum. Figure 18 shows the absorption cell which was constructed for this purpose. Two thin (3 mil) beryllium windows are sealed to the copper cell by 50 mil indium wire gaskets clamped with iron rings. Brass screws were used to prevent loosening at low temperatures. Liquid hydrogen or liquid helium can be introduced into the cell to provide a cold surface. The distance between the parallel faces was accurately machined to 0.437 inch. The absorption at 3.9 A of liquid hydrogen of this thickness was estimated to be 6 per cent; 76,77 of liquid helium 25 per cent. Two 2 mil thicknesses of beryllium

76. Compton and Allison, op cit, p 802.

77. The absorption of liquid helium at 3.86 A was accurately determined during the course of the experiment.

were used as heat shields on the cryostat, the total 10 mils of beryllium having an estimated absorption of 63 per cent at 3.9 A.

Figure 19 is a section through the absorption cell apparatus. The cell is part 14, the window mounting plates, parts 15. The plate 6 is the bottom of the inner vessel of the cryostat, whose volume was approximately 600 cc of liquid hydrogen or helium. The absorber gas is introduced through the fine nickel tube at the left and directed against the beryllium window. The nickel tube extends through the outer wall of the cryostat to a high vacuum needle valve, thence to the gas supply. The inconel tube 20 may be
NOTE: To solder into hole in cover plate. See Dwg. 6.
NOTE: Position Helium Cold Chamber on inconel supporting tubes so that all windows are accurately aligned. Tighten part 8 on threads firmly before cutting flats & slits 8A.
electrically heated to prevent condensation on its surface. The nickel tube extends only within about 1 cm of the absorption cell to permit the absorber gas to diffuse evenly over the surface of the window. Figure 20 is a view into the bottom of the cryostat showing the absorption cell equipment in place.

The method of mounting the beryllium windows to the absorption cell proved satisfactory. However, the thin beryllium windows themselves showed evidence of a leak at low temperatures after several cycles of cooling and heating. The windows were replaced and the new windows served for several experiments before also developing a leak. Changing gaskets proved of no value so new windows, this time 5 mil, were mounted. Only one experiment was performed with this pair. The indium gaskets fused firmly to the copper and fitted tightly to the beryllium so it is believed that they were not the cause of the leaks.

Figure 21 is a view of the entire cryostat assembly while Figures 22 to 35 are detail drawings of the various components. The copper sleeve (8) (Figure 21) and the inner vessel, composed of parts (5), (6) and (10), were highly polished to reduce radiation heat transfer. Six one inch diameter holes were bored near the top of the copper sleeve to provide vacuum communication.

Assembly of the cryostat was begun by soldering the inconel connecting tubes into the bushing in the inner vessel. The end of the 1/8 inch tube was filed off at 45° to permit using it to blow out the inner pot. The tubes were then passed through the bushings
Figure 20. View of Bottom of Cryostat, Bottom Plate Removed
0-Ring groove. 6" ID x 0.055 wide, 0.100 deep (±0.002)

NOTE: 5" ID to receive standard 5" brass tube. See Dwg. 14.

All dimensions ±1/64, except as shown.

5" Drill thru, 12 holes equally spaced on 7/8 BC.
All dimensions are 1/64, except as shown.

Fig. 23

Ohio State University
Brass Tube
Project No. 20; Dwg. No. 14
Scale: Full; No. Req.: 1
Date: 7-15-52
Mat'l: Brass
Inst's: To fit part. Dwg4 & Dwg13
All dimensions ±1/64, except as shown.

#6 Drill thru.

1/4-20 NC-2 Tap

6 holes, equally spaced on 61/4 B.C. These holes to be drilled after assembly.

Lay out B.C. only.

NOTE: 5" ID to receive standard 5" brass tube. See Dwg. 14.

0-Ring groove 51/2 ID x 0.165 wide; 0.100 deep (+0.002)

Section X-X

FIG. 24
Drill thru.
6 holes equally spaced
on 6\(\frac{1}{4}\) B.C. These holes
are to be drilled after assembly.
Lay out B.C. only.

NOTE: 4" ID to receive
standard 4" Inconel
tube. See Dwg. 9.

All dimensions ±\(\frac{1}{64}\), except as shown.
All dimensions ± 1/64, except as shown.

Note: Lay out this hole, but do not drill.
Fig 28

All dimensions ±1/64 except as shown.

NOTE: To be machined after soldering to Inconel tube, Dwg 9.

Ohio State University
Cover Plate
Project No. 20; Dwg. No. 7
Scale: Full; No. Req.: 1
Date: 7-15-52
Mat'l: Copper
Inst's: To fit parts, Dwg 9, Dwg 9
#32 Drill x \frac{1}{2} deep.
6: 32 NC-2 Tap 4 holes equally spaced on 3\frac{3}{16} BC

NOTE Finish inside to 3\frac{1}{4} if necessary, to fit part, Dwg. 3.

NOTE: See also Dwg 15 for detail.

Section X-X

3\frac{3}{16} - 32 NC-3 Thread to fit part, Dwg 7.

All dimensions ±\frac{1}{64}, except as shown.
NOTE: Lay out this hole, but do not Drill.

\(-\frac{3}{8}\) Drill & Ream

\(\frac{3}{8}\) Drill & Ream

\(\frac{1}{4}\) Drill & Ream

Note: To be machined after soldering to copper tube, Dwg. 10.

All dimensions \(\pm \frac{1}{64}\) except as shown.

**Ohio State University**

Cover Plate

Project No. 20; Dwg. No. 5; Finish

Scale: Full; No. Req.: 1

Date: 7-15-52; Mat'l: Copper

Inst's: To fit part, Dwg. 10.
All dimensions ± 1/64 except as shown.

NOTE: Finish ends only, 
1/2 deep each end, to fit parts, Dwg 5, Dwg 6

Fig. 31

OHIO STATE UNIVERSITY
Cold Chamber
Project No. 20 ; Dwg. No. 10
Scale: Full ; No. Req.: 1
Date: 7-15-52;
Mat'l: Copper
Inst's: To fit parts, Dwg 5, Dwg 6
NOTE: To be machined after soldering to copper tube, Dwg. 10.

All dimensions ± 1/64, except as shown.

Fig. 32
- Mill flat. See Detail A for layout of holes.

Bottom View
Flat See 1B for layout of £ slit.

## Detail A

- #19 Drill thru 2.56 tap
- 4 holes, equally spaced on 1/4 B.C. to match part. Dwg #16, Detail #19
- 1" bore

## Detail B

- #19 Drill thru 2.56 tap
- 3 holes equally spaced on 1/4 B.C. to match part.
- Dwg #16, Detail #19

### NOTE:
Mill flats on Cover Plate, Dwg 3, to match flats on Cold Chamber.

### Ohio State University
Cold Chamber: End Detail

- Project No.: 20
- Dwg. No.: 8A
- Scale: Full
- No. Req.: /
- Date: 2-20-53
- Mat'l: Copper
- Inst's: As shown
#49 Drill thru 6 holes equally spaced on 0.760 BC
Align with holes of part, Dwg. 14, to fit in any position

Chamfer these edges around slit

NOTE: Make 2 flanges. Drill 4 tap holes for 2-56 screws.
Drill #1.5 clearance for 2-56 screws in second.
Drill to receive two Inconel tubes

#40 Drill thru. 2.56 top
6 holes, equally spaced
on 1/8 B.C.

1/16 deep groove
to receive
2.00 Inconel
tube

Section A-A

DETAIL #16
Copper Flange

#43 Drill thru
3 holes, equally spaced
on 1/8 B.C. to match part
16 Dwg. SA in any position.

Section A-A

DETAIL #19
Copper Flange
#43 Drill thru. 3 holes equally spaced on 1/8 B.C. to match holes in part, Detail A. #16, in any position.

#44 Drill thru 4 holes equally spaced on 1/225 B.C. (1/230 after trim.

0.040 Drill thru. Tangent to inner hole. Approx. as shown.

DETAIL #18
Lavite insulator

DETAIL #20
Inconel tube

OHIO STATE UNIVERSITY
Parts for Argon Orifice
Project No. 20; Dwg. No. 16
Scale: Twice; No. Req.: 1 each
Date: 2-19-53
Mat'l: Lavite, Copper, Inconel
Inst's: Solder as shown
in part 7 and in part 12. With a brass ring of 1.545 inch axial length to support the helium vessel, part 12 was pressed firmly in place and the tubes soldered to it. The jig could then be removed and the tubes soldered to the bushings in part 7.

The copper sleeve 8 was aligned by inserting a pointed plug in the sample tube hole in part 6. An eyepiece mounted over one window (Detail A, Figure 33) and a hair line over the opposite window permitted the windows to be aligned with the plug by adjusting the rotation of the sleeve on its precision threads. Slight filing of the shoulder on part 7 allowed the sleeve to be turned snugly to the correct position, within 0.005 inch. At this point, the absorption cell, part 14, could be soldered in place, using a Jig to align it accurately with the windows in the outer sleeve 6. Three lucite screws tapped in this sleeve allow the inner vessel to be adjusted and held accurately in proper alignment in the center of the cryostat within 0.005 inch. A fine line scratched on the bottom plate 3 of the cryostat marked the axis of the x-ray beam through the windows for alignment of the entire system in the spectrometer. At this point the cryostat was thoroughly leak tested using a helium mass spectrograph leak detector manufactured by Consolidated Vacuum Corporation.

The outer brass cylinder of the cryostat was mounted permanently in place on the spectrometer and final alignment was begun. With the Gaussian telescope at the elevation of the x-ray beam (six inches above the spectrometer base plate) and accurately horizontal, the
inner cylinders of the cryostat were lowered into place and the spectrometer evacuated. Observations were recorded of the vertical and horizontal motions of the cryostat as the spectrometer bell deflected under vacuum, and then as the cryostat was cooled to liquid nitrogen temperature. It was assumed that further cooling to liquid helium temperature would produce negligible contraction. Table VII lists the various motions observed; lateral motion was negligible. Following this experiment, a shim plate to fit between parts 4 and 11 was machined, of proper thickness to bring the center of the cryostat windows into accurate vertical alignment with the x-ray beam. Screws tapped through part 11 into the shim held it permanently in position. All flanges at the top of the cryostat were sealed with neoprene O-rings. Three brass C-clamps held the flanges 4 and 11 tightly together, permitting full freedom of angular adjustment.

