AN EXPERIMENTAL DETERMINATION OF THE ELECTRON DENSITY DISTRIBUTION IN METALLIC LITHIUM

DISSERTATION

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AN EXPERIMENTAL DETERMINATION OF THE ELECTRON DENSITY DISTRIBUTION IN METALLIC LITHIUM

Introduction

There have been few accurate determinations of electron densities in crystals and some of the most important ones can be briefly mentioned.

The older work is that of Compton,[1] Havighurst,[2] James[3] and his coworkers, on various simple ionic crystals. James[4] has discussed these early investigations in detail. Later Brill,[5] Grimm, Hermann, and Peters made measurements on rocksalt, diamond, hexamethylene tetramine, magnesium and aluminum with the particular view of finding something out about the nature of the bonding in these substances. More recently Ageev[6] and coworkers have studied several metals, aluminum, copper, nickel and the compound NiAl with the express purpose of investigating the distribution of the valence electrons. NaCl has been reinvestigated by Renninger,[7] and Stambaugh[8] has made a study of LiH. Robinson,[9] in the course of his work on the compound Mn_3SiAl_9, attempted to find the valence electrons in order to decide questions of valence charge transfer which had been raised previously.

The extent to which investigations such as the ones mentioned have been successful is rather uncertain. Discussions and criticisms involving some of the work cited raise strong doubts as to the validity of some of the claims put forward regarding the detailed charge distribution in solids, but also encourage the feeling that such information can be obtained.

The present investigation is another attempt to find the charge distribution in a crystal and the metallic element lithium was chosen for this purpose. Lithium, crystallizing in a body-centered cubic cell and possessing three electrons per atom, is the simplest metal, from the point of view of both the lattice structure and electronic structure, that exists. In principle it should be the metal most amenable to theoretical treatment and its physical properties easiest to understand. However, as a survey and a comparison of the theoretical and experimental values of very many physical properties of lithium show, it cannot yet be said to be well understood. Experimental data are always welcome under such circumstances and this study was undertaken to see if some information could be contributed with respect to its electronic structure. Also, the possibility of success in gaining information about the valence electrons is greater the greater the fraction of total charge contributed by the valence electrons. In this respect a more favorable division of charge between "core" and "valence" is to be found in lithium than in any of the metals except beryllium. Furthermore, it was desired to check some data of Griffith[10] obtained in this laboratory some years ago. His results suggested an accumulation of charge at the point midway between atoms along the cell edge.

Previous x-ray work on lithium can be summarized in a few statements. Hull,[11] many years ago, suggested the body-centered cubic structure on the basis of Debye-Scherrer photographs. The correctness of this structure was demonstrated successively by Bijvoet[12] and by Simon[13] and Vohsen. Later, Pankow[14] derived atomic form factors from Debye-Scherrer photographs taken at various temperatures and used them to evaluate the characteristic temperature. Griffith[10] utilized a powder spectrometer with ionization chamber to obtain f-values and electron densities in the lithium lattice.

Experimental

Preparatinn of crystals.

The lithium used was C. P. metal lump obtained from Eimer and Amend. No analysis or list of impurities was furnished with the sample. All handling of the lithium and all manipulations involved in the preparation of the crystals were carried out in a dry box under a dry atmosphere of hydrogen or helium.

The crystals were grown and prepared for examination by the following procedure: A lump of lithium was taken from the reagent bottle and small (roughly one to two millimeters on an edge), clean pieces were cut from it with a razor blade. These pieces were placed in little glass cups which were then inverted (since the density of Li is less than that of paraffin) and immersed in a beaker of hot melted paraffin. A small hot plate heated the paraffin to a temperature somewhat above 188°C, the melting point of lithium. When the lithium had melted, it was agitated by placing the inverted cup over a glass rod and rotating the cup. The agitation caused the piece of lithium to break up into numerous globules. The paraffin was then permitted to cool and, the globules froze as the temperature passed through their melting point. The little spheres of lithium were removed from the paraffin, the residual paraffin clinging to them was in turn removed by adsorbent tissue paper, and the spheres were mounted on small glass capillaries with shellac. When the shellac had dried the specimens, ranging in size from 0.5 mm. to 1 mm. in diameter, were dipped in melted paraffin to furnish them with a thin protective coating. Bioloid embedding paraffin, m.p. 56-58°C, was used both for heating the lithium and for coating the spheres.

When first formed under paraffin the globules were shiny but by the time they had reached the coating stage the surface had darkened somewhat. However, being coated they could stand in air for many days or evan weeks without deterioration beyond the initial tarnishing.

The specimens were removed from the dry box, mounted on goniometer heads and examined with x-rays to see whether or not they were single crystals. Many batches of spheres were prepared in this fashion, and one sphere in about seven or eight resulted in a single crystal. When a crystal was obtained, it was aligned photographically and transferred to a spectrometer for intensity measurements.

Measurement of Intensities

For the measurement of the Laue-Bragg scattering a single crystal spectrometer was used in conjunction with a General Electric XRD-3 X-Ray Diffraction Unit. The spectrometer is the same one used by earlier investigators in this laboratory, Van Horn[15] in his study of Li_2O, Griffith[10] in his study of lithium, and Stambaugh[8] in his study of LiH, but modified for single crystal intensity measurements. The powder specimen holders and accompanying low temperature apparatus formerly employed have been replaced by a goniometer head for the crystal and new accessories for low temperature measurements. Provision has been made for the motion of the receiving slit and geiger counter along a vertical arc in addition to its motion along the horizontal arc making possible the measurement of reflections on non-equatorial layers of the reciprocal lattice. Also the spectrometer has been equipped with a gearing assembly so that the central shaft carrying the goniometer head can be driven at a series of different speeds which are in simple ratio to one another. Figure 1 shows the apparatus.

The x-ray unit contains its own recording instruments and geiger tube and is described fully in the instruction manual accompanying the instrument.

The crystal is positioned with respect to the x-ray beam and the reflections are produced in exactly the same manner as in the ordinary rotating crystal photographic method.

