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ELASTIC PROPERTIES OF GERMANIUM SELENIUM GLASSES AND METASTABLE COBALT FILMS

DISSERTATION

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

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* * * * *

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ABSTRACT

Brillouin light scattering in binary Ge$_x$Se$_{1-x}$ ($0.15 < x < 0.33$) glasses reveals the longitudinal acoustic (LA) mode frequency, $v_{LA}(x)$, to increase quasi-linearly with $x$ at low probe illumination-power $P_r(< 3\text{mW})$. At increased power ($4\text{mW} < P_r < 6\text{mW}$) a reversible softening in $v_{LA}(x)$ commences near $x = 0.15$ which grows with $P_r$ leading to a deep, 25%, suppression in frequency centered at $x \sim 19\%$. The photo-driven transitions rapidly diminish beyond this concentration and are fully suppressed at $x = 25\%$. The selective interaction of photons with the network that supports weakening Se-bond bending constraints beyond $x \sim 15\%$, progressive cross-linking, and eventual percolation of Ge-centered isostatically rigid fragments account for the observed behavior.

The wave vector and directional dependence of the Rayleigh and higher order Sezawa elastic waves in single crystalline epitaxial fcc Co layers are measured by Brillouin light scattering at room temperature. The dispersion of the mode velocities allows for the independent elastic constants and elastic moduli to be determined for this cubic phase of cobalt. These results compare very favorably to previous determinations of the elastic constants measured above 700 K from the high-temperature fcc phase of pure Co. Deviations from theoretical estimates are discussed.
Dedicated to my family
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CHAPTER 1

INTRODUCTION

A floppy to rigid transition in covalent networks was predicted [1,2] in the early 1980's using mean-field constraint counting algorithms wherein the inter-atomic valence forces were translated to bond bending and bond stretching mechanical constraints. Calculations show [2] that for an N-atom random network composed of n_r atoms having r-fold coordination, the r/2 bond stretching (α) constraints and (2r-3) bond bending (β) constraints lead to a solitary floppy to rigid transition when the connectivity or mean coordination \( \bar{r} \) of the network increases to 2.4. This critical point, identified with a network elastic stiffness transition, has broad fundamental importance. It not only coincides, in a mean field description, with the optimal glass forming ability in inorganic solids such as oxides and chalcogenides [1], but the underlying theory has also filtered into other fields of science such as biology [3], granular matter [3] and computational science [4]. Experimentally, new details of the floppy to rigid transition have emerged [5-7] in binary (Ge or Si)_xSe_{1-x} glasses by Raman scattering and T-modulated Differential Scanning Calorimetry (MDSC). In contrast to the numerical calculations on random networks, these experiments show that the rigid phase \((x > x_c(2) = 0.26 \text{ or } \bar{r}_c(2) = 2.52)\) is compositionally separated from the floppy phase \((x < x_c(1) = 0.20 \text{ or } \bar{r}_c(1) = 2.40)\) by an intermediate phase \((x_c(1) < x < x_c(2))\). Here the mean coordination number [7] \( \bar{r} \) [1]...

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These experimental results, on the other hand, are much closer to the recent numerical simulations [8] on self-organized networks that predict two transitions, a second order transition from a floppy to an unstressed rigid phase, followed by a first order transition from an unstressed rigid to a stressed rigid phase. Extension of the constraint theory to include atoms with broken $\beta$ constraints has also emerged [9]. In the case of pure Se glass, the existence of unbroken $\beta$ constraints is evident from the agreement of neutron data [10] to predictions [11] of the fractional vibrational density of states associated with the floppy Se-chain segments. As illustrated in the case of oxide [9] and chalcogenide glasses [6], the flexibility of the linkages that accompany broken bond bending constraints invariably leads to reduction in the network strain and to the fulfillment of the optimal glass condition at a higher connectivity than when the constraints were intact. Thus it follows that for the Ge$_x$Se$_{1-x}$ glasses there exists a Ge concentration at which the bond bending constraint must begin to weaken as evident in Raman data [6]. Early Mossbauer and Raman data [12] associated with tuning the number of constraints by replacing cations to erase some of the $\beta$ constraints highlight the delicate interplay between strain fields and valence-force fields that determine the equilibrium state of a network glass.