The spectrometer cover, carrying the cryostat, was lifted and the center line of the x-ray beam marked by clamping a steel straight edge to the flange of the bell. With the straight edge as an index the cryostat was rotated on flange 4 until the scratch line mentioned earlier was accurately parallel to the beam. The entire assembly was then tilted slightly by inserting two 0.003 inch shims, swinging the cryostat approximately 0.030 inch at the bottom, and into alignment with the beam. It is believed that the maximum accumulated positioning error of the cryostat was less than 0.015 inch in any direction. The sequence of adjustments outlined above
<table>
<thead>
<tr>
<th>Description</th>
<th>Movement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflection of base plate at cryostat position</td>
<td>1/64 inches up</td>
</tr>
<tr>
<td>(spectrometer evacuated)</td>
<td></td>
</tr>
<tr>
<td>Deflection of cryostat and spectrometer lid</td>
<td>1/32 inches down</td>
</tr>
<tr>
<td>(spectrometer evacuated)</td>
<td></td>
</tr>
<tr>
<td>Motion of cryostat windows</td>
<td>3/32 inches up</td>
</tr>
<tr>
<td>(cooled to 90 K)</td>
<td></td>
</tr>
</tbody>
</table>
was repeated twice during the course of the experiments with similar results.

Since experiments similar to those of Parratt on argon gas were also planned, a system for accurate pressure control of the sample gas was required. Figure 36 shows the gas handling apparatus constructed. A short length of tygon tubing connects the system to the cryostat. For the solid measurements, this connection was made to the high vacuum needle valve connected to the nickel inlet tube. For measurements of gas absorption, the gas was fed directly into the inner vessel of the cryostat, replacing the cold liquid in the space between the beryllium windows. In this case, liquid oxygen rather than nitrogen was used in the upper reservoir of the cryostat to prevent condensing the argon gas at high pressures. (Boiling point of oxygen is 90°K, of argon 87°K and of nitrogen 77°K). The mercury manometer on the right measures the absolute pressure of the gas in the system and the 2 liter bulb at the top serves as a reservoir. The valves at the bottom provide for introducing the sample gas and for evacuating the entire sample system. The glassware is mounted on an iron lattice fastened to a wooden base which permits it to be placed on the spectrometer bell next to the cryostat when experiments are in progress.

For the measurement of the krypton gas absorption it was found that the 1.11 cm path of the absorption cell of the cryostat would require a krypton pressure in excess of one atmosphere to produce an optimum density of absorber. For lower pressure at the necessary
Figure 36. Gas Handling Apparatus
density an absorption cell was constructed as shown in Figure 37 consisting of a hollow copper cylinder 1 1/4 inch long faced with 1 mil aluminum windows clamped in place on indium wire gaskets. At 0.86 Å, the absorption in the windows was calculated to be approximately 14 per cent. A short length of copper tubing and a vacuum valve permit connecting the cell to a krypton source for filling. Since air absorption is small at 0.86 Å, the experiment on krypton gas could be done in an air atmosphere. The spectrometer bell was lifted out of the way and the absorption cell held in place in the x-ray beam by a clamp and stand. The solid krypton absorption was measured using the technique developed for argon. In this case the spectrometer vacuum was required only to insulate the cryostat.
Figure 37. Krypton Absorption Cell
III. EXPERIMENTS AND RESULTS

3.1 Preliminary Experiments Using Quartz Crystals

After alignment of the crystal axes the Fe Kα, radiation from a Machlett tube was observed in the (2, +2) position. Data were taken with a Geiger counter at various angles of tilt of the second crystal from its axis and at atmospheric pressure. Data were also taken using the proportional counter. Table VIII lists the values of rocking curve width at half maximum intensity which were obtained. Figure 38 is the best curve obtained, corresponding to a tilt of 6 minutes of arc. Fine control of the tilt of the crystal was achieved by rotating the second axis through the desired angle while monitoring the crystal with the Gaussian telescope reflecting from a small mirror stuck to the crystal surface. The cross hairs of the telescope were set at 45° so that horizontal and vertical deflections of the crystal could be compared. The crystal axis was rotated the desired amount and the crystal was then tilted until the resultant motion placed the reflected crosshairs 45° from their original position. Errors with this method are probably ±0.25 minute of arc.

Following the rocking curve data, the second quartz crystal was realigned parallel to the axis and an attempt made to locate the argon K edge without resetting the crystals. The wavelength of the Fe Kα1 is almost exactly half the wavelength of the argon K edge. Argon gas was admitted to the absorption cell at 64 cm pressure. Using 6.5 KV, 29.5 ma x-rays, an intensity jump from 4 to 14 counts
## TABLE VIII

Iron Kα, Width in (2, +2) Position: Quartz

<table>
<thead>
<tr>
<th>Tilt</th>
<th>Pressure</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geiger counter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 min</td>
<td>1 atm</td>
<td>231 sec</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>229</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>227</td>
</tr>
<tr>
<td>7½</td>
<td>1</td>
<td>232</td>
</tr>
<tr>
<td>Proportional counter</td>
<td>10 min</td>
<td>1 atm</td>
</tr>
<tr>
<td>0</td>
<td>vacuum</td>
<td>221</td>
</tr>
</tbody>
</table>
per minute was observed near the center of the region scanned, occurring in an angular interval of 2 minutes of arc. With the absorbing gas removed, intensities were of the order of 40 counts per minute and uniform with wavelength. A second experiment using 25.6 cm argon pressure confirmed the first result. Figure 39 shows the relative absorption coefficient of argon gas versus wavelength as obtained from these preliminary experiments. Data were taken at 11.5 cm of argon using 7.4 KV, 22 mA x-rays. For the data reported the pulse analyzer was set to reject only very large pulses. No dependable pulse height distribution data could be taken due to the very low intensities available, although an effort was made to obtain some data of this type.

A preliminary experiment was then performed using liquid helium to prepare a solid argon sample. After transferring the liquid helium to the inner vessel of the cryostat, the high vacuum valve was opened slightly to admit argon gas against the absorption cell window. The pressure of the argon supply used was 3 cm. The pressure within the spectrometer rose from about 2 to 4 × 10⁻⁷ mm as measured by an ionization gage on the spectrometer bell, and fell immediately upon closing the valve. The x-ray intensity on the short wavelength (high absorption) side of the argon K edge was monitored continuously during filling and was observed to fall from 120 total counts per minute to 70, at which point the argon gas input was stopped. The 70 counts per minute remaining were predominately second order
radiations, rejected by the pulse height analyzer but recorded by the counting rate meter in the hookup used. A search showed the solid argon absorber to have an edge approximately at the same wavelength as the gas. No absorption structure could be observed. The helium evaporation rate was steady at 3 liters per minute and no increase in rate could be observed while freezing the argon film. The experiences in preparing the solid argon film were repeated many times in subsequent experiments without notable exception. The amount of liquid helium in one filling required approximately two hours and forty minutes to evaporate. Evaporated helium gas was passed through a gas flow meter to monitor the quantity lost.

Several additional experiments were made in an attempt to increase the x-ray intensity to usable values. In particular, an improved pulse height distribution curve was obtained using 10 KV, 38 mA x-rays. Intensity of the first order radiation was approximately 380 counts per minute; the second order, 220 counts per minute.

In view of the limitation on intensity imposed by the quartz crystals, a calculation was made of the suitability of calcite crystals. Table IX lists values of the principal features of the two types of crystals from which it was deduced that the intensity reflected from a calcite pair would be approximately twelve times that reflected from a quartz pair. The inner K level of argon is known to be 0.58 volts wide \(^78\) compared to the contribution to the

---

\(^78\) Parratt, L. G., *Phys. Rev.* 56, 295 (1939)
### TABLE IX

Comparison of Calcite and Quartz (110) Near 3.9\AA 

<table>
<thead>
<tr>
<th></th>
<th>Quartz</th>
<th>Calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Reflection</td>
<td>20.4% (3.35\AA)*</td>
<td>57% (3.708\AA)**</td>
</tr>
<tr>
<td></td>
<td>16% (4.15\AA)*</td>
<td>57% (3.907\AA)**</td>
</tr>
<tr>
<td></td>
<td>19% (3.9\AA)***</td>
<td></td>
</tr>
<tr>
<td>(1,-1) width</td>
<td>15.5 sec (3.35\AA)*</td>
<td>27 sec (3.708\AA)**</td>
</tr>
<tr>
<td></td>
<td>18 sec (4.15\AA)*</td>
<td>29 sec (3.902) **</td>
</tr>
<tr>
<td></td>
<td>17 sec (3.9\AA)***</td>
<td></td>
</tr>
</tbody>
</table>

* Parratt, L. G., Rev. Sci. Inst. 6, 113 (1935)
** Parratt, L. G., Phys. Rev. 41, 561 (1932)
*** Interpolated
width of 0.18 volts by calcite, and 0.09 volts by quartz. From this it was decided that the loss of effective resolving power by using calcite would be of the order of 15 per cent, while the gain in intensity would be 1200 per cent. Accordingly a program was undertaken to prepare a pair of "perfect"\(^79\) calcite crystals.

\footnote{79. Parratt, L. G., Rev. of Sci. Inst. 6, 387 (1935)}

### 3.2 Preparation of Calcite Crystals

Table I shows the widths obtained with several calcites under various conditions. Crystals A, B, and D were prepared by polishing with TiO\(_2\) dust and etching in 0.70 normal HCl. Crystals E and F were prepared by cleaving only; E' and F' are the same crystals after polishing and etching. Crystals G and H are matching faces of a large crystal which was carefully cleaved as described in section 2. Comparison of the data for crystals G and H with that obtained by Bearden and Shaw \(^80\) shows that they may be considered Class I crystals \(^79\).