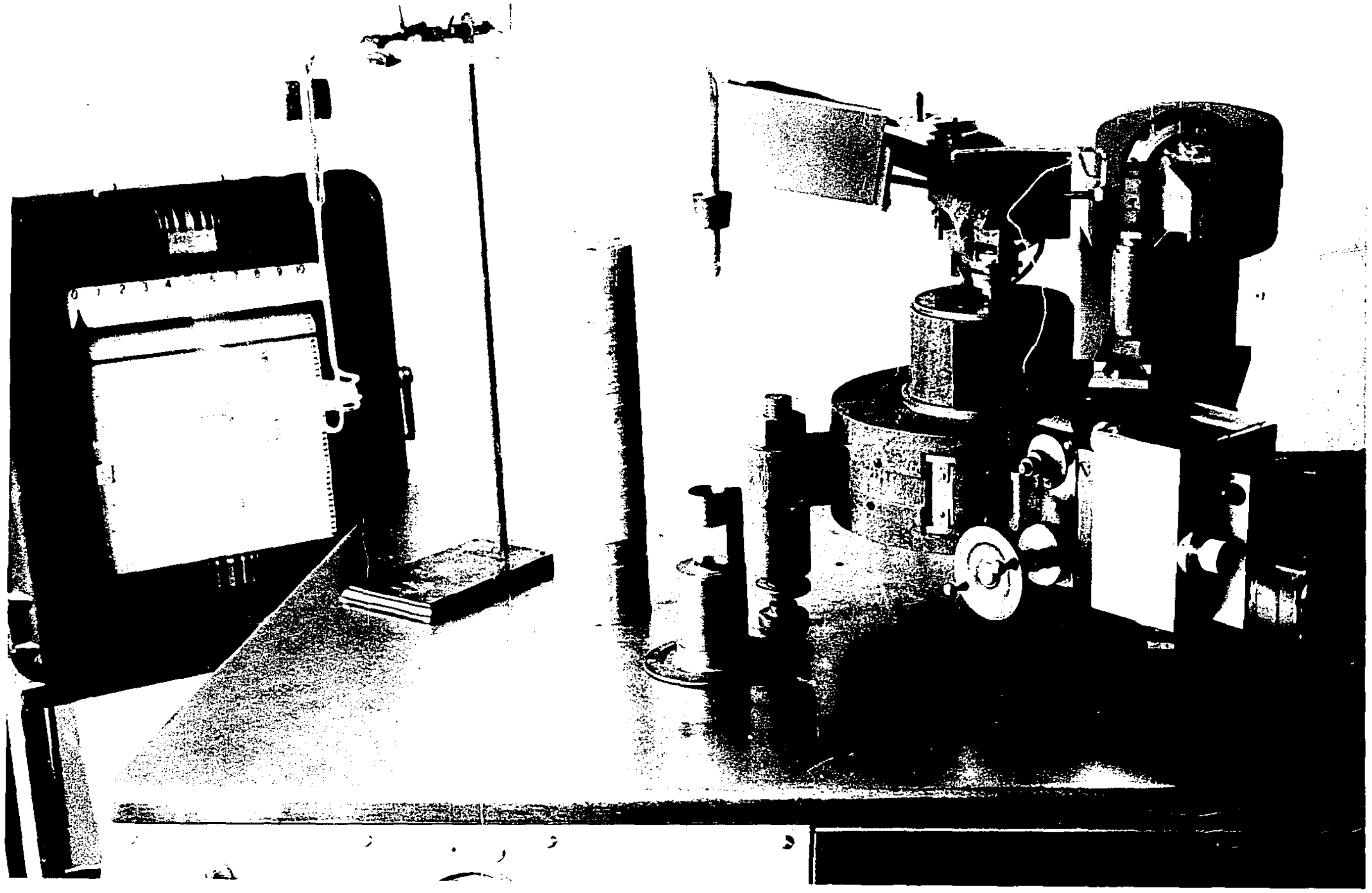


Figure 1. Spectrometer

For examination of a crystal, a table was made up giving the reflections occurring on each layer line, the angular setting of the geiger counter for each reflection as determined from the Bragg relation, (for non-zero layer line levels this will include the polar angle as well as the azimuthal angle) and the relative crystal orientation for each reflection as given by a simple reciprocal lattice construction, all appropriate to the crystallographic axis about which the crystal happened to be aligned. This information allows any reflection to be picked up readily after one reflection has been found. At any temperature each reflection is characterized by its integrated intensity I_T, a quantity whose absolute value is given by the well known equations[16]

$$I_T = \frac{E_T \omega}{I_0} = \left(\frac{e^2}{mc^2}\right)^2 \frac{N^2 \lambda^3}{\sin 2\theta} \quad \frac{1+\cos^2 2\theta}{2} |F|^2 \times \text{Absorp. factor} \quad (1)$$

where E_T = total energy reflected by the crystal as it rotates through its reflecting range

ω = angular velocity of crystal rotation

I_0 = intensity of incident beam

Then, to measure the integrated intensity of a reflection the geiger counter was set at the proper position to receive the diffracted beam, the crystal was driven through its range of reflection, the geiger counter being held stationary, and the total energy was measured as the number of counts recorded by the scaler for the period of time the crystal was rotated. It was not possible to derive absolute values of the integrated intensities because I_0 was unknown. Therefore, the measured energy of a reflection was taken directly as a relative integrated intensity (after correcting for background radiation as mentioned below) without multiplication by ω , which had the same value, ω_0, for most reflections. In the few cases where a different was used the energies were multiplied by the ratio ω/ω_0 to bring them on the same relative scale as the others.

While the crystal was rotating through its reflection the chart recorder simultaneously drew the shape of the reflection and any irregularities could easily be noted.

In order to make low temperature measurements the crystal was cooled in a manner similar to that described by Rhodes.[17] Nitrogen was boiled from a dewar reservoir through cooling coils immersed in liquid nitrogen into a dewar transfer tube. This tube led into a chamber which fitted over the goniometer head and crystal. The exit end of the transfer tube was situated immediately above the crystal which was then cooled by the cold gas issuing from the tube. The dewar transfer tube consisted of two concentric glass tubes. The inside surface of the outer tube and the outside surface of the inner one were silvered and the space between the two evacuated. A cellophane window on the chamber permitted the passage of the incident and diffracted beam with low absorption.

The method of cooling precluded the use of a thermocouple for temperature measurement, and the temperature was only estimated from the change in Bragg angle for a high order reflection relative to its value at room temperature, together with the known lattice constant and coefficient of expansion of lithium at 95°K.

Accurate temperature measurements were not made and it was only determined that the data were obtained at temperatures in the range 77°K - 110°K. This can be seen from the following considerations. From Lonsdale[18] and Hume-Rothery's values of the lattice constant at room temperature and at 90°K the shift in the Bragg angle for the 330 reflection was computed from Bragg's equation in difference form

$$\Delta\theta \ (\text{degrees}) = 57.3 \tan\theta \ \frac{\Delta a_o}{a_o}$$

and numerically was $1^{\circ}8'$ for CuKα radiation. Measured displacements of the 330 reflection came to this amount within errors of measurement of $\sim 6'$ in 2θ or $\sim 3'$ in θ. So the temperature was around 90°K with an uncertainty corresponding to an uncertainty in Δ of around $3'$. Setting $\Delta\theta = 3/60$ degrees and solving for Δa_o gives a change in cell constant of .001 A$^{\circ}$. At 95°K the coefficient of linear expansion of lithium is 17×10^{-6} deg^{-1} according to Simon and Bergmann.[19] The temperature change corresponding to a cell constant change of .001 A$^{\circ}$ was calculated from the definitinn of the coefficient of linear expansion as

$$\alpha = \frac{1}{a_o} \frac{\Delta a_o}{\Delta T}$$

$$\Delta T = \frac{\Delta a_o}{a_o \alpha} = \frac{.001}{3.48 \times 17 \times 10^{-6}} \simeq 17^{\circ}.$$

This is the estimation of uncertainty in the temperature and is the basis for the above statement that the measurements were carried out in the range 77°K - 110°K. The agreement of the low temperature data from crystal to crystal suggests that either the temperature was closely the same in all cases or that the intensities were not very temperature sensitive in the range 77°K - 110°K.

At the low temperature the zero level layer line reflections only were examined because the cold gas transfer tube was situated so close to the crystal as to interfere with a non-equatorial reflected beam. Thus one crystal did not suffice to furnish complete data and other crystals aligned along different axes and which gave different equatorial reflections had to be mounted. Naturally some reflections appeared on the zero level for several rotation axes while others appeared for just one. This is the reason more measurements were made on some index types than others.

At room temperature the data did not extend beyond the (400) reflection. This limit arose with copper radiation because of the condition imposed by Bragg's law that the indices of the highest order reflection possible must be such that

$$\sqrt{h^2 + k^2 + l^2} \leqslant \frac{2a_o}{\lambda}$$

Letting $a_o = 3.5$ A^o and $\lambda = 1.54$ A^o this gives

$$\sqrt{h^2 + k^2 + l^2} \leqslant 4.55$$

and the highest order reflection possible is the (420) for which $\sqrt{h^2 + k^2 + l^2} = 4.47$. In practice even this wasn't observable because the geiger counter and receiving slit were blocked by the incident beam collimator mounting before they could reach the high Bragg angle at which the (420) reflection occurs, and measurements ended at the (400) reflection. Attempts to overcome these limitations by using a shorter wave length were unsuccessful. For molybdenum Kα radiation, $\lambda = .71$, the restriction on the indices is

$$\sqrt{h^2 + k^2 + l^2} \leqslant 9.86$$

In principle reflections out to the (844) for which $\sqrt{h^2 + k^2 + l^2} = 9.80$ are accessible to observation. Experimentally, however, the intensities of the reflections beyond the (400) were too weak to be measured. This was a consequence of the low scattering power of lithium for molybdenum radiation (equation 1 shows that the integrated intensity is proportional to λ^3), and the weakening effect of the lattice thermal motion on the intensities.

Both radiations were also used at the low temperature. Again the copper data were necessarily restricted to $\frac{\sin\theta}{\lambda}$ values not greater than that corresponding to the (400) reflection $\left(\frac{\sin\theta}{\lambda} \sim 0.64\right)$. But the reduced thermal motion of the lattice resulted in an increase of the intensities great enough to allow measurements with molybdenum radiation out to a $\frac{\sin\theta}{\lambda}$ value of .908 corresponding to the (620) reflection.