In the first section of this thesis the technique of Brillouin Light Scattering (BLS) has been used to analyze the rigidity transition of germanium selenium chalcogenide glasses. In Chapter 2, BLS as an experimental technique and the reason for why it is a valuable tool to study the rigidity transition will be discussed. A brief introduction to chalcogenide glasses will be given in Chapter 3 along with an explanation of the mean field constraint theory. Chapters 4 and 5 will focus on the experiments performed on
chalcogenide glasses and the results obtained. An examination of those results in light of current theory and other available experiments will be included.

The second section of this thesis deals with the BLS study of cobalt in its metastable face centered cubic (fcc) phase. The ability to grow materials as pseudomorphic films on a substrate has enabled the stabilization of novel phases of materials having new, and often, unusual properties [13-16]. The well-defined anisotropic homogeneous strain within the epitaxial film that arises from the mismatch between the unit grid of the film in its unstrained state and that of the substrate and related elastic energies are central to the stabilization of these meta-stable phases. The situation associated with magnetic films (such as cobalt) is especially interesting since the Stoner exchange correlation parameter is sensitive to the lattice constant, and hence to the induced strain [17]. In these cases the energy difference between two crystal structures may be comparable to the small energy differences associated with magnetic effects giving rise to a delicate competition between two distinct ground states in the strained film.

Cobalt, which is a strong ferromagnet and stable in the hexagonal close packed (hcp) phase under ambient conditions, is a good example. The face centered cubic (fcc) structure, which is normally a high-temperature phase of Co realized beyond 693K, has been synthesized at room temperature by epitaxial growth on Cu,[18,19] while Prinz first succeeded in stabilizing body centered cubic (bcc) Co films on GaAs over a decade ago [20]. Total energy spin-density energy band calculations show that, while the fcc phase has the lowest energy in the paramagnetic state, when magnetic order is introduced, the hcp phase is lowered in energy, and becomes more stable, relative to the stable
paramagnetic fcc phase [17]. The total energy of the ferromagnetic bcc phase was found to be close to that corresponding to the face centered phase with its stabilization in the laboratory requiring careful tuning of the lattice mismatch strain [20]. It follows that the interplay between structural and magnetic energies in cobalt is indeed subtle with the stability of the bcc and hcp phases originating from the magnetic order.

The experimental procedure of BLS study on fcc cobalt is described in Chapter 6. The independent elastic constants and moduli of fcc cobalt stabilized at room temperature are presented and compared to elastic properties of the high temperature fcc phase.
CHAPTER 2

BRILLOUIN LIGHT SCATTERING

In this study of the Ge$_x$Se$_{1-x}$ chalcogenide glass system, the experimental technique of Brillouin Light Scattering (BLS) was used. BLS is based on an instrument known as the Fabry-Perot interferometer. Bouloch first described the instrument that was then called the reflection multiple-beam-interferometer in 1893. Fabry and his coworkers "fully explored the behavior, characteristics and use of this device to the extent that it is called the Fabry-Perot interferometer"[21]. Much advancement has been made since this time, but the physical concepts upon which BLS was founded remain the same. In this chapter the fundamental theory behind this technique will be explored, a description of the modern BLS system will be given, and why this system is an effective tool for the research performed will be explained.

2.1 Multiple-Beam interference

To fully understand Brillouin scattering knowledge of multiple-beam interference is essential. Following the argument of Hecht[22], interference will be considered for a situation where the film, substrate, and surrounding medium are transparent dielectrics (see Figure 2.1).
Notation conforms to letting $r$ and $t$ be reflection and transmission amplitudes respectively. The symbol $r'$ represents reflections inside the film and $t'$ is the fraction transmitted when the wave leaves the film. $E_0$ is defined to be the amplitude of the initial incoming wave. The arrows denote the wave propagation and the electric field will oscillate perpendicular to this propagation.