\footnote{80. See Section 2, Table VI}

at the Fe K\(\alpha\) wavelength. However, later data taken on the silver lines and on the argon gas absorption indicated that they were inferior at the longer wavelengths although no \((1, -1)\) rocking curves were taken at the longer wavelengths. Figures 40, 41, and 42 are the rocking curves obtained with this pair of crystals on the Fe K\(\alpha\), line in the \((1, -1), (1, +1)\) and \((2, +2)\) positions respectively,
<table>
<thead>
<tr>
<th>Crystal Pair</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A, B)</td>
<td>18 sec</td>
</tr>
<tr>
<td>(D, A)</td>
<td>20 sec</td>
</tr>
<tr>
<td>(D, B)</td>
<td>22 sec</td>
</tr>
<tr>
<td>(E, F)</td>
<td>15 sec</td>
</tr>
<tr>
<td>(E', F')</td>
<td>21 sec</td>
</tr>
<tr>
<td>(G, H)</td>
<td>13 sec</td>
</tr>
<tr>
<td>(G, H) (1, 1)</td>
<td>66 sec</td>
</tr>
</tbody>
</table>
Figure 40. Rocking Curves: Fe Kα₁ in (1,-1) Position with Calcite Crystals
using the iron anode Machlett tube.

Before continuing with the argon absorption experiments the performance of the proportional counter-pulse height analyzer system was studied. Figure 43 shows the pulse height distribution curves for the continuous spectrum from a gold x-ray target at various target voltages. The curves are plotted as counts per minute per 2 volt analyzer channel as a function of the channel base line voltage. The logarithmic scale is chosen only to make the display of the data clearer. The counter was filled to a total pressure of only 15.5 cm and so was not very sensitive to short wavelength radiation. All pulses were amplified with the preamplifier-linear amplifier system described in Section 2.3. The ability of the proportional counter to discriminate against high energy radiation is evident. Prior to each experiment performed a pulse height distribution curve was obtained and the pulse height analyzer, linear amplifier combination adjusted to accept 95 per cent of the desired radiation. No long time drift was observed for these settings, but slight variations occurred from one experiment to another due to changes in amplifier gain and similar effects. A later experiment on argon gas showed that the apparent absorption coefficient of argon was constant for all x-ray tube voltages, further indicating that all second order radiation was rejected by the detecting system.

3.3 Argon Gas Absorption

A number of measurements of argon gas absorption was made using
the calcite crystals. Ordinary commercial grade argon gas of unknown but high purity, was used for all the experiments reported here. Typical intensity with the absorber removed was 2700 counts per minute using 8.8 KV potential, and 30 ma current on the x-ray tube, or approximately eleven times that obtained with the quartz crystals. Various absorber densities were used (by varying gas pressure) to obtain optimum contrast over the different parts of the structure. The complete argon spectrum, covering some 15 X-units in the region of the absorption edge, was taken first, at 16 cm argon pressure in the absorption cell. Then the short wavelength structure was examined using a 24 cm gas pressure. A series of accurate measurements of the transmission of the absorber on the long and short wavelength sides of the absorption edge, far (>10 X-units) from the edge structure was then undertaken using argon pressures from 8 cm to 65 cm. Figure 44 shows this data plotted on semi log paper with the expected relative error of each point (± N \sqrt{N/2}) depicted by the conventional brackets. From the curves the function $\mu_0 \psi \gamma$ can be calculated according to

$$\mu_0 \psi \gamma = - \frac{1}{\ln T}$$

(34)

For all of the experiments on argon gas, an uncertainty exists in the absolute values of the absorption coefficients, or in the values of gas density. The cryostat equipment was maintained at liquid oxygen temperature (90°C) for all of the argon gas data. The inner vessel was well enough insulated that it could have been warmer than this even after several days of operation, giving a smaller density
of argon gas in the cell than that calculated from the known pressure and the \(90^\circ\) temperature. No thermometer was built into the cryostat inner vessel to measure temperature of the absorbing gas. From Figure 44

\[
\rho = 19 \pm 5\text{cm } \mu_s/\rho
\tag{35}
\]

where \(\rho\) is in cm, \(\mu_s\) is the short wavelength absorption coefficient in \(\text{cm}^2/\text{gm}\), \(\rho\) is in \(\text{gm/cm}^3\) and \(x\) is in cm. Similarly from Figure 44

\[
\rho = 175 \pm 25 \mu_s/x
\tag{36}
\]

From equations (35) and (36), it is seen that the jump ratio

\[
\frac{\mu_s}{\mu_l} = \frac{175 \pm 25}{19 \pm 5} = 9.2 \pm 1.3
\tag{37}
\]

is in satisfactory agreement with the accepted value

\[
\frac{\mu_s}{\mu_l} = 9.9 \pm 1.5
\tag{38}
\]

---

81. Spencer, R. J., Phys. Rev. 38, 1932 (1931)

The thickness of the absorption cell is known to be 1.11 cm, so using equation (35) above and Spencer's value for \(\mu_s (= 1465)\)

\[
\frac{\rho}{\rho} = (31 \pm 8) \times 10^3 \text{cm}^3/\text{gm}
\tag{39}
\]

From the equation of state of a perfect "argon" gas

\[
\frac{\rho}{\rho} = 15\omega \text{ cm}^4/\text{gm} \cdot \text{K}
\tag{40}
\]
and from equations (39) and (40), the temperature of the absorber is $200 \pm 5\%$. The press of the program on solid argon precluded temperature experiments to confirm this result.

Precise measurements of the argon absorption structure were made, taking 6000 counts per point. In addition, the structure in the region of the principal absorption maximum was repeated at the end of the entire argon program to serve as a calibration reference. The structure observed in each experiment was in complete agreement with the others, except for the first survey taken. Here, all features of the structure were observed displaced 20 seconds toward shorter wavelengths. A 0.0015 inch piece of grit under one of the bearing pads could have caused such a displacement and since it was not repeated it was thought to be unimportant. Figure 45 shows the argon gas absorption curve obtained in this first experiment. Figure 46 shows the argon gas absorption as measured prior to the investigation of solid argon. The data were repeated afterward for a check on wavelength calibration and was found to agree in all details. Figures 45 and 46 do not agree, however, not only in the wavelength displacement mentioned but also in the resolution of the absorption lines. Apparently a shift of the crystals or some other perturbation had occurred. The statistical accuracy of the plotted points is approximately $\pm 15 \text{ cm}^2/\text{gm}$ uniformly. The data are plotted as absolute absorption coefficient versus energy, and the absolute scale error is probably of the order of $\pm 30 \text{ cm}^2/\text{gm}$ due to the method of estimating absorption coefficients. The scale
ARGON GAS
ABSORPTION
Fig. 46
was chosen to make the extrapolated absorption coefficients equal to 1460 and 148 cm\(^2\)/gm far to the short and long wavelength limits of the spectrum respectively. This could be done by a simple formula of the type

\[ \mu = -A \log \frac{I}{I_{\text{inc}}} \]  

(41)

with appropriate choice of \( A \). The empirical parameter \( A \) was calculated for both limits of the spectrum as a check, and the ratio \( A_2/A_1 \), compared to the jump ratio 1460/148. Including one point at (-11) volts not shown in Figure 45, the agreement was within 2 per cent. The zero energy point has been chosen to be 2.71 volts to the high energy side of the principal absorption line, following the system of Parratt.\(^\text{82}\) The actual data were recorded using the millimeter micrometer readings of the spectrometer. The voltage scale of the figure has been calculated using the formulae

\[
\Delta \Theta = 1000/3 \times 4.85 \times 10^{-6}
\]

(42a)

\[
\lambda = 2d \sin \Theta
\]

(42b)

\[
\Delta \lambda = 2d \cos \Theta \Delta \Theta
\]

(42c)

\[
V = \frac{hc}{e \lambda} \times 10^8
\]

(42d)

\[
\Delta V = -\frac{hc}{e \lambda^2} \Delta \lambda \times 10^8
\]

(42e)

where \( \Theta \) is in radians, \( S \) is the micrometer scale reading in mm, \( \lambda \) and \( d \) are in Angstroms, \( V \) is in volts, \( h \) is in joule-sec, \( c \) is in cm/sec, and \( e \) is in coulombs. The resulting calibration formula,
using standard values of the physical constants, $d_{\text{calcite}} = 3.029 \ \text{A}$, and $\lambda = 3.86 \ \text{A}$, is

$$\Delta V = + 6.238 (\Delta s + c)$$

(43)

where $c$ is the appropriate correction term in mm obtained from Figure 13.

3.4 Argon Solid Absorption

A leak developed in the cryostat system during the first helium filling, preventing the attainment of a high vacuum and doubling the helium evaporation rate. The argon film was formed as previously described, to give a transmission of about 40 per cent on the short wavelength side of the absorption edge (see Section 5.1 for discussion of "optimum" film thickness). Due to the limited time available to the experiment, data were recorded with the counting rate meter and Leeds and Northrup chart recorder, the micrometer screw being turned at approximately constant speed by hand. Data obtained were very crude but did show evidence of absorption structure in the solid which was confirmed by later experiments. After the leak had been repaired, two determinations of the structure of the absorption spectrum of solid argon in the region of the absorption edge were made, the two curves agreeing in all details. Figure 47 shows the combined result of these experiments with statistical errors indicated by brackets. The voltage scale of Figure 45 has been used, zero
volts corresponding to the series limit of the potassium-like optical levels of excited gaseous argon atoms. However, the scale has been greatly compressed to include the entire energy spectrum scanned in this experiment. The jump ratio of the absorption coefficients on the two sides of the absorption edge agreed with the value determined in the gas experiments within experimental error. This was taken as an indication of the uniformity of the solid argon film. No absolute determination of absorption coefficient could be made in this experiment but the data were fitted to the absolute scale by assuming the total absorption coefficient in the solid to be equal to that of the gas\textsuperscript{83} in the regions far from the absorption edge structure. Statistical error of each point is approximately $\pm 30 \text{ cm}^2/\text{gm}$ while the error in the absolute absorption scale is probably also about $\pm 30 \text{ cm}^2/\text{gm}$ as in Figure 45.