The experimental intensities, i.e., the number of counts recorded by the scaler, had to be corrected for background radiation before use could be made of them in calculations. To this end hundred second counts were taken with the receiving slit held at the Bragg reflection angle and with the crystal set stationary three or four degrees off the reflection peak. The chart recorder was a convenient guide in fixing the crystal settings for these readings. Counts taken on each side of the reflection were averaged to give the mean background intensity over the reflection range. The average background counting rate was multiplied by the time during which counts were taken when the reflection was measured, and the result subtracted from thetotal number of counts recorded. The remainder was taken as the true relative integrated intensity of the reflection. The dead time of the geiger tube used is about 25×10^{-6} seconds. The average counting rate seldom exceeded 600 counts per second and no correction for missing counts was necessary. The integrated intensities of non-equatorial reflections were multiplied by $\sqrt{\frac{\sin^2\mu}{\sin 2\theta}}$,[20] where μ is the angle between the equatorial plane and the reflected beam, and

θ is the Bragg angle. This quantity is the modification to the Lorentz factor which corrects for the longer time the reciprocal lattice point spends passing through the sphere of reflection. The resulting values for the integrated intensities are those which would have been measured directly had the reflection occurred on the zero level.

With these corrections the experimental intensities are listed in Tables I and II. Table I shows the room temperature results and Table II shows the low temperature results. The number heading a column identifies the same crystal throughout.

Table I

hkl	1	2	3	4	5	6	13
110	18510	58367	23512	91775	10774	113047	93233
200	6536	-	8308	33917	3966	40519	-
211	2797	9796	3616	13833	1618	17197	13682
220	1298	4847	1808	6600	767	7930	7020
310	-	-	815	3587	390	4332	-
222	408	-	515	2068	239	2663	-
321	-	966	325	1278	153	1596	1334
400	186	-	227	910	-	1190	-
330	161	582	202	753	84	963	864

Table IIa

hkl	1	2	3	4	5	6
110	20986	5993	52503	9836	14250	-
200	-	-	-	4285	-	29776
211	5227	1478	12206	2334	3389	-
220	3237	838	7446	1367	1992	9230
310	2043	-	-	-	1314	-
222	-	-	-	715	-	4811
321	-	367	3117	-	-	-
400	-	-	-	547	-	3800
330	-	386	-	-	-	-

Table IIb

hkl	7	7	8	8	9	10	11	12
110	62241	-	97104	-	-	-	-	-
200	27775	-	-	-	-	-	-	-
211	-	-	24872	-	-	-	-	-
220	9018	-	16790	-	-	-	-	-
310	5859	50110	-	-	-	-	-	32472
222	-	-	-	-	-	-	-	-
321	-	-	4056	25576	-	16830	-	-
400	-	13760	-	-	-	-	-	-
330	-	10384	2194	14434	-	9006	6526	6836
411	-	-	-	-	-	-	5602	5707
420	-	5710	-	-	-	-	-	-
332	-	-	-	-	-	-	2713	2797
422	-	-	-	3834	-	2617	1785	1967
510	-	1995	-	-	2093	-	-	-
431	-	-	-	2798	-	1654	-	-
521	-	-	-	-	-	-	-	788
440	-	-	-	1590	1104	1082	-	-
530	-	-	-	-	665	-	-	-
600	-	-	-	-	607	-	-	-
532	-	-	-	468	-	-	-	-
620	-	-	-	-	285	-	-	-

The room temperature data listed in Table I were all taken on crystals which had been cooled to around 100°K before measurement. Crystals which had not been previously cooled exhibited large differences from crystal to crystal in the intensities of the low order reflections but after cooling the intensities of these reflections from different crystals came into agreement and were also considerably higher. For example the intensities at room temperature of the(110) reflections from the different crystals were of the order of thirty percent greater than the intensities of the same reflection from the same crystals at room temperature before cooling. Evidently the crystals grew with a rather high degree of perfection which resulted in considerable extinction.

Treatment of the Experimental Data

For the normal beam single crystal arrangement the relative integrated intensity of an equatorial reflection is given by equation (1) rewritten as

$$I'_T = \frac{1 + \cos^2 2\theta}{\sin 2\theta} \; F'^2_T \text{ x absorption factor} \qquad (2)$$

where F'_T signifies a relative structure amplitude per unit cell at temperature T. Since the specimens were spherical in shape, and since the linear absorption coefficient of lithium is small so that the product μ R is also small,[21] the absorption factor is essentially independent of θ and can be incorporated into the relative structure amplitude. Also, since F = 2f for lithium, where f is the atomic form factor, the discussion can be carried out in terms of the atomic structure factor rather than the structure amplitude, and the relative integrated intensity at temperature T can be set down as

$$I'_T = \frac{1 + \cos^2 2\theta}{\sin 2\theta} \times f'^2_T \qquad (3)$$

f'_T being a relative atomic form factor at temperature T.

The experimental relative integrated intensities of the Laue-Bragg reflections listed in Tables I and II were converted into relative atomic form factors through use of the above equation written as

$$f'_T = \sqrt{I'_T \quad \frac{\sin 2\theta}{1 + \cos^2 2\theta}} \quad . \qquad (4)$$

The resulting sets of f'_T 's were on independently arbitrary scales and it was necessary to place them on a common scale for averaging. To this end one set was designated as a reference set with relative form factors $f'_{T(\text{reference})}$. Another set had relative form factors $f'_{T(x)}$. The ratio

$$\frac{f'_{T(\text{reference})}}{f'_{T(x)}}$$

was computed for reflections common to each set. This ratio would be the same for all reflections if the measurements were exact and the two crystals gave exactly the same relative intensities. In practice these circumstances do not hold and the above ratio was averaged for the reflections common to the two sets and this average was used as a multiplication factor to bring the values $f'_{T(x)}$ to the same scale as the reference set.

Crystal number four was taken as reference for the low temperature data and number six for room temperature. The reflections at higher values of $\sin\theta/\lambda$, those beyond the (330), were averaged separately and fitted to the lower ones through reflections common to both. The relative atomic form factors obtained in this manner are given in Tables III and IV. Table III gives the room temperature results and Table IV the low temperature results.

Table III

hkl	1	2	3	4	5	6	13	av.
110	203.1	190.8	203.4	201.4	203.1	200.8	199.5	200.3
200	152.8	-	153.0	155.0	155.9	152.2	-	153.8
211	115.7	114.5	116.9	114.5	115.3	114.8	112.1	114.5
220	86.6	88.5	90.8	87.2	87.2	85.6	88.2	87.8
310	-	-	63.3	66.6	64.6	65.8	-	65.1
222	49.6	-	49.5	49.8	49.7	50.7	-	49.9
321	-	37.6	36.7	36.4	37.1	36.6	36.6	36.8
400	27.5	-	27.0	27.1	-	27.9	-	27.4
330	21.1	21.2	21.0	20.3	19.9	20.7	21.4	20.9

Table IVa

hkl	1	2	3	4	5	6	7
110	57.90	58.93	59.37	59.53	59.28	-	61.08
200	-	-	-	49.75	-	50.09	50.18
211	42.44	42.97	42.04	42.58	42.46	-	-
220	36.59	35.47	35.98	35.71	35.67	35.44	34.43
310	30.10	-	-	-	30.00	-	29.75
222	-	-	-	26.15	-	25.91	-
321	-	22.00	21.82	-	-	-	-
400	-	-	-	18.51	-	18.63	-
330	-	16.00	-	-	-	-	-

Table IVb

hkl	7	8 and 10	9	11 and 12	av
110	-	-	-	-	59.83
200	-	-	-	-	49.95
211	-	-	-	-	42.38
220	-	-	-	-	35.72
310	29.87	-	-	29.65	29.88
222	-	-	-	-	26.07
321	-	21.10	-	-	21.61
400	18.34	-	-	-	18.50
330	16.89	17.08	-	16.63	16.72
411	-	-	-	15.30	15.30
420	13.22	-	-	-	13.22
332	-	-	-	11.50	11.50
422	-	10.01	-	9.80	9.90
510	8.60	-	8.86	-	8.73
431	-	8.49	-	-	8.49
521	-	-	-	6.79	6.79
440	-	7.13	6.93	-	7.06
530	-	-	5.49	-	5.49
600	-	-	5.32	-	5.32
532	-	4.01	-	-	4.01
620	-	-	3.74	-	3.74

A relative form factor given in Tables III and IV is a product of the absolute atomic form factor at the particular temperature and an arbitrary constant, c,

$$f'_T = cf_T \tag{5}$$

Under the assumption that the effect of thermal vibrations and zero point vibrations is given correctly by the Debye-Waller expression $e^{-B_T \frac{\sin^2\theta}{\lambda^2}}$, equation (5) becomes

$$f_T' = c f_0 e^{-B_T \frac{\sin^2\theta}{\lambda^2}} \tag{6}$$

where f_o is the absolute atomic form factor for lithium at rest in the crystal. If f_o were known c and B_T could be found as follows: Equation (6) gives the following sequence:

$$\frac{f'_T}{f_o} = c\, e^{-B_T \frac{\sin^2\theta}{\lambda^2}}$$

$$\ln \frac{f'_T}{f_o} = \ln c - B_T \frac{\sin^2\theta}{\lambda^2} \tag{7}$$

Then a plot of $\ln \frac{f'_T}{f_o}$ against $\frac{\sin^2\theta}{\lambda^2}$ would yield a straight line of slope $-B_T$ and intercept $\ln c$.