If the incident wave is depicted as $E_0e^{i\omega t}$ then the components of the wave contributing at a point $P$ where the reflected light is focused are given by:

\[
\begin{align*}
E_{1r} &= E_0 r e^{i\omega t} \\
E_{2r} &= E_0 t r' t' e^{i(\omega t - \delta)} \\
E_{3r} &= E_0 t r^3 t' e^{i(\omega t - 2\delta)} \\
&\vdots \\
E_{Nr} &= E_0 t r^{(2N-3)} t' e^{i(\omega t - (N-1)\delta)}
\end{align*}
\]

(2.1)
where \( \delta, 2 \delta, \ldots, (N-1)\delta \) are phase changes due to differences in optical path length between adjacent rays. \( \delta \) is given by \( \kappa_0 \Lambda \) where \( \kappa_0 \) is the wavevector and \( \Lambda \) is the difference in optical path length, \( 2n_r d \cos(\theta) \). \( n_r \) is the index of refraction of the film and \( d \) is the film thickness. The resultant reflected scalar wave is then:

\[
E_r = E_{1r} + E_{2r} + E_{3r} + \ldots + E_{Nr}
\] (2.2)

which can be rewritten as:

\[
E_r = E_0 e^{i\omega t} \left[ 1 + \frac{r + r' t' e^{-i\delta}}{1 - r^2 e^{2i\delta}} \right] (2.3)
\]

For \( (r^2 e^{i\delta}) < 1 \) and for \( N \) approaching infinity the series in brackets converges giving:

\[
E_r = E_0 e^{-i\omega t} \left[ 1 + \frac{r + r' t' e^{-i\delta}}{1 - r^2 e^{2i\delta}} \right] (2.4)
\]

A relation between the primed and unprimed coordinates is obtained through the following illustration developed by Sir George Gabriel Stokes[22]. Consider the transmission and reflection of light at a single barrier (see Figure 2.2).

---

**Figure 2.2[22]: Reflection and transmission according to the Stokes treatment.**

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As in Figure 2.2a, the incident light strikes the barrier and is partially reflected and partially transmitted. If there is no absorption then the same process must also be possible in reverse (see Figure 2.2b). Now consider the case of two incident beams (Figure 2.2c). Equating the processes in b and c yields the relations:

\[ E_{0i}tt' + E_{0i}tr = E_{0i} \]  
\[ E_{0i}rt + E_{0i}tr' = 0 \]

Equations (2.5) may then be transformed to give:

\[ tt' = 1 - r^2 \]  \hspace{1cm} (2.6a) \n\[ r' = -r \]  \hspace{1cm} (2.6b)

Returning to the discussion of multiple beam interference, equation (2.4), in the case of zero absorption, can be rewritten as:

\[ E_r = E_0 e^{-i\phi} \left[ \frac{r(1 - e^{-i\delta})}{1 - r^2e^{-i\delta}} \right] \]  \hspace{1cm} (2.7)

where equations (2.6) were used to remove the primed amplitudes. An expression for the reflected flux density at P is obtained from the reflected scalar wave using the relation:

\[ I_r = (1/2) E_r E_r^* \]  \hspace{1cm} (2.8)

The reflected flux density becomes:

\[ I_r = I_l \frac{2r^2(1 - \cos\delta)}{(1 + r^4) - 2r^2\cos\delta} \]  \hspace{1cm} (2.9)

where \( I_l = (1/2)E_0^2 \).
A similar treatment can be performed for the transmitted wave whose components are of the form:

\[ E_{1t} = E_0 e^{i\omega t} \]
\[ E_{2t} = E_0 e^{i(\omega t - \delta)} \]
\[ E_{3t} = E_0 e^{i(\omega t - 2\delta)} \]
\[ \vdots \]
\[ E_{Nt} = E_0 e^{i(\omega t - (N-1)\delta)} \]