During these experiments, a series of measurements of the absorption of liquid helium was made. The spectrometer was set far (30 volts) to the long wavelength side of the argon absorption edge and the x-ray intensity recorded with and without helium in the absorption cell. Measurements were made quickly to prevent appreciable warming of the cell windows between helium fillings. No detectable change in transmission on the short wavelength side of the edge was observed, indicating that the argon film had no chance

\textsuperscript{83} Compton, A. H. and Allison, S. K., op. cit., p 512
to evaporate. Section 3.6 describes the results of the measurements on helium absorption as well as experiments on oxygen and nitrogen absorption. In addition to the absolute helium absorption at one point, about 1000 counts per point were taken at 1.5 volt intervals out to 45 volts from the argon edge to affirm that no structure in the helium transmission was present to confuse the argon spectrum obtained.

Evidence of possible Kronig type structure on the short wavelength side of the absorption edge seemed inadequate, so it was decided to continue the data out to several hundred volts from the absorption edge. In order to do this the center positions of the spectrometer axes had to be shifted slightly (1.5 degree) to smaller angles. Before the axes were moved the spectrometer was calibrated by recording the Fe Kα lines in the (2, +2) position. The absolute wavelength of the iron lines has been carefully measured by Bearden and Shaw. The positions of the peaks of the iron lines are recorded in Figures 46 and 47 for calibration references. The position of the Kα, line agreed precisely with that obtained in the initial alignment of the crystals.

In searching for Kronig structure in the absorption spectrum of solid argon a total of 6000 counts per point was accumulated with the points spaced at approximately 1.3 volt intervals. Figure 48 shows the absorption measurements made in searching for Kronig structure. The
voltage scale used is an extension of that used in Figure 46. The two curves were fitted by means of the iron and silver calibration lines mentioned. Relative absorption is plotted in Figure 48 in arbitrary units since no direct measurement of absorption coefficient is possible. No fine structure can be distinguished in the curve shown in Figure 48. The high dispersion, point by point method of x-ray registration is not as well suited to recording the broad, faint Kronig structure as are the photographic techniques.

A faint line was observed in the continuous spectrum from the gold target at 3.73 Å. The cadmium Lα line at 3.730 Å was selected as being the most probable of several possible lines including bismuth M_{111}^1 and potassium Kα_{1,2}.

To calibrate the spectrometer at the settings used for the far short wave side of the argon edge a silver target was prepared. Figure 49 shows the silver L_{α_2}, L_{α_3} and L_{α_5} lines recorded. Wavelengths of these lines in the silver L spectrum have been accurately measured by Parratt 85. The positions of these silver lines are marked in Figure 48.

Figure 50 shows the principal features of the argon absorption curves in the region of the absorption edge, with the gas and the solid absorption plotted to the same scale, and with the Fe Kα_1 calibration line indicated.

85. Parratt, L. C., Phys. Rev. 54, 99 (1938)
3.5 Absorption Edge Structure of Krypton

The spectrometer was adjusted to a Bragg angle of 8.2° and the tungsten target Machlett tube installed in the spectrometer base plate. The wavelength of the krypton absorption edge, 0.86 Å, is too short for air absorption to reduce the transmitted intensity appreciably. Accordingly the krypton gas absorption cell was clamped directly in front of the x-ray tube and the absorption edge structure measured through a 90 cm path of atmospheric air. Two experiments were performed, with 30 KV and then with 38.8 KV on the x-ray tube and 30 ma current. A total of 5000 counts per point were recorded on the high absorption side of the edge. The incident intensity was also recorded for each point. The krypton used for these and the subsequent experiments was high purity gas, although its exact analysis is unknown. It was obtained in sealed flasks whose markings showed that they had been used as spectroscopic standards.

Figure 51 shows the shape of the absorption edge observed. The zero volt point has been arbitrarily set at the calculated values of the series limit for the optical p states of rubidium similar to the calculation described by Shaw. No absolute absorption scale has been prepared since the pressure of the krypton gas in the cell was unknown. Absorption structure is plotted in arbitrary units, proportional to log I/I_trans. The energy coordinates of Figure 51 were calculated similarly to those of Figure 45 using the

86. Shaw, C. H., Phys. Rev. 57, 877 (1940)
formulae (41a---------e) and \( \lambda = 0.8637 \) A. The resulting dispersion equation is

$$\Delta \nu = 149.1 (\Delta s + c)$$

(44)

The first attempt to measure the absorption structure of solid krypton was successful only in locating the edge and affirming the technique of forming the krypton film. The edge had not yet been measured in the gas and the point chosen for monitoring the solid film thickness was inadvertently at too long a wavelength. A film was formed having a 30 per cent transmission on the long wavelength side of the krypton edge; intensities on the short wavelength side were too weak to measure. A considerable quantity of gas was evolved when the film was finally allowed to evaporate.

A second attempt to perform the experiment was terminated by a leak at the absorption cell windows. The cell would hold liquid nitrogen or oxygen with a small leak (spectrometer pressure 8 \( \times \) 10\(^{-6}\) mm), but was not adequate to hold liquid helium. The absorption of the two heavier liquids was then measured at 0.861 A as described in section 3.6.

The data on solid krypton absorption were finally taken after modifying the absorption cell by installing 5 mil beryllium windows. The cryostat was cooled to liquid hydrogen temperature and the krypton film formed. Figure 52 shows the resulting absorption structure in the solid krypton film, plotted to the same scale as Figure 51. The absorption units were made identical to those of
Figure 51 by fitting the curves at the long and short wavelengths far from the absorption edge structure. No absolute measurement of the wavelength of the absorption edge was made, the center value of 0.8637 Å being taken from the tables of Cauchois and Hulubei.


No measurements were made on the absorption of liquid hydrogen at this wavelength. It is presumed that the hydrogen absorption was without structure in the wavelength region studied. The hydrogen absorption was less than 3 per cent. Figure 53 shows the absorption of solid krypton in the region of the absorption edge, with the gas absorption curve superimposed for reference.

3.6 Measurements of Absorption Coefficients of Helium, Nitrogen and Oxygen

In the course of the absorption structure experiments, the absolute absorption coefficients of the liquified gases helium, nitrogen and oxygen were determined. Table XI lists the transmission of the three elements and the wavelengths at which it was measured. Statistical error in the transmission is also recorded.

The absolute mass absorption coefficient can be calculated from

$$
\mu = \frac{\ln \frac{I}{I_0}}{\rho x}
$$

where $\rho$ is the density of the absorber in $\text{gm/cm}^3$ and $x$ is the thickness of the absorption cell, 1.11 cm in this case. The absorption coefficients obtained are also recorded in Table XI. The
HRYPTON

ABSORPTION

ENERGY, ELECTRON VOLTS

MICROMETER SCALE (MM)
### TABLE XI

**Absorption: Liquid Helium, Oxygen, and Nitrogen**

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength</th>
<th>T</th>
<th>M0 X</th>
<th>( \rho ) ( \text{g} / \text{cm}^3 )</th>
<th>( \mu ) ( \text{cm}^2 / \text{g} )</th>
<th>( \mu_{\text{standard}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>3.87 A</td>
<td>.802 ± .008</td>
<td>221 ± .01</td>
<td>.1251* 1.59 2.90***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>.861 A</td>
<td>.063 ± .003</td>
<td>2.77 ± .04</td>
<td>1.14** 2.19 2.05***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>.861 A</td>
<td>.286 ± .003</td>
<td>1.25 ± .01</td>
<td>.808** 1.39 1.42***</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


*** Compton, A. H. and Allison, S. I., op cit, p 802. Values are interpolated from data given.

**** Victoreen, V. A., p 20, 1141 (1949)
absorption coefficients obtained here are in good agreement with those reported by Compton and Allison for neighboring wavelengths, except in the case of helium. A theoretical discussion of absorption coefficients was presented by Victoreen in a recent paper in which general formulae were derived, suitable for calculation of absorption coefficients. Tables were presented giving the absorption coefficients of the principal elements as a function of wavelength. The values in all cases tested were in good agreement with available experimental results. The theoretical absorption coefficient of helium at 3.86 Å is approximately 3.2 as interpolated from Victoreen's tables. Apparently the measurement of helium absorption reported here is in error, possibly due to rapid boiling in the absorption cell with resulting low helium density. A repeat experiment is contemplated using liquid helium at 1.5°K where the super fluid properties prevent bubbling in the liquid.
SECTION IV. INTERPRETATION OF RESULTS; CONCLUSIONS

4.1 Argon Absorption: Correction for Resolving Power

The data reported in Figure 45 show distinct absorption lines corresponding to the transitions ls→4p, ls→5p, ls→6p, as previously reported by Parratt. The statistical accuracy of the data of Figure 46 was not sufficient to resolve the third maximum. The width of the principal line observed can be obtained from Figure 45 directly by measuring the half width at half maximum absorption, to get 0.076 mm scale, or 0.475 ± 0.025 volts. The resulting line width is 0.95 ± 0.05 volts. The rocking curve width of Class I calcite crystals in the (1, -1) position at several wavelengths was reported by Parratt in an early paper. Interpolation of the data presented there gives a rocking curve width of 30 seconds of arc at 3.9 A, or 0.34 X units. In a later work Parratt showed that the contribution to the observed width, W, in X units of an x-ray line reflected from calcites in the (N,+N) position could be approximated by

\[
W'_{\text{CORRECTION}} (N,N) = -2.9 \frac{W'}{\text{OBSERVED}} (N,-N) \tag{46}
\]

For Class I calcites at 3.9 A, the correction is 0.45 X units, or 0.19 volts. Since Parratt reports the corrected width of the argon

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90. Parratt, L. G., Phys. Rev. 41, 561 (1932)

91. Parratt, L. G., Rev. of Sci. Inst. 6, 387 (1935)

92. Parratt, L. G., Phys. Rev. 41, 561 (1932)
lines to be 0.58 ev, his observed line width was apparently 0.77 ev. If the figure of 0.58 ev be taken for the true natural line width of the ls state of argon, (the contribution by the 4p state is negligible) then the contribution of the crystals used in the present work must have been of the order of 0.37 ev, making them definitely inferior crystals at this wavelength. No direct determination of the (1, -1) rocking curve width of these crystals was made at 3.9 A.