Theoretical calculations show that the f_o values for the isolated lithium atom and ion differ markedly only at values of $\frac{\sin\theta}{\lambda}$ less than two tenths. Experimental points do not extend into this region and so over the range of experimental observation the third electron would not be expected to cause great departures from the theoretical f curves of the free atom or ion. Consequently theoretical f_o values were inserted in equation (7) and values of c and B_T derived as outlined above. If the points of the plot of $\ln \frac{f_T}{f_o}$ vs. $\frac{\sin^2\theta}{\lambda^2}$ had fallen precisely on a straight line the true f_o values for the crystal would have been equal to the theoretical f_o's used in making the plot within the limits of validity of the temperature expression. The actual plots, given in figures 2 and 3 for the room temperature data and 100°K data respectively, though allowing straight lines to be drawn, do show scatter which, if the temperature factor is correct and the experimental measurements accurate, is to be attributed to deviations of the true f_o values from the theoretical ones. These true f_o values could then be calculated by the converse process through equation (6) using the c and B_T obtained from the plots.

These plots were made (Figures 2 and 3) using f_o's for the ion as derived from a simple analytic wave function given by Lowdin.[22] This function represents with good accuracy the numerical solution of the Hartree-Fock equations as calculated by Fock and Petrashen[23] andthe expression for f_o resulting from it could be evaluated readily for any reflection.

It was attempted to establish the absolute basis for the atomic form factors experimentally through a direct comparison of the intensity of a reflection from a lithium crystal with the intensity of a reflection

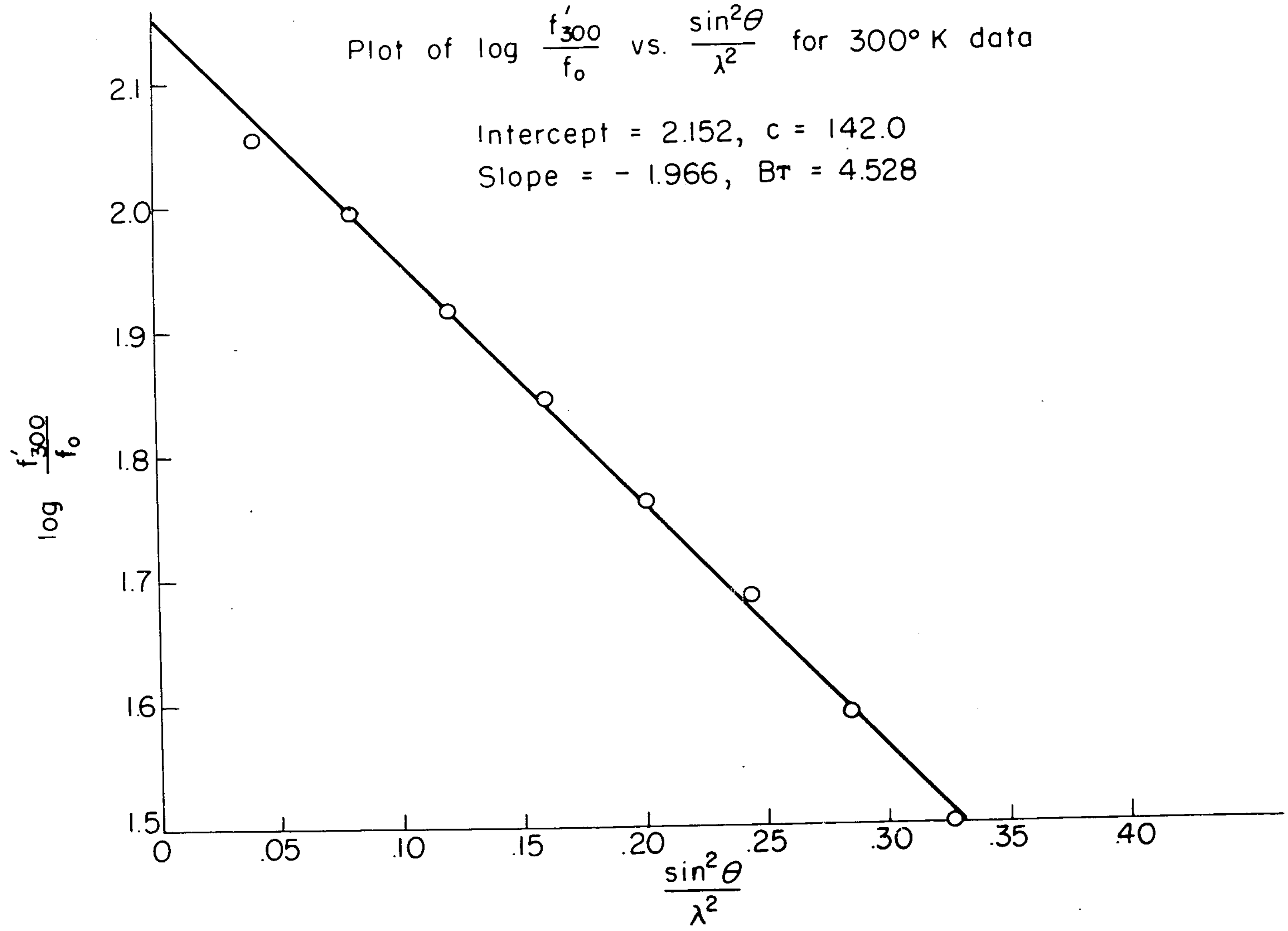
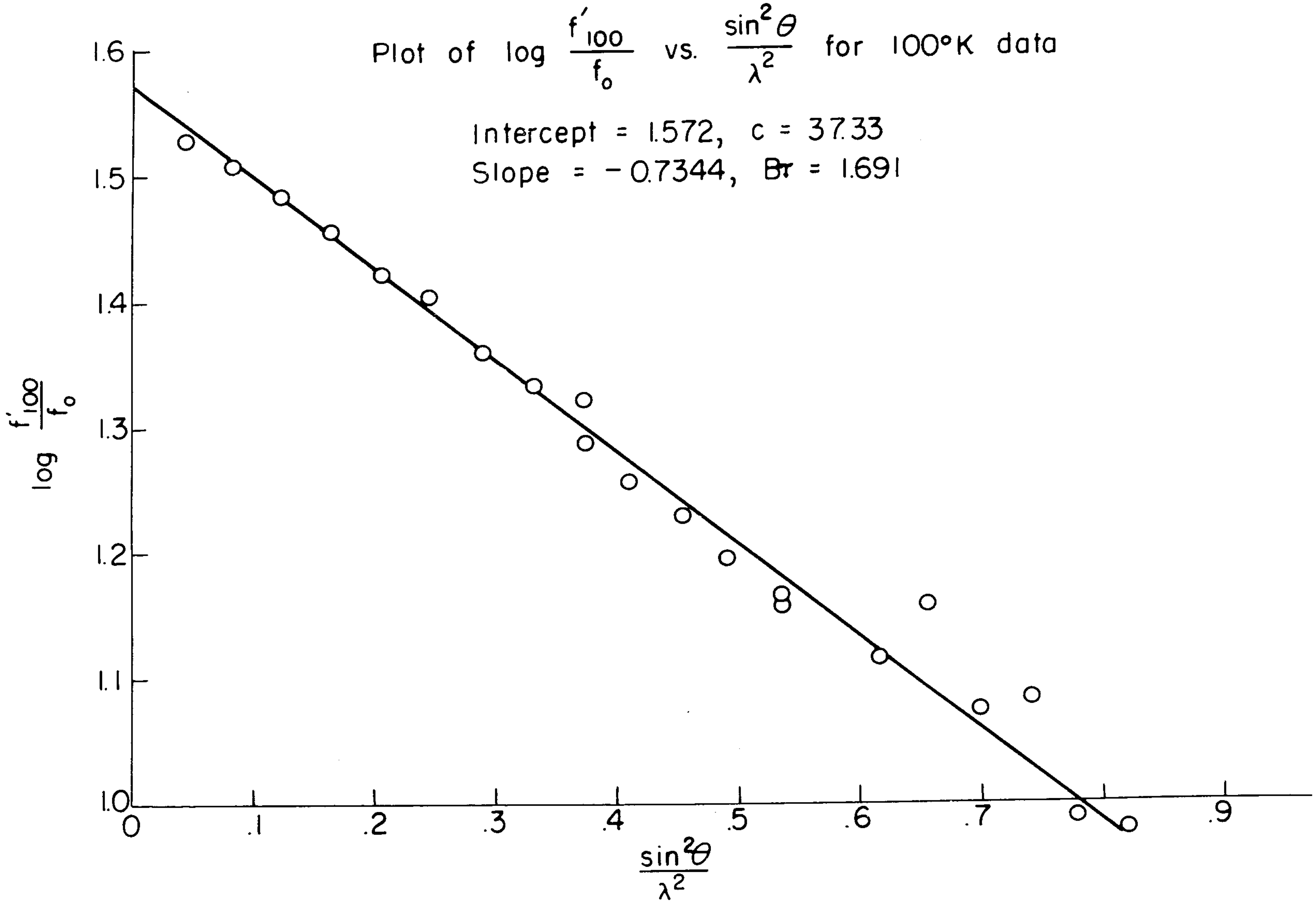