Adding these components gives a transmitted scalar wave:

\[ E_t = E_0 e^{-\frac{nt'}{1 - r^2 e^{-id}}} \]  

(2.10)

The irradiance of the transmitted wave becomes:

\[ I_t = I_i \frac{(nt')^2}{(1 + r^4) - 2r^2 \cos \delta} \]  

(2.12)

Using the identity \( \cos(x) = 1 - 2 \sin^2(x/2) \) from trigonometry allows \( I_r \) and \( I_t \) to be:

\[ I_r = I_i \frac{\left[ \frac{2r}{1 - r^2} \right]^2 \sin^2\left(\frac{\delta}{2}\right)}{1 + \left[ \frac{2r}{1 - r^2} \right]^2 \sin^2\left(\frac{\delta}{2}\right)} \]
\[ I_t = I_i \frac{1}{1 + \left[ \frac{2r}{1 - r^2} \right]^2 \sin^2\left(\frac{\delta}{2}\right)} \]  

(2.13)

Examination of equations (2.13) propose the introduction of the quantity:

\[ F = \left( \frac{2r}{1 - r^2} \right)^2 \]  

(2.14)

This quantity is called the coefficient of finesse. Written in terms of the coefficient of finesse the denominator of equations (2.13) can be redefined as:

\[ A(\theta) = [1 + F \sin^2(\delta/2)]^{-1} \]  

(2.15)
where \( A(\theta) \) is called the Airy function. A graph of the Airy function corresponding to different values of \( F \) (and therefore \( r \)) is shown in Figure 2.3:

![Airy Function Graph](image)

Figure 2.3[22]: Airy Function

It can be seen that with an increased coefficient of finesse the Airy function becomes sharply peaked at \( \delta/2 = m\pi \), where \( m \) is an integer. As the value for \( r \) gets closer to one (corresponding to larger values of \( F \)), the sharper the contrast between different peaks will become. As will be demonstrated in the following sections, high contrast is a very desirable trait for Brillouin spectroscopy.
2.2 Fabry-Perot Interferometer

The Fabry-Perot interferometer is the primary instrument necessary for Brillouin spectroscopy. This interferometer consists of two highly reflecting surfaces that are separated from each other by a distance d that can be varied (see Figure 2.4).

These surfaces act to produce multiple-beam interference as discussed in the previous section. However, high reflectivity is usually obtained by using semi-silvered or aluminized glass. These materials will absorb some of the light incident upon them, so the theory of the previous section must be altered accordingly. The statement[22]:

\[ T + R = 1 \]  \hspace{1cm} (2.16)

(which is equivalent to equation 2.6a where T=tt' is called the transmittance and R=r^2 is called the reflectance) is no longer valid. A new term A, the absorptance, must be added[22]:

\[ T + R + A = 1 \]  \hspace{1cm} (2.17)

A change in the phase shift (\(\delta\)) must also be made. The new \(\delta\) is represented as[22]:
where $\varphi$ is a function of the incident angle (under normal situations, $d$ is large enough and $\lambda_0$ small enough that $\varphi$ can be neglected[22]). The ratio between the transmitted and incident intensities now becomes[22]:

\begin{equation}
\frac{I_t}{I_i} = \left(\frac{T}{1-R}\right)^2 \frac{1}{1 + \left[\frac{4R}{(1-R)^2}\right] \sin^2\left(\frac{\delta}{2}\right)}
\end{equation}

To obtain a measure of the sharpness of the fringes produced by the light transmitted through the interferometer it is sufficient to find the width of the peak, in radians, when the transmitted intensity is equal to half of its maximum value. This width is called the half-width and is represented by $\gamma$. For large $F$, $\gamma$ can be represented by[22]:

\begin{equation}
\gamma = \frac{4}{\sqrt{F}}
\end{equation}

Once again, the magnitude of $F$ becomes important. The larger $F$ is, the sharper the peaks will appear.