It is also significant to compare the observed absorption coefficients at the peak of the line. Parratt\(^\text{92}\) reports a peak absorption approximately 1.84 times the short wavelength continuous absorption, whereas that ratio was measured here to be 1.88±.10. It seems difficult to understand how the absorption peak could remain relatively high while the line is broadened by poor crystals.

The separation of the optical levels 4p→5p as measured from Figure 45 is 1.44 ev, identical with the value reported by Parratt\(^\text{92}\). The 5p→6p separation is 0.50 ev compared to Parratt's value of 0.53 ev.

Figure 46 shows the argon gas absorption as measured for wavelength calibration purposes. The entire spectrum was displaced 0.038 mm from that of Figure 45. However, in addition, the resolution seems much poorer. The principal line of Figure 46 is 1.05±0.05 ev wide, and has a peak to continuous absorption ratio of only 1.63. Although the adjustment of absolute absorption coefficients is
rather arbitrary, the possible errors do not account for the differences between Figures 45 and 46. It seems quite possible that some change occurred in the crystals.

The solid absorption curve shown in Figure 50 definitely represents transitions into some sort of continuum of empty states. The discrete exciton levels suggested for an absorption process of this type are completely obscured by the broad bands observed. Following the suggestion of Richtmyer, Barnes and Ramberg\(^{93}\) the width of the


sharp leading edge of the principal feature of the solid absorption spectrum has been determined. The width from 1/4 to 3/4 maximum absorption is 0.82±0.05 ev. This is surprisingly less than the width of the 4p line as measured in the gas, but is in excellent agreement with the 0.77 ev predicted by Parratt's\(^{92}\) results. Figure 54 shows the arc tangent curve suggested by Richtmyer\(^{93}\) fitted to the argon absorption edge. The arc tangent curve has the form

\[
M = 150 + 2400 \left[ \frac{1}{2} - \frac{1}{\pi} \arctan \left( \frac{2E - 5.18}{0.52} \right) \right]
\]  \hspace{1cm} (47)

Apparently the absorption observed in the solid has one or more "lines" superimposed on the continuum of empty levels, since neither the arc tangent curve, nor discrete optical lines alone are sufficient to describe the observed spectrum.

Figure 55 shows an attempt to resolve the principal features of
Mass Absorption Coefficient

Solid Argon Absorption

Fig. 55
the argon absorption spectrum into components. The absorption maxima near the discontinuity are clearly asymmetrical, having a sharp rise on the low energy side and a gentle slope on the high energy side. The resolution of the principal absorption band into two similar bands is believed to be justified by the data. For convenience, the various bands of Figure 55 have been labeled A, A', B, C, D respectively from the main edge. The \((A, A')\) notation of Veldkamp has been used to designate the absorption maxima and minima. Table XII lists the positions of these features and their energy relative to the ionization potential of the excited gaseous argon atom.

### 4.2 Krypton Absorption

The width of the krypton absorption edge of Figure 51 is \(2.5 \pm 0.3\) ev using the \(1/4, 3/4\) criterion suggested by Richtmyer, Barnes and Ramberg. Admittedly this can only be approximate since the transitions involve discrete optical levels rather than a continuum. The crystal correction for Class I calcites at \(0.86\) Å can be obtained as in Section 4.1, equation 45. The \((1, -1)\) width is interpolated from Parratt's data to be 6.1 seconds of arc, or 0.090 \(X\) units.
## TABLE XII

**Argon Absorption Structure**

<table>
<thead>
<tr>
<th>Band</th>
<th>Position</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A edge</td>
<td>12.8 mm</td>
<td>-2.8 volts</td>
</tr>
<tr>
<td>A' edge</td>
<td>12.9 mm</td>
<td>-2.2</td>
</tr>
<tr>
<td>B edge</td>
<td>14.1 mm</td>
<td>5.3</td>
</tr>
<tr>
<td>C edge</td>
<td>14.7 mm</td>
<td>9.0</td>
</tr>
<tr>
<td>D edge</td>
<td>16.0 mm</td>
<td>17.2</td>
</tr>
<tr>
<td>AA' peak</td>
<td>13.0 mm</td>
<td>-1.6</td>
</tr>
<tr>
<td>B peak</td>
<td>14.4 mm</td>
<td>7.2</td>
</tr>
<tr>
<td>C peak</td>
<td>15.0 mm</td>
<td>19.9</td>
</tr>
<tr>
<td>D peak</td>
<td>16.6 mm</td>
<td>20.9</td>
</tr>
<tr>
<td>α</td>
<td>14.0 mm</td>
<td>4.7</td>
</tr>
<tr>
<td>β</td>
<td>14.6 mm</td>
<td>8.4</td>
</tr>
<tr>
<td>γ</td>
<td>16.0 mm</td>
<td>17.2</td>
</tr>
<tr>
<td>δ</td>
<td>17.8 mm</td>
<td>28.4</td>
</tr>
</tbody>
</table>
The correction is calculated to be 0.049 $X$ units, 3.4 seconds of arc, or 0.76 ev, so the "natural" width of the edge is approximately $1.7 \pm 0.3$ ev. This is somewhat less than the estimate of 2.07 ev by Shaw, but is not in serious disagreement due to the approximations required. Shaw also sketches the resolution of the edge into component lines.

The solid krypton absorption curve of Figure 53 differs considerably from the solid argon absorption. Only two component bands appear. The principal absorption edge has an arc tangent slope which can be seen to be identical with that of the gas absorption but displaced from it 4.6 volts to higher energies. The second absorption band does not have the characteristic edge. Table XIII gives the relative positions of the two bands observed, measured from the ionization potential of the excited krypton gas atom. It is significant that no absorption occurs in solid krypton to energies less than the gas ionization potential, whereas an absorption maximum occurs at -1.6 ev in solid argon.

4.3 **Simplified Theory of Kronig Structure**

Fine structure in the x-ray absorption spectrum of a crystal occurs because of the diffraction of the conduction electrons by the crystal lattice. Not all momenta are available to the electrons
TABLE XIII

**Krypton Absorption Structure**

<table>
<thead>
<tr>
<th>Band</th>
<th>Position</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A edge</td>
<td>12.760 mm</td>
<td>2.4 ev</td>
</tr>
<tr>
<td>A peak</td>
<td>12.780</td>
<td>5.4</td>
</tr>
<tr>
<td>B peak</td>
<td>12.850</td>
<td>15.8</td>
</tr>
<tr>
<td>X</td>
<td>12.810</td>
<td>9.8</td>
</tr>
</tbody>
</table>
released from the inner atomic core; those momenta which reflect from the crystal planes are forbidden and x-ray transitions which would result in such momenta do not occur. The actual calculation of the relative transition probabilities in any real crystal is very complicated; however, Kronig\textsuperscript{98} pointed out that in the limiting case in which the electrons were nearly free, the energies corresponding to minimum transition probabilities could be estimated directly from knowledge of the crystal structure. The forbidden momenta correspond exactly with the Brillouin zone boundaries predicted by the crystal symmetry.

The Schroedinger equation for the motion of the electron in the lattice is

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi + (\mathbf{V} - E) \psi = 0 \tag{48}
\]

where \( \mathbf{V} \) has the periodicity of the lattice. According to a theorem of Bloch, the solutions of 48 may be written

\[
\psi(r) = X(r) e^{2\pi i \mathbf{k} \cdot \mathbf{r}} \tag{49}
\]

where \( X(r) \) has the same periodicity as \( \mathbf{V} \). A perturbation calculation may be made using

\[
\psi = \psi^0 + \psi' + \ldots
\]

\[
E = E^0 + E' + \ldots
\]

\[
V = V^0 + V' + \ldots \tag{50}
\]
If $V$ is chosen to be constant and equal to zero by appropriate choice of energy scale, the free electron energy is obtained directly, as

$$E^0 = \frac{\hbar^2 k^2}{2m}$$

(51)

and

$$\psi^0 = \frac{1}{\sqrt{2}} e^{2\pi i \cdot \mathbf{k} \cdot \mathbf{r}}$$

(52)

It turns out that the $\psi^0$ so obtained are not adequate for the solution of the perturbed equation, since they lead to terms of the type

$$E' = \frac{1}{e^{\mathbf{k} \cdot \mathbf{r}} \frac{e^{2\pi i (\mathbf{k}' \cdot \mathbf{r})}}{E_k - E_k'}} \int e^{2\pi i (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} V' d\mathbf{r}'$$

(53)

which blow up when $(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}$ equals an integer and $E_k$ equals $E_k'$. A new set of $\psi$ functions can be formed from the $\psi^0$ however, so that the numerators of the offending terms in the sum of equation (53) vanish. With this modification, the perturbing energy $E'$ can be calculated and the resulting total energy is similar to that shown in Figure 2. Of more concern here however are the conditions on the $k$ vectors at the discontinuities in the energy. They are

$$(\mathbf{k}' - \mathbf{k}) \cdot a = \text{an integer}$$

(54)
where \( \mathbf{a} \) is a lattice vector and
\[
\frac{\left| \mathbf{k}' \right|^2}{\left| \mathbf{k} \right|^2} = \frac{\left| \mathbf{k}' \right|^2}{\left| \mathbf{k} \right|^2}
\] (55)

The equations 54 and 55 are just the conditions for Bragg reflection of the electron wave from the crystal lattice and may also be written
\[
\mathbf{M} : (\mathbf{M} \pm 2\mathbf{k}) = 0
\] (56)

if \( \mathbf{M} \) is a lattice vector of the reciprocal lattice equal to \( (\mathbf{k}' - \mathbf{k}) \).