Plot of log $\frac{f'_{300}}{f_o}$ vs. $\frac{\sin^2\theta}{\lambda^2}$ for 300° K data
Intercept = 2.152, c = 142.0
Slope = − 1.966, Bτ = 4.528
log $\frac{f'_{300}}{f_o}$
2.1
2.0
1.9
1.8
1.7
1.6
1.5
0
.05
.10
.15
.20
.25
.30
.35
.40
$\frac{\sin^2\theta}{\lambda^2}$

FIGURE 2



Plot of $\log \frac{f'_{100}}{f_o}$ vs. $\frac{\sin^2\theta}{\lambda^2}$ for 100°K data

Intercept = 1.572, c = 37.33

Slope = −0.7344, B_T = 1.691

FIGURE 3

from a sodium chloride crystal. Two sets of measurements were made with two different sodium chloride crystals and two different lithium crystals. The NaCl crystals were ground into spheres of size comparable to the lithium crystals making possible simple absorption corrections. The ratios of intensities were reduced to ratios of structure factors using well known formulae. In the one case the lithium (211) reflection was compared with the (444) and (440) NaCl reflections, and in the other case the lithium (211) and (220) reflections were compared with the NaCl (600) reflection, in both cases at room temperature. Absolute values of the structure factors for NaCl at room temperature were available from several sources, principally from the measurements of James and Firth,[24] Havighurst,[2] Brill[5] et.al., and Renninger.[7] Examination of the values these people give shows there is wide disagreement, and because it could not be decided which of these data were the more reliable, the absolute atomic form factors found by the procedure used in the preceding paragraph were used in the calculations for the electron densities discussed later. However, for comparison, the values of $f(211)$ and $f_{(220)}$ for lithium, as determined by directly comparing intensities and using the structure amplitudes of the various authors mentioned above, are listed in table V. The column headings identify the authors (J.F. means James and Firth, etc.) whose data were used to evaluate the absolute atomic form factors for lithium. The last column gives the absolute f-values for lithium at room temperature taken from table VI below.

Table V

Reflections compared	f_{Li} (abs.) computed from data J.F.	H.	B.	R.	f_{300}
NaCl (444) and Li (211)	0.793	0.759	0.859	0.925	0.806
NaCl (440) and Li (211)	0.775	0.746	0.791	-	0.806
NaCl (600) and Li (211)	0.788	-	0.823	0.900	0.806
NaCl (600) and Li (220)	0.592	-	0.618	0.676	0.618

Table VI gives the values of f'_T's, taken from tables III and IV, the absolute values f_T computed from equation (5) and absolute values for f_o calculated from equation (6). These f_o values are for the lattice at rest becauee the effect of zero point vibration has beenn included in the Debye-Waller exponential B_T.

The data are plotted in figure (4). It is immediately apparent from either the table or the plot that the experimental curve is well represented by the theoretical one over the range of in which observatinns were made. Some differences occur which are considered real.

The value at $\frac{\sin\theta}{\lambda}$ =0.201 (corresponding to the (110) reflection) is too low at each temperature and, through the manner of evaluating it, is necessarily too low for the lattice at rest. The experimental value of 1.700 is the average of 1.705 ~~as~~ given by the low temperature data and 1.695 as given by the room temperature data. Each of these values in turn is the average of seven

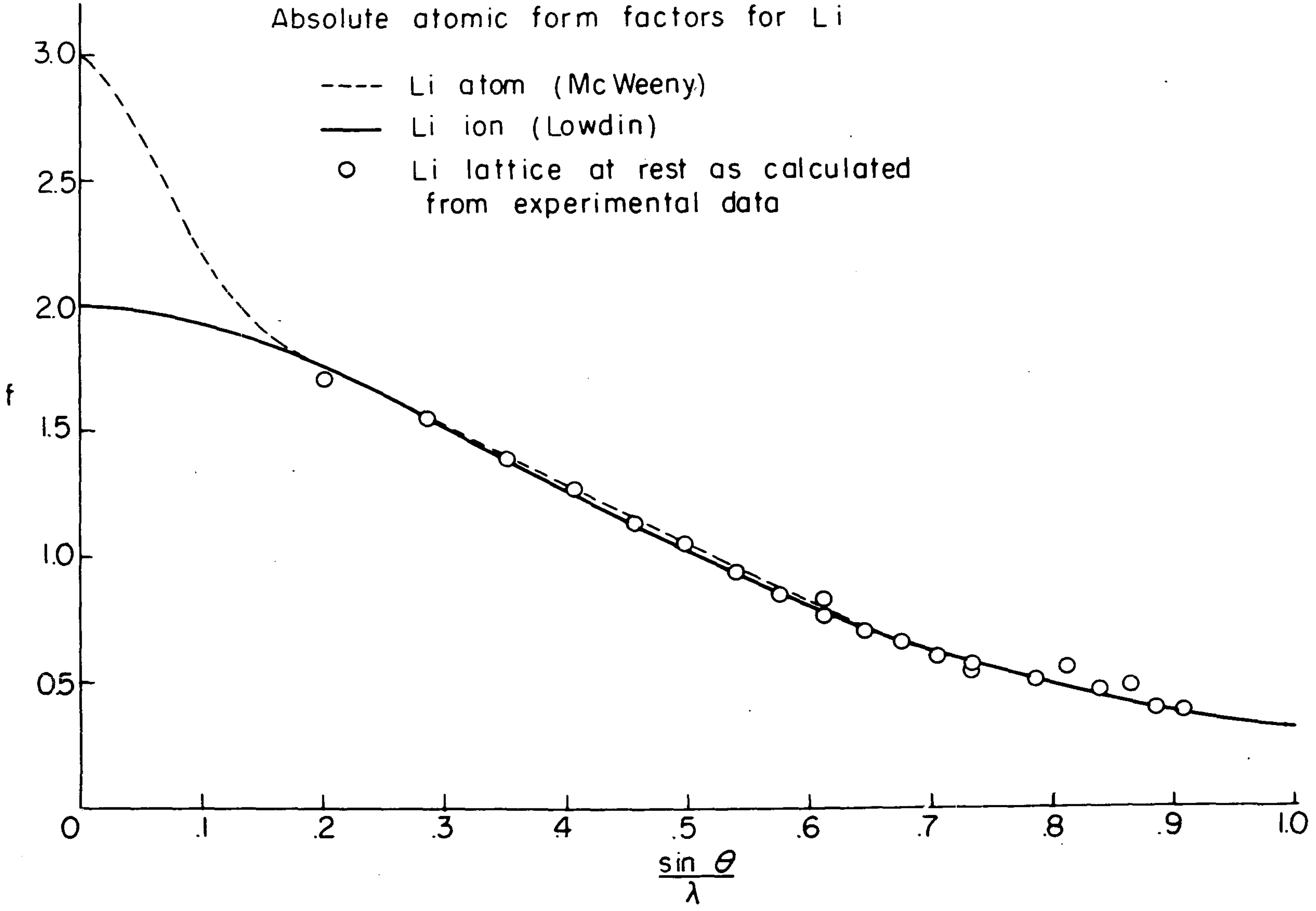

Absolute atomic form factors for Li
---- Li atom (Mc Weeny)
— Li ion (Lowdin)
○ Li lattice at rest as calculated from experimental data
f
3.0
2.5
2.0
1.5
1.0
0.5
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
$\frac{\sin\theta}{\lambda}$