Another important quantity, closely related to the half-width, is the reflectivity finesse[22]:

\begin{equation}
F_r = \frac{\pi \sqrt{F}}{2}
\end{equation}

This quantity corresponds to the ratio of the separation of adjacent maxima to the half-width. In the Brillouin system used during the course of this thesis the reflectivity of the mirrors was $R=0.94$ at a wavelength of 514.5nm, leading to a reflectivity finesse of $F_r=50$. 

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The optical flatness of the mirrors also contributes to the finesse. This portion of the finesse is given by\cite{21}:

\[
F_s = \frac{m}{2}
\]  \hspace{1cm} (2.22)

where \(m\) is a measurement of the flatness given in terms of wavelength. The system utilized in this work has plates flat to within \(\lambda/150\). This produces a surface flatness finesse of 75.

Taking the reflectivity finesse \((F_R)\) and the surface flatness finesse \((F_s)\) into account gives a total finesse \((F_T)\) of about 40, where \(F_T = \left[ \frac{1}{(F_R)^2} + \frac{1}{(F_S)^2} \right]^{-1/2}\). Diffraction and pinhole finesse contributions will further decrease the total finesse \((F_T)\) to about 30.

The finesse can be used to define another important parameter for Brillouin spectroscopy, the contrast. The contrast is the peak to trough ratio or the ability for the interferometer to distinguish between strong and weak peaks that appear in the same spectrum. An expression for the contrast is given by\cite{21}:

\[
C = 1 + \frac{4}{R^2} F_T^2
\]  \hspace{1cm} (2.24)

With \(R=0.94\) and \(F_T\) being the total finesse corrected for flatness, diffraction and pinhole contributions, the value of \(C\) becomes about 350. Figure 2.5 gives an illustration of contrast effects for varying values of finesse.
Figure 2.5[21]: Contrast between two emission lines. The smaller features on either side of the central peak are 1/100 of the central one. The curves differ in reflectivity: 0.98(narrowest), 0.81, 0.65, and 0.45(widest).

The values of 30 for F and 350 for C are those obtained for a single pass through a Fabry-Perot interferometer. These values fall short of the requirements for Brillouin spectroscopy. Most Brillouin spectroscopy measurements require full width at half-maximum values on the order of 0.2 GHz. This would need a total finesse of 125. In addition the signals that are examined by Brillouin spectroscopy are often $10^6$-$10^{10}$ times weaker than the elastic laser line that also scatters from a sample. This type of measurement needs a significantly larger contrast than 350. The solution to this dilemma can be found in multi-passing. Multi-passing consists of sending the same beam through
a Fabry-Perot interferometer several times. Significant improvements are obtained with this method. The effect is seen through the equations[23]:

\[
F_n = \frac{F}{\sqrt{2^{\frac{1}{n}} - 1}} \\
C_n = C^n
\]

(2.25)

where \( n \) represents the number of passes the beam makes through an interferometer. For the interferometer used in this study \( n=6 \), yielding \( F_n=250 \) and \( C_n=2\times10^{15} \).

With the finesse and contrast being within requirements for Brillouin spectroscopy, one more problem must be overcome. When a spectrum is taken by continuously varying the spacing \( L \) between two plates, peaks from different orders may overlap. The relation between the spacing \( L \) and the order \( m \) is given by[22]:

\[
2L = m\lambda
\]

(2.26)

To avoid the problem of order ambiguity it is sufficient to pass a beam through two interferometers at different spacings. One order will be selected while the other orders are reduced (see Figure 2.6).

![Figure 2.6](image_url)

Figure 2.6[24]: Transmission of a single order due to the use of two Fabry-Perot interferometers in tandem.
This is due to the fact that the wavelength shift $\delta \lambda$ of the inelastically scattered light from the wavelength $\lambda$ of elastically scattered light must satisfy both of the following relations simultaneously:

$$\frac{\Delta L_1}{L_1} = \