The mean energy at the discontinuity is obviously \( E^0 \), from which it follows that
\[
E_{\text{dis}}^0 = \frac{\hbar^2}{2m} \frac{\mathbf{k}^2}{\mathbf{M}^2} = \frac{\hbar^2}{8} \frac{\mathbf{M}^2}{\mathbf{m}^2}
\] (57)

or
\[
E_{\text{dis}}^0 = \frac{\hbar^2}{8m} \left( \frac{\mathbf{H}^2}{d_1^2} + \frac{\mathbf{K}^2}{d_2^2} + \frac{\mathbf{L}^2}{d_3^2} \right)
\] (58)

where \( \mathbf{H}, \mathbf{K}, \mathbf{L} \) are the Miller indices of the particular Bragg reflecting plane involved and the \( d \)'s are the lattice parameters.

Sandstrom\(^{99} \) has taken advantage of this result to compare the observed structure at the aluminum K edge with that predicted by Kronig theory. Results are in good agreement with the theory for energies greater than the Fermi energy of the conduction electrons.

Argon crystallizes in a face centered cubic lattice for which

---

99. Sandstrom, A., Ach. f. Mat. Ast. och Fys. 28A No 12 (1941) and 29B No 3 (1942)
equation (58) becomes

\[ X = \frac{h^2}{8md^2} (H^2 + K^2 + L^2) \]  

(59)

Because of the face centering, certain reflections are extinct\(^{100}\)


and for reflection to occur it is necessary that all three sums, \(H+K, K+L, L+H\), be even. This limits the usable planes to the fifteen shown in Table XIV plus those with larger indices. The lattice spacing of argon is 5.43 Å from which the first energy discontinuity can be calculated to be

\[ E = 3h^2/8md^2 = 6.12 \times 10^{-12} = 4.03 \text{ electron volts} \]  

(60)

Table XIV lists the energies of minimum absorption predicted by Kronig theory. Figure 56 shows the minima of Table XIV superimposed on the solid argon absorption of Figure 47. To the energy scale of the calculated Kronig structure has been added a constant potential to fit the points to the minima in the observed absorption spectrum. A limited agreement between calculated and observed structure is observed in Figure 56.

Similar calculations for the krypton lattice, using \(d=5.59\) Å, give the results shown in the last column of Table XIV. Figure 57 shows these results as fitted to the krypton spectrum.

4.4 Conclusions

The absorption spectrum of solid argon consists of several
TABLE XIV

Forbidden Energies of Crystalline Argon

<table>
<thead>
<tr>
<th>Planes</th>
<th>$H^2 + K^2 + L^2$</th>
<th>$E_{\text{argon}}$</th>
<th>$E_{\text{argon}}^{(\text{avg})}$</th>
<th>$E_{\text{krypton}}$</th>
<th>$E_{\text{krypton}}^{(\text{avg})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>3</td>
<td>4.0</td>
<td>4.8</td>
<td>3.8</td>
<td>4.5</td>
</tr>
<tr>
<td>002</td>
<td>4</td>
<td>5.7</td>
<td></td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>002</td>
<td>8</td>
<td>10.7</td>
<td>10.7</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>113</td>
<td>11</td>
<td>14.8</td>
<td>15.4</td>
<td>14.0</td>
<td>14.5</td>
</tr>
<tr>
<td>222</td>
<td>12</td>
<td>16.1</td>
<td></td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>004</td>
<td>16</td>
<td>21.5</td>
<td>21.5</td>
<td>20.3</td>
<td>20.3</td>
</tr>
<tr>
<td>133</td>
<td>19</td>
<td>25.5</td>
<td>26.2</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>024</td>
<td>20</td>
<td>26.9</td>
<td></td>
<td>25.4</td>
<td>24.7</td>
</tr>
<tr>
<td>224</td>
<td>24</td>
<td>32.2</td>
<td>32.2</td>
<td>30.4</td>
<td>30.4</td>
</tr>
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<td>333</td>
<td>27</td>
<td>36.2</td>
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<td>34.2</td>
<td>34.2</td>
</tr>
<tr>
<td>115</td>
<td>27</td>
<td>36.2</td>
<td></td>
<td>34.2</td>
<td></td>
</tr>
<tr>
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<td>32</td>
<td>42.9</td>
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<td>40.5</td>
<td>40.5</td>
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<tr>
<td>135</td>
<td>35</td>
<td>47.0</td>
<td>47.6</td>
<td>44.4</td>
<td></td>
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<tr>
<td>244</td>
<td>36</td>
<td>48.3</td>
<td></td>
<td>45.6</td>
<td>45.0</td>
</tr>
<tr>
<td>006</td>
<td>36</td>
<td>48.3</td>
<td></td>
<td></td>
<td>45.6</td>
</tr>
</tbody>
</table>
Mass
Absorption
Coefficient

Fig. 56
Absorption

Solid Krypton Absorption

Fig. 57
absorption bands including one very strong band at the absorption edge. The existence of a sharp edge on the long wavelength side of this band is established.

It has been suggested that the absorption spectrum of insulating crystals should show sharp lines corresponding to transitions into impurity or exciton levels closely bound to the ionized atom. If this be true, such levels might be expected to have a width similar to the optical levels of the isolated gas atom, but spaced more closely by the factor $\frac{1}{\alpha^2}$, where $\alpha$ is the high frequency dielectric constant. Such sharp closely spaced lines may in fact be responsible for the unusual shape of the principal absorption feature of the solid argon spectrum. This sharp edge is not completely described by transitions into a continuum of states of approximately equal transition probabilities, nor by transitions into lines alone. Resolution of this feature into a band and an exciton series requires information about the high frequency dielectric constant $\alpha$.

The sharp rise in absorption at the main absorption edge agrees closely with the arc tangent form suggested by Tichtmyer, Barnes and Rumberg except near the absorption maximum. The arc tangent form is calculated on the basis of a sharp discontinuity in the density of states at the edge of a band of uniform density of states as shown in Figure 56(a). The absorption of solid argon indicates a sharp discontinuity in the density of states curve approximately
of the type shown in Figure 38(b). Skinner has shown that the density of states of an insulator band is assymetrical, but with the sharp discontinuity on the high energy edge. A discontinuity of the type observed on the low energy side of the absorption band might reasonably be expected in a metal, where it results, not from the density of states function, but from the effect of the sharp Fermi level.

An attempt to correlate the observed absorption minima in the argon spectrum with those predicted by Kronig theory was made. The zero energy point of the Kronig series was adjusted arbitrarily to give the best agreement with the observed spectrum. The first minimum (α) can not be fitted, but the three succeeding minima (β, γ, δ) agree fairly well with the predicted strong Kronig minima. Other minima, predicted by the Kronig theory to be weak, are not positively observed. The spacing of successive minima in the observed spectrum, about 11 volts, agrees closely with the Kronig prediction. The zero of the energy scale for the Kronig lines is set at +2.9 volts relative to the ionization energy of the free atom.

The absorption spectrum of solid krypton is surprisingly different from that of argon. The initial edge is again steep but
the maximum absorption is much less. Only two strong absorption bands are observed having nearly equal intensities. The width of the principal band is about 5 volts. The principal absorption edge of solid krypton occurs at approximately +3 volts from the ionization potential of the gas, whereas the solid argon edge occurs at -1.6 volts from the ionization potential of argon gas.

The Kronig series of absorption minima cannot be fitted as well to the krypton spectrum as to the argon because of the smaller number of observed minima in the krypton spectrum. The zero energy point of the Kronig series was adjusted arbitrarily to give the best agreement with the observed spectrum. The two minima observed are at approximately 10 volt spacing, in agreement with the Kronig values.

The high resolving power two crystal spectrometer is well suited to measurements of the absorption structure details in the region of the absorption edge. The instrument lends itself to measurements of band shapes in which the confirmation of "edges" is of first importance. In the present work the existence of sharp discontinuities, corresponding to band edges, in the solid argon spectrum is clearly shown and calculations affirm that a continuum of energy states must exist, at least in the region of the observed edges.

For a more complete picture of the density of electron states in the solid, two additional experiments must be performed. The high energy Kronig structure is very weak and the lines reported by
other observers are of irregular shape. The high resolution spectrometer is not well suited to the investigation of this phenomenon. A single crystal, photographic registration instrument would undoubtedly be better suited to such measurements since resolving power could be exchanged for intensity. Precise determination of relative intensities and interesting structure could then be undertaken using a high resolution instrument, without the excessive counting time consumed in scanning the spectrum.

An experiment of great significance in understanding the nature of the electron bands is the measurement of the emission spectrum in the region of the absorption discontinuity. Such measurements would demonstrate the existence of the insulator gap in solids such as argon, and might also be more fruitful in demonstrating the existence of exciton levels than the absorption measurements have been. Exciton levels are predicted to exist below each band, filled and unfilled, when the band structure is observed by ionizing a lattice atom.

Measurements of the absorption spectrum at the L absorption edges, when coupled with data on the K edge structure, might be expected to give additional understanding of the effect of screening on the absorption transitions observed. The impurity effect produced by an L ionized atom in the solid should be considerably less than that of a K ionized atom and the possible exciton states should lie much closer to the bands. The krypton L absorption edges lie in the
6.5 Å region and so may be experimentally accessible for absorption measurements using quartz crystals. The argon L edges are found near 50 Å and are experimentally impossible with the present apparatus. Although no K absorption structure data is available for Xenon ($\lambda = 36$ Å), the L edge structure at 2.4 Å is readily available and will probably be investigated soon. The L edge structure has the additional advantage of showing the effect of selection rules on the absorption transitions. The $L_1$ transitions are of $2s \rightarrow np$ character while the $L_2$, $L_3$ transitions are $2p \rightarrow ns$, $nd$ types.