FIGURE 4

Table VI

	f'_{100}	f_{100}(abs)	f_o(abs)	f'_{300}	f_{300}(abs)	f_o(abs)	f_o(avg)	Lowdin f_o(theoretical)
110	59.36	1.590	1.705	200.3	1.411	1.695	1.700	1.756
200	49.95	1.338	1.538	153.8	1.083	1.564	1.551	1.555
211	42.38	1.135	1.399	114.5	.806	1.394	1.397	1.389
220	35.72	.957	1.264	87.8	.618	1.287	1.275	1.249
310	29.88	.800	1.133	65.1	.458	1.147	1.140	1.131
222	26.07	.698	1.060	49.9	.351	1.057	1.058	1.029
321	21.61	.579	.943	36.8	.259	.937	.940	.941
400	18.50	.496	.866	27.4	.193	.839	.853	.864
330	16.72	.448	.839	(20.9)	.147	-	.839	.797
411	15.30	.410	.768	(20.9)	.147	-	.768	.797
420	13.22	.354	.710	-	-	-	.710	.737
332	11.50	.308	.663	-	-	-	.663	.684
422	9.90	.265	.611	-	-	-	.611	.637
510	8.73	.234	.579	-	-	-	.579	.594
431	8.49	.227	.561	-	-	-	.561	.594
521	6.79	.182	.517	-	-	-	.517	.523
440	7.06	.189	.576	-	-	-	.576	.491
530	5.49	.147	.480	-	-	-	.480	.463
600	5.32	.143	.501	-	-	-	.501	.437
532	4.01	.108	.406	-	-	-	.403	.392
620	3.74	.100	.403	-	-	-	.403	.392

individual determinations and in every case the experimental form factor is lower than the theoretical. The measurements definitely pull this point off the theoretical curve. The low temperature measurements show a splitting of the (330) and (411) reflections ($\sin\theta/\lambda$ = 0.608) which reflect at the same Bragg angle. This separation, though not great was certainly observed experimentally. Finally, also at low temperature, the high order (440) reflection was measured three times and its derived f_o value was consistently high. The (600) reflection is also high but it is the result of measurements on one crystal only and less reliance is placed on it.

If the experimental f_o values had fallen exactly on the theoretical f_o curve one would have been justified in supposing the lattice to consist of spherical ions, having the same charge distribution as the isolated ion, superimposed on a uniform charge distribution for the third electron. It is now necessary to see to what extent this picture must be modified as a consequence of the observed small departures of the f_o values from the theoretical ones. Since these departures are small it is to be expected that the corresponding electron density distribution in the lattice will differ little from that of the model of spherical ions in the uniform distribution of the free electron.

The electron density at any point in the unit cell of the lithium structure is given by a Fourier expansion,[4] the expansion coefficients being the atomic form factors,

$$\rho_{xyz} = \frac{Z}{V} + \frac{Z}{V} \sum_{h} \sum_{k}{}_{-\infty}^{\infty} \sum_{l} f_{hkl} \cos 2\pi (hx + ky + lz) \qquad (8)$$

where, ρ (x,y,z) = electron density at the point (x,y,z),

x,y,z are spatial coordinates given as fractional parts of the cell edge,

Z = total number of electrons in the unit cell,

V = volume of the unit cell,

f_{hkl} = atomic form factor for that value of $\frac{\sin\theta}{\lambda}$ corresponding to the (hkl) reflection,

Z/V = average electron density in the unit cell.

This equation was employed to calculate the electron density along the [100] , [111] , and [110] directions in the unit cell from the experimental f_o values. For the calculation to yield the most accurate representation of ρ an infinite number of terms in the sum is necessary. Experimentally the measurements did not extend beyond the (620) reflection and the number of coefficients available for the summation was therefore limited. Under such circumstances series termination errors must be expected and the calculated experimental electron density ρ $(x,y,z)_c$ differs from the true experimental density ρ (x,y,z) by the series termination error $\Delta\rho$.

Thus

$$\rho(x,y,z) = \rho(x,y,z)_c + \Delta\rho \tag{9}$$

The series termination error was evaluated in a manner now to be described.

The calculations for the electron densities $\rho(x,y,z)$ were repeated after replacing the experimental f_0 values by the theoretical values for the ion. The summations were cut off at the same term as before, and, as before, there resulted a calculated electron density distribution which differed from that for the model of lithium ions and a uniform background distribution, which the calculation was supposed to represent, by a series termination error. But in this case the true distribution of the model was easily set up from Fock and Petrashen's theoretical values of the radial distribution function for the ion. Therefore the termination error $\Delta\rho_{\text{theoretical}}$ could be evaluated. The values so obtained are the same as the $\Delta\rho$ values in equation (9) to the approximation that, for $\frac{\sin\theta}{\lambda}$ values greater than 0.908 (corresponding to the (620) reflection), the atomic form factors for lithium at rest in the crystal have the same values as inthe free ion. This does not have to be, but the closeness of the experimental values to the theoretical values at lower $\frac{\sin\theta}{\lambda}$ values suggests that it probably isn't a bad approximation to consider the two $\Delta\rho$ values to be equal. Therefore $\Delta\rho_{\text{theoretical}}$ was substituted for $\Delta\rho$ in equation (9) and corrected electron densities computed.

The corrected electron densities for the lattice at rest shown in figure (5) where $\rho\ (x, y, z)$ is plotted as a function of r, the distance from the atomic center, and in each case the last point marks the half-way distance to the nearest atom in the direction considered.

In the discussion describing the procedure used for establishing the absolute basis it was mentioned that its correctness depended on the validity of the Debye-Waller theory of the temperature effect. It is well known that according to this theory, if atomic form factors are derived at two temperatures T_1 and T_2, a plot of $\log_e \frac{f_{T_1}}{f_{T_2}}$ against $\frac{\sin^2\theta}{\lambda^2}$ shauld give a straight line of zero intercept and slope $B_{T_2}-B_{T_1}$ where $x = \frac{\Theta}{T}$ and

$$B_T = \frac{6h^2}{mk\Theta}\left\{\frac{\phi(x)}{x} + \frac{1}{4}\right\} \qquad (10)$$

and all symbols have their usual meanings.[4] The plot was made with the present experimental data and is shown in figure (6). Trial and error solution of the equation

$$B_{T_2}-B_{T_1} = \text{slope} \qquad (11)$$

gave a value of 325°K for the characteristic temperature.

Discussion of Results

Attention is first directed to the electron density plots. The point of reference for the discussion is the model of a theoretical lithium ion lattice immersed in the uniform distribution of the free or valence electrons. The charge density of this structure is

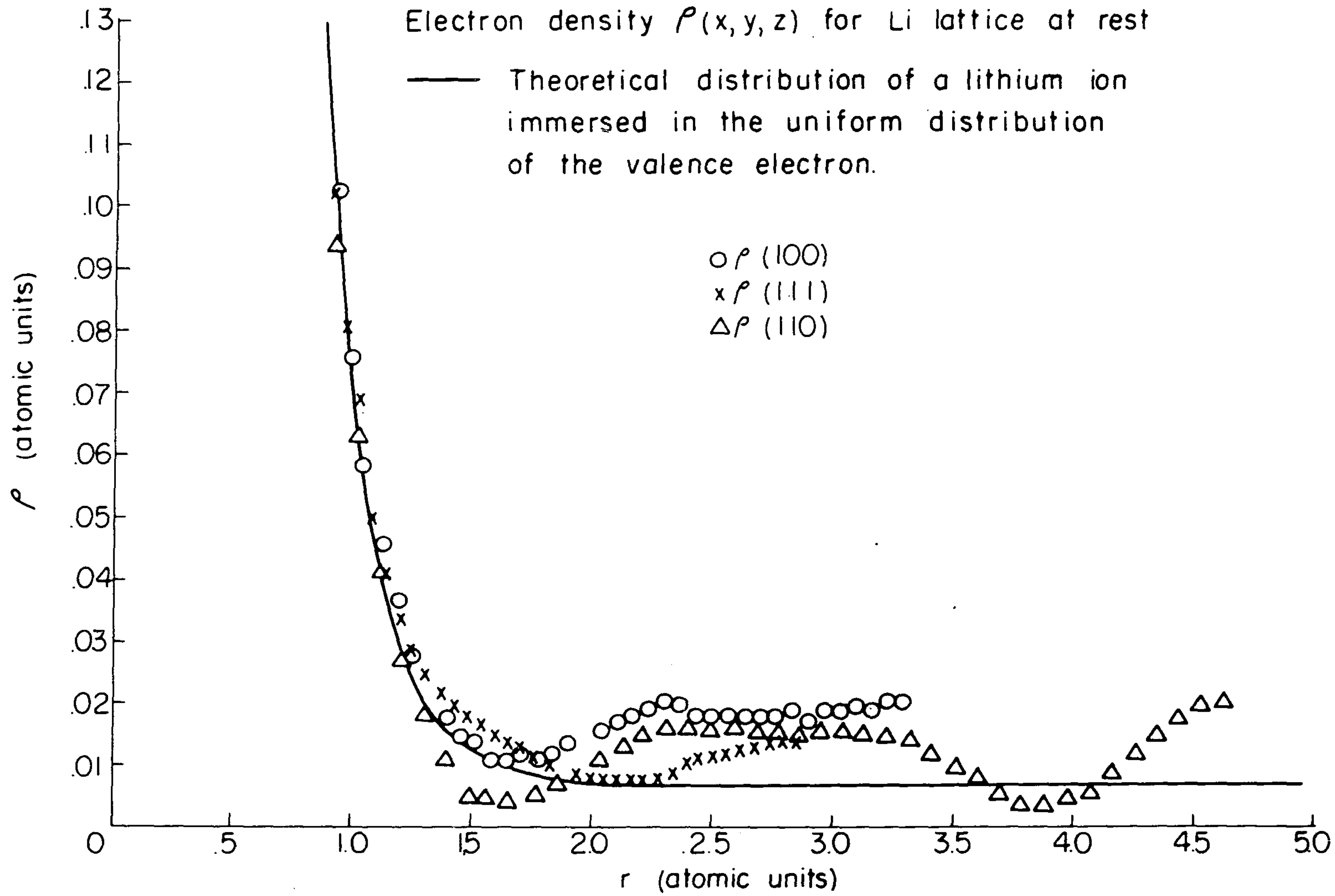

Electron density $\rho(x, y, z)$ for Li lattice at rest
Theoretical distribution of a lithium ion immersed in the uniform distribution of the valence electron.
○ ρ (100)
x ρ (111)
△ ρ (110)
ρ (atomic units)
r (atomic units)
.13
.12
.11
.10
.09
.08
.07
.06
.05
.04
.03
.02
.01
0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

FIGURE 5

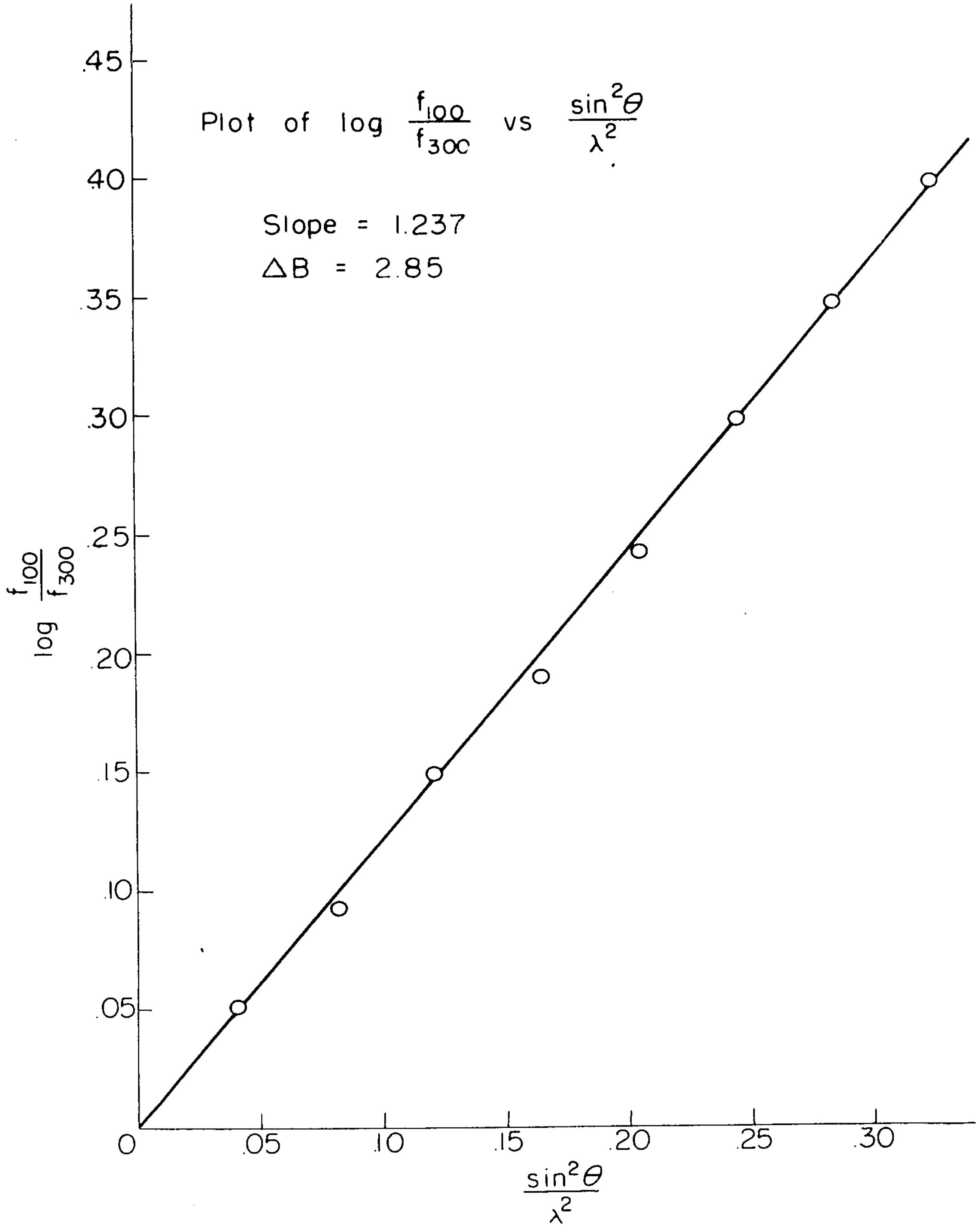

Plot of $\log \frac{f_{100}}{f_{300}}$ vs $\frac{\sin^2\theta}{\lambda^2}$
Slope = 1.237
ΔB = 2.85
$\log \frac{f_{100}}{f_{300}}$
.45
.40
.35
.30
.25
.20
.15
.10
.05
0
.05
.10
.15
.20
.25
.30
$\frac{\sin^2\theta}{\lambda^2}$

FIGURE 6

given in figure (4) for comparison with the experimental values.

Out to a distance of about one in atomic units all the curves are indistinguishable on the plot. The calculations show that the reference curve lies a little above the others by amounts which increase as r decreases, and which are largest at $r = 0$, but, even then, the difference only amounts to three or four tenths of a percent.

In the interesting region outside the ion core it is seen at once that all the curves are confined to ρ values in the range $\rho = .004\, e/V$ to $\rho = .020\, e/V$, where e/V means electrons per unit volume in atomic units. Though it would be unwise to place too much confidence in the fine details of the plots, the facts that they do not differ widely from one another and numerically do not exceed 0.02e/V a.u. were considered worthy of attention.

Pauling has given a theory for metals involving directional covalent binding. This theory assumes a particularly simple form in the case of lithium and has been discussed in an elementary manner by Coulson.[25] According to this theory 0.22 electrons are to be assigned to the bond between nearest neighbors, that is to say, between an atom at the unit cell corner and the atom at the center of the cell, and roughly 0.03 electrons to the bond between next nearest neighbors, those at the cell corners. Reasonably volumes in which these electrons would lie can be estimated and some idea of the electron density to be expected in the bond can be obtained. The length of the cell edge is 6.6 a.u. The ion cores are, say, 1.7 a.u. radius so that the bond charge for next nearest neighbor bonds ought to be located in a distance of 6.6-3.4 = 3.2 a.u. between the ion cores along the cube edge. The bond is supposed to be strongly directional and its charge density ought to decrease rapidly in a direction perpendicular to the bond's direction. Then it would not be unreasonable to say that the bond's charge is contained in the volume of a cylinder of length 3.2 a.u. and axial radius unity. The volume of such a cylinder is 10 cubic atomic units. Three hundredths electrons are to be assigned to this volume to give an average charge density of .003 electrons per unit volume. For the bond between nearest neighbors a similar calculation can be carried out which, because of the greater charge alloted to this bond and the smaller distance between atoms, yields a considerably higher value for the electron density. The corresponding cylinder is of length 2.3 a.u. giving an average density of 0.03 electrons per atomic unit volume. As these are average electron densities in the bond it is reasonable to suppose the actual densities along the lines joining atomic centers would be somewhat greater. This simple calculation thus predicts that the electron density along the [111] direction ought to be of the order of ten times greater than the charge density along the [100] direction and that numerically it ought to be greater than .03 electrons per unit volume. As is apparent from the plots the experimental data do not support these conclusions. The electron density nowhere exceeds 0.02 e/V and the values for ρ [111], far from exceeding by tenfold the values of ρ [100] are seen to lie beneath the latter. It can therefore be said that the experimental data stand in contradiction to the notion of strong directional bonding as given by Pauling's theory when applied to lithium.