Additional rocking curve data on the calcite crystals are necessary before attempting more precise determinations of line widths and edge widths. A set of measurements of the $(l, -l)$ widths as a function of wavelength is required to determine precisely the contribution of the crystals to the observed widths.
5.1 Optimum Absorber Thickness

Parratt has suggested that the optimum thickness of the absorber be that which gives the greatest contrast between two points whose absorption coefficients are $\mu_1$ and $\mu_2$. From this, the difference in intensity observed is given by

$$I = I_1 - I_2 = I_0 (e^{-\mu_1 x} - e^{-\mu_2 x})$$

(61)

and

$$\frac{\delta I}{I_0} = (\mu_2 e^{-\mu_1 x} - \mu_1 e^{-\mu_2 x}) \rho \delta x$$

(62)

For maximum $I$, $\delta I = 0$, and

$$\mu_2 e^{-\mu_1 x_0} = \mu_1 e^{-\mu_2 x_0}$$

(63)

$$\ln \mu_2 - \ln \mu_1 = (\mu_2 - \mu_1) \rho x_0$$

(64)

and the optimum thickness, $x_0$, is given by

$$x_0 = \frac{1}{\rho} \frac{\ln \mu_2 / \mu_1}{\mu_2 - \mu_1}$$

(65)

A more significant definition of the optimum thickness is one based on error considerations. That is, the optimum thickness is that which gives the smallest statistical deviation in $\mu$ for a given
observation time. For the purposes of calculation the incident intensity is assumed to be known precisely, in which case
\[ \mu \rho x = \ln I_o - \ln I \]  \hspace{1cm} (66)
and
\[ \rho x \Delta \mu = - \frac{\Delta I}{I} \]  \hspace{1cm} (67)
\[ \frac{\Delta \mu}{\mu} = \frac{\Delta I}{I} \ln \frac{I}{I_o} \]  \hspace{1cm} (68)

The intensity I is recorded as N total counts with a statistical deviation \( \sqrt{N} \). It is convenient to define \( \frac{\Delta \mu}{\mu} \equiv \varepsilon \), the expected relative error in the absorption coefficient \( \mu \); and in \( I/I_o = T \), the transmission of the absorber. With these substitutions equation 68 above becomes
\[ \varepsilon = \frac{\sqrt{N}}{\sqrt{N} \ln T} = \sqrt{\frac{N}{N \ln T}} \]  \hspace{1cm} (69)

Since the observed number of counts \( N \), is obtained from the number of counts incident, \( N_o \), by
\[ N = T N_o \]  \hspace{1cm} (70)
equation 69 becomes
\[ \varepsilon^2 = \frac{1}{N_o T (\ln T)^2} \]  \hspace{1cm} (71)
The optimum transmission can be defined from equation (71) as that value of \( T \) which minimizes \( \varepsilon \). Since \( \varepsilon \) is everywhere positive,
equation (71) can be differentiated directly.

\[ 2N_0 \epsilon \frac{d\epsilon}{dT} = -\frac{1}{(T \ln T)^2} - \frac{2T}{(T \ln T)^3} = 0 \]  

(72)

Thus

\[ \ln T = -2 \]  

(73)

\[ T = 0.135 \]  

(74)

This result may be substituted in equation (71) to give

\[ \epsilon^2 N_0 = 1.85 \]  

(75)

Thus for an \( \epsilon \) equal to 1 per cent, 18,500 counts must be incident on the absorber and 2500 counts will be transmitted.

5.2 Properties of Argon and Krypton

Ditchburn and Gilmour report the vapor pressure curve of argon to be given by

\[ \log_{10} P_{\text{mm}} = -\frac{A}{T} + C \]  

(76)

where

\[ A = 357.7, \ C = 6.970 \] from 84 to 90 K and
\[ A = 412.5, \ C = 7.622 \] from 70 to 84 K.

The melting temperature of argon is 83.9 K and the heat of fusion is measured to be 1120 joules/gm atom. The heat of fusion calculated
from the equation of state is \( \frac{1050 \text{ joules}}{\text{gm atom}} \).

A similar equation for krypton between the triple and critical points was presented by Meinuisen and Crommelin 105.

\[
\log P_{\text{atm}} = -899.979/T - 12.55400 \log T + 31.50311 + 0.0175105T \quad (77)
\]


No data are available on vapor pressures of these gases at low temperatures. A solid argon film was formed on helium cooled windows in one experiment after the liquid helium had evaporated, the temperature presumably being in the 15° to 25°K region. Experience with another cryostat offered some basis for estimating the warm up time of the cryostat used for the absorption experiments. The argon films evaporated rapidly at temperatures in the 30°- 50°K region. The solid krypton film was formed at 20°K (liquid hydrogen) without any detectable vapor pressure effects. It, too, evaporated somewhere below solid oxygen temperature.

Figure 59 is a plot of the measured absorption coefficients of strontium, krypton and bromine from which the jump ratio at the krypton K edge can be estimated. Absorption coefficients of 162 and 20.5 are obtained from the graph, yielding a jump ratio of 7.9.

5.3 Theory of Van der Waals Forces for Noble Gases

The following calculations follow essentially these outlined by
Margenau and Seitz. Many of the original calculations were

106. Margenau, H., Rev. Mod. Phys. 11, 1 (1939)

107. Seitz, F., op. cit., p 392

made by F. London.


The individual noble gas atoms consist of closed electron
shells and hence have no static dipole or multipole moments.
However, since the average uniform charge density is obtained by
motions of the electrons in the charge cloud the atom does instan­
taneously have electric force moments which act on the electron
distributions of neighboring atoms, tending to produce a phase
relationship between the charge clouds. This polarization is respon­
sible for the Van der Waal's attractions.

For an electron cloud of \( n \) electrons the field at a point \( R \)
distant from the nucleus is given by

\[
\phi = \frac{2}{R^3} \sum e_i \frac{1}{R^3} \left( \frac{x}{R} \cdot \sum e_i x_i \sum e_i j_i + \frac{7}{R} \sum e_i g_i \right) \\
+ \frac{1}{R} \left( \frac{3x^2}{R^2} - 1 \right) \sum e_i x_i^2 + \ldots + \frac{3xy}{R^2} \sum e_i x_i y_i + \ldots \Bigg) \\
+ \frac{1}{R^4} \left[ \text{etc.}\right]
\]

(78)

The potential terms above are, in order, the static potential, \( (1/R) \)
the dipole potential \( (1/R^2) \), the quadrupole potential \( (1/R^3) \) and so
forth.
The interaction energy occurring when a second similar charge distribution is placed at \( R \) is given by

\[
V = \sum_j \varepsilon_j \Phi(R + \rho_j)
\]

(79)

To simplify the calculation, we assume that \( R \gg \rho_j \), that \( \varepsilon \varepsilon_i = \rho \rho_j = 0 \) and that \( \rho_i = \rho j = 0 \) for all positive charges. Then the potential energy is given by

\[
V = -\frac{1}{R^3} \sum_{ij} \varepsilon_i \varepsilon_j \left( \rho_i \rho_j - x_i \rho_j - y_i \eta_j \right)
+ \frac{3}{2R^2} \sum_{ij} \varepsilon_i \varepsilon_j \left[ \rho_i^2 \rho_j - 2 \rho_i \rho_j + 2 \left( x_i \rho_j + 2 \eta_i \eta_j - 3 \rho_j \rho_j \right) \right]
+ \frac{3}{4R^2} \sum_{ij} \varepsilon_i \varepsilon_j \left[ \rho_i^2 \rho_j + 2 \left( y_i \rho_j - 3 \rho_j \rho_j \right) \right]
+ \ldots
\]

(80)

where Latin letters refer to electrons of one atom, and Greek letters refer to electrons of the other atom. The \( \rho_i \) and \( \rho_j \) axes are taken parallel to \( R \). The expression for \( V \) converges only if the \( r \)'s and \( \rho \)'s are smaller than \( R \), which is the equivalent of requiring the charge distributions not to overlap. Figure 60 shows the radial electron distribution of argon as observed and as calculated using the Hartree method. The assumption that the electron clouds are discrete in the solid (whose lattice distance is 5.43 Å) is clearly justified.

Simplification of equation (80) has been attempted by several
Electron density of argon

Fig. 60
The resulting interaction energy is then obtained from \( (F^2)_{\text{ave}} \) as

\[
v = - \alpha \left( 2p^2/R^6 + 3t^2/R^8 + \ldots \right)
\]  

(82)

where \( p = \sum e_i \gamma_i \) and

\[
t^2 = (\sum e_i x_i^3) + (\sum e_i y_i^3) + \ldots - (\sum e_i x_i^2) - (\sum e_i y_i^3) - (\chi)
\]  

(83)

and the \( x_i, y_i, \tau_i \) refer to either atom. Strictly speaking the quantity \( (F^2)_{\text{ave}} \) should be replaced by \( (F e^{-\frac{F}{kT}})_{\text{ave}} \) in which (82) above is only the first term.

The more rigorous method employed by London was to calculate the mean value of \( V \) from equation (80) using the quantum mechanical method and \( \psi \) functions of the unperturbed, isolated atoms. In this case, if \( \psi_\lambda \) is the state function describing the electron density
of the charge clouds in their unperturbed state then the contribution to the total energy of the system by the interaction is given by

$$\delta E = \int \psi_k^* \psi_\lambda \, d\tau + \sum_i \left( \int \psi_k^* \psi_i \, d\tau \right)^2 \frac{\epsilon_k - \epsilon_i}{E_k - E_i}$$

(84)

The $\psi$ functions of the unperturbed atoms are given by products of the spherical harmonics used to describe the individual charge clouds as

$$\psi_k = \mathcal{P}_l^m (\cos \Theta_1) \mathcal{P}_{l_1}^{m_1} (\cos \Theta_2)$$

(85)

For convenience in calculating, consideration will be limited to the $1/R^3$ term of equation (80) which may be written

$$v = e^2 / R^3 \left( r_1 \sin \Theta_1 \cos \Phi_1, r_2 \sin \Theta_2 \cos \Phi_2 - 2r_1 \cos \Theta_1 \cos \Theta_2 \right)$$

(86)

where $r_1 \sin \Theta_1 \cos \Phi_1 \equiv X_i \equiv X_i$, etc.