On the other hand, the distribution is not exactly that of the theoretical model of spherical lithium ions immersed in the uniform distribution of two free electrons per unit cell. Some accumulation of charge between the atoms is indicated and the electron density does not fall off uniformly with distance in the outer region of the ion, but decreases less rapidly along the [111] direction than along the [100] or [110] directions. Some estimate of the amount of charge in the region occupied by the ion core could be obtained if this region could be defined. The distance from the center of charge corresponding to the minimum in the electron density curve for each direction, $r_{minimum}$, was assumed as the distance beyond which there was no ionic charge. It is to be remembered that, according to the model, "free" charge may also exist in this region. Radial distribution values were computed for the different ρ curves under the temporary assumption of spherical symmetry of each distribution. Numerical integration out to the r_{minimum} gave the number of electrons in each spherical distribution. Then an average r was computed by weighting each r_{minimum} with the multiplicity of the direction concerned. These multiplicities are six for the [100] direction, eight for the [111] direction, and twelve for the [110] direction. The number of electrons in each distribution was averaged into a single value in the same manner using the same weights. A kind of averaged spherical core thus resulted from a weighted smoothing out of the electron densities in the 26 directions. The following table gives the results:

Direction	$r_{\text{min.}}$ a. u.	Number of electrons in spherical distribution
[100]	1.580	2.146
[111]	1.939	2.314
[110]	1.664	2.049
avg.	1.73	2.15

The average value of 2.15 electrons can be compared with the corresponding value given by the theoretical ion model. The number of electrons contained within a radius $r_{\text{avg.}}$ in the theoretical ion can be calculated from Lowdin's radial wave function, u, (see appendix) according to the equation

$$\text{Number of electrons} = 2\int_0^{r_{\text{avg.}}} u^2 dr. \qquad (12)$$

Evaluation of the integral for $r = r_{avg.} = 1.73$ a.u. yields 1.99 electrons. There must be added to this the number of electrons contained in a sphere of radius $r_{avg.}$ if the charge density within the sphere is that for the uniform density of the free electrons. The volume of the unit cell is 283 cubic units (a.u.). There are two free electrons. Therefore the uniform charge density of two electrons per unit cell is .007 e/V a.u. The volume of a sphere of radius $r_{avg.}$ is 21.65 a.u. The amount of uniform free charge in this volume is $.007 \times 21.65 = .15$ electrons. The total charge in the sphere of radius $r_{avg.}$ is the sum of 1.99 and .15 or 2.14 electrons, agreeing closely with the value 2.15 found by the averaging of the individual distributions described above.

The number of electrons remaining for the rest of the volume in the cell is correct to give the uniform distribution value .007 e/V. The densities along the lines joining atoms are greater than this and there certainly must be compensating smaller values someplace in the cell. A full calculation for (x, y, z) throughout the cell would be necessary to reveal them. A calculation of ρ for a single point, (1/2, 1/4, 0), which is not located on a line joining atoms, gave a value of .014 e/V, again higher than that of the uniform distribution.

Rather than to speculate on the meaning of the ρ curves for the space between ions a few remarks will be made in defense of the principal claim already made. Admittedly the calculations of electron densities to be expected in the bonds on Pauling's model are of the crudest sort. But it is felt liberal allowance was permitted in the directions which were most disadvantageous to the conclusions. It is believed the data cannot possibly be in such error that, if corrected, it would raise the density along [111] to anything like ten times that along [100]. One of Snow's criticisms of Ageev's work was that Ageev forced convergence of his summations with an implausibly high artificial temperature factor and series terminatinn errors of some kind still remained. Errors due to finite termination of series were certainly considerably reduced, if not eliminated, by the method of treatment of data used here - hence, these results are not subject to this type of criticism. Finally it is worth pointing out that the values ρ given by the last points of the [100] and [110] curves are equal. These two points on the curves correspond to equivalent points in the b.c. cell and really must be equal. It is pleasing the calculations make them so.

It might be objected that in the determination of the absolute basis the choice of the theoretical lithium ion f-values rather than the theoretical atomic f-values involves an unjustified arbitrariness. Indeed, since the atomic f-curve lies above the ionic f-curve over the range of $\frac{\sin\theta}{\lambda}$ which is experimentally accessible, and touches the ionic curve at the $\frac{\sin\theta}{\lambda}$ value corresponding to the (110) reflection, and since the experimental f-value for the (110) relfection was relatively too low, it can reasonably be said the experimental f-curve would give as good or better overall fit with the theoretical atomic f-curve. This may or may not be. But even if the experimental curve did give a better fit with the atomic f-curve it would not necessarily follow that the unit of structure would be more like an atom than ion. To discuss such questions directly from the f-curve, experimental values must be available in the low range of $\frac{\sin\theta}{\lambda}$ where the f-values are more sensitive to the distribution of the valence electrons. However, the absolute scattering factors F_{hkl} were determined using the theoretical f-values of the atom as given by McWeeny.[26] The results differed insignificantly from these already had. The f-values were increased by a percent or less and the temperature factors differed but slightly from the earlier ones. These differences are not important. What was important was to be able to set up a ficticious structure of which both the density distribution and the f-values derivable from it were exactly known. Since the model of the ion lattice with a uniform background distribution satisfied these conditions the calculations and discussion have been carried out with it as a reference point.

Appendix

The theoretical lithium ion f_0 values were computed with the aid of a wave function given by Lowdin. This function is a normalized, radial, 1s wave function:

$$u_{1s} = 6.6641re^{-2.4346r} + 2.561re^{-4.4250r} \qquad (1)$$

where r is the distance from the nucleus in atomic units. The total radial distribution function for both electrons is

$$U(r) = 2u_{1s}^{2}\,. \qquad (2)$$

The atomic form factor is a function of the radial distribution function and $\frac{\sin\theta}{\lambda}$ through the relation

$$f\left(\frac{\sin\theta}{\lambda}\right) = \int_0^\infty U(r)\,\frac{\sin kr}{kr}\,dr\,; \quad k = 4\pi\,\frac{\sin\theta}{\lambda} \qquad (3)$$

After substituting from equations (1) and (2), performing the integration, expressing λ in Angstroms, and reducing, there results

$$f\left(\frac{\sin\theta}{\lambda}\right) = \frac{1.539}{\left(1+1.864\,\frac{\sin^2\theta}{\lambda^2}\right)^2} + \frac{0.4231}{\left(1+0.939\,\frac{\sin^2\theta}{\lambda^2}\right)^2} + \frac{0.0379}{\left(1+0.564\,\frac{\sin^2\theta}{\lambda^2}\right)^2}$$

This is the equation used in the calculation of the f_0's.

Summary

In this research the following has been accomplished:

1. Single crystals of metallic lithium have been grown.

2. The relative integrated intensities of the Laue-Bragg reflection have been measured at room temperature and at $\sim 100^{\circ}$K.

3. Relative atomic form factors for metallic lithium at room temperature and at 100°K have been derived from the measured relative integrated intensities and are tabulated.

4. Absolute atomic form factors at room temperature and 100°K have been obtained from the relative values with the aid of the theoretical f-values of the lithium ion, and are tabulated.

5. Absolute atomic form factors for the lattice at rest have been derived and are tabulated.

6. Electron densities along the [100], [111], and [110] directions have been calculated for the lattice at rest.

7. The characteristic temperature for lithium has been evaluated.

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Autobiography

I, Paul Leroy Splitstone, was born in Fremont, Michigan, January 29, 1926. I received my secondary school education at the Fremont Public High School. My undergraduate training was obtained at Western Michigan College, from which I received the degree Bachelor of Arts in 1948. I commenced my graduate studies at The Ohio State University in the fall of 1948. For three years I held an appointment as teaching assistant in the Department of Chemistry. In the spring of 1952 I was appointed a Research Fellow under the auspices of the Ohio State University Research Foundation and I held this position for three and a half years while completing the requirements for the degree Doctor of Philosophy.