For atoms with closed electron shells, the $\psi_k$ are S states and the matrix elements, $(k_1|v|k_2)$ of the dipole energy vanish. The interaction energy is then

$$\delta E = e^2 \sum_{i,j} \left[ \frac{\lambda_{i,m_i} \lambda_{j,m_j} \lambda_1 \lambda_2}{R^3} \right] \frac{\epsilon_i - \epsilon_j}{\epsilon_i - \epsilon_j} \left( \frac{\lambda_{i,m_i} \lambda_{j,m_j} \lambda_1 \lambda_2}{R^3} \right)$$

(87)

The matrix elements in equation (87) can be calculated using various approximation methods and the properties of the $\psi_i$'s. In the case of the noble gases considered here, it will be assumed that the atoms have spherical symmetry in the states $\lambda_1$ and $\lambda_2$; therefore it can
be shown that all the cross product terms in the squared expression above, such as \((\ell', m', \lambda', \mu_i)(\ell, m, \lambda, \mu_i)\), vanish when summed over \(\lambda', \mu_i\). Also,

\[
\sum_{\mu_i} \vert (\ell_i, m_i, \lambda_i, \mu_i) \vert^2 \leq \sum_{\lambda_i} \vert (\lambda_i) \vert^2 = \sum_{\lambda_i} \vert (\ell_i, \lambda_i) \vert^2
\]

\[
\equiv \frac{1}{3} \vert (\ell_i / R | \lambda_i) \vert^2
\]  

(88)

The interaction energy of equation (88) simplifies to

\[
\delta \mathcal{E} = \frac{2 \mathcal{E}^y}{3 R^3 \lambda_i \lambda_i} \leq \sum' \left( \frac{\ell_i | R | \lambda_i}{} \right) \left( \frac{\lambda_i | R | \lambda_i}{} \right)
\]

\[
= \frac{1}{3} \sum \frac{f_{\ell_i} \lambda_i}{\ell_i \lambda_i}
\]

(89)

London suggested a convenient way of simplifying equation (89) by taking advantage of known oscillator strengths and avoiding the calculation of matrix elements entirely. By definition

\[
\frac{f_s (x)}{f_s (y)} = \frac{f_s (x)}{f_s (y)} \equiv \frac{1}{3} \frac{f_{\ell_i} \lambda_i}{\ell_i \lambda_i}
\]

(90)

Substitution of (90) into (88) yields

\[
(\ell_i / R | \lambda_i)^2 = \frac{3}{2} \frac{K^2}{m} \frac{f_{\ell_i} \lambda_i}{(E_{\ell_i} - E_{\lambda_i})}
\]

(91)

Equation (89) then becomes

\[
\delta \mathcal{E} = \frac{3 \mathcal{E}^y K^2}{2 R^3 m^2 \lambda_i \lambda_i} \left( \frac{f_{\ell_i} \lambda_i | f_{\lambda_i} \lambda_i}{} \right) \left( \frac{E_{\ell_i} - E_{\lambda_i}}{} \right) \left( \frac{E_{\lambda_i} - E_{\ell_i}}{} \right) \left( \frac{E_{\ell_i} - E_{\lambda_i}}{} \right)
\]

(92)

where \(M\) is the electron mass, \(h\) is the Planck constant \((\frac{\hbar}{2 \pi})\), \(f_{\lambda_i} \lambda_i\) the oscillator strength for the \(\ell_i \rightarrow \lambda_i\) transition, and the \(E_i\)'s are the steady state energies of the \(\ell, \lambda\) states.

The \(f\) values needed to evaluate (92) directly can often be
obtained from the dispersion formula

$$\alpha_l = \frac{e^2 \hbar^2}{m} \sum \frac{f_i}{(E_i - E_f)^2 + \hbar^2 \omega^2}$$  \hspace{1cm} (93)

London approximated the effect of the equation (93) by assuming that it could be simplified to the single term

$$\alpha_l = \frac{e^2 \hbar^2}{m} \frac{f_i}{\Delta E_i}$$  \hspace{1cm} (94)

Substitution of (94) into (92) using $\Delta E_i = \hbar \nu_i$ yields

$$\Delta E = \frac{3}{2} \frac{\hbar^2 \nu_i \nu_2}{K (\nu_i + \nu_2)} \alpha_l \alpha_l$$  \hspace{1cm} (95)

For the simple lattice in which the atoms are identical $\nu_i = \nu_2$ and $\alpha_l = \alpha_l$, so $\Delta E$ becomes

$$\Delta E = \frac{3 \hbar \nu \alpha^2}{4 K^6} = \frac{C_1}{R^6}$$  \hspace{1cm} (96)

Using a similar technique, Margenau calculated the quadrupole interaction and got a term

$$\Delta E = \frac{15}{4} \frac{\alpha^2 (\hbar \nu)^2}{f e^2 R^8} = \frac{C_2}{R^8}$$  \hspace{1cm} (97)

Numerical values of $\hbar \nu$, $\alpha$, and $f$ are available for argon and krypton and may be used to calculate the dipole and quadrupole energies. When the interaction energy is expressed as

$$\Delta E = - \frac{C_1}{R_6} - \frac{C_2}{R_8}$$  \hspace{1cm} (98)

the constants $C_1$ and $C_2$ may be calculated as shown in Table XV.
### TABLE XV

**Van der Waal's Constants for Argon and Krypton**

<table>
<thead>
<tr>
<th>Element</th>
<th>$h\nu$ (cm$^{-2}$)</th>
<th>$f$</th>
<th>$C_1$ (erg cm$^6$)</th>
<th>$C_2$ (erg cm$^8$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>$1.63 \times 10^{-24}$</td>
<td>4.54</td>
<td>$5.54 \times 10^{-10}$</td>
<td>$1.20 \times 10^{-76}$</td>
</tr>
<tr>
<td>Krypton</td>
<td>2.46</td>
<td>4.90</td>
<td>107</td>
<td>275</td>
</tr>
</tbody>
</table>
An estimate of the possible errors in the coefficients is shown by
Slater and Kirkwood's values of $C_1$ for argon and krypton respectively:

Slater, J. C., and Kirkwood, J. G., Phys. Rev. 37, 682 (1931)

69.5 and 129, compared to Margenau's 55.4 and 107. Even greater
uncertainty exists in $C_2$.

The total cohesive energy of the face centered cubic lattice
of argon can be calculated in the straightforward Madelung fashion.

The energy contributed by the first 62 ($r = d$) near neighbors is

$$E = 110.907 \frac{C_1}{d^6} + 200.429 \frac{C_2}{d^8}$$

(99)

For large distances from the source atom, the atomic distribution is
practically uniform and

$$\Delta E = - \frac{C_i}{R^{4+2i}} \frac{dN}{dV} \Delta V$$

(100)

where

$$\Delta V = 4\pi R^2 \Delta R$$

(101)

and

$$\frac{dN}{dV} = 4 \text{ atoms/unit cell} = 4/d^3$$

(102)

$$\delta E = \sum \Delta E = \int_{r_d}^{\infty} \frac{16\pi C_i}{R^{4+2i}} \frac{dR}{d^3}$$

(103)

$$= \frac{16\pi C_i}{(1+2i)} \frac{n^{4+2i}}{n^{4+2i}} d^{4+2i}$$

(104)

Equation 104 gives a "tail" term, $0.626 d^6$, for atoms as far
away as $3d$ and $0.31C_2/d^8$ for atoms as far away as $2d$. 

London calculated the dipole contribution due to $^{45}S$ near neighbors ($n = 3$) and got 117.42. From these approximations, the binding energy of the lattice is

$$E = \frac{118}{2} N \frac{C_1}{a_6} + \frac{205}{2} N \frac{C_2}{a_8}$$

(105)

Substitution of numerical values in equation (105) yields, for argon with $d = 5.43$ Å,

$$E_{\text{calc}} = 1.84 + 0.23 \text{ K cal/mole}$$

(106)

and

$$E_{\text{obs}} = 1.77 \text{ K cal/mole}$$

(106a)

and for krypton with $d = 5.59$ Å,

$$E_{\text{calc}} = 2.98 + 0.43 \text{ k cal/mole}$$

(107)

and

$$E_{\text{obs}} = 2.67 \text{ k cal/mole}$$

(107a)

The repulsive energy of neon has been calculated by Deitz, using

the equation

\[ V(R) = 1.888 \times 10^{-8} e^{-R/0.209} \text{erg/atom}. \]  

(108)

considering only nearest neighbor interactions he found that the repulsive energy was nearly as large as London's calculated attractive energy for neon. No suitable repulsive term similar to (107) has been calculated for argon but probably the term is large enough to produce a considerable discrepancy between the calculated values and the observed values of equations (106a) and (107a). In each case, the calculated attractive energy is probably too small.
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AUTobiography

I, Jack Arbuthnott Soules, was born in Ashtabula, Ohio, January 26, 1928. I received by secondary school education in Howland School, Warren, Ohio. My undergraduate training was in the Engineering College of the Ohio State University, from which I received the degree Bachelor of Science in Physics in 1948. I continued in the Graduate School of the Ohio State University, receiving the degree Master of Science in 1950. I have held the following honors and positions while at the Ohio State University: Graduate Assistant, 1948 - 1949; Research Assistant, 1949 - 1950; Research Fellow, 1950 - 1951; Graduate School Fellow, 1951 - 1952, DuPont Fellow, 1952 - 1953; Assistant Instructor, 1953 - 1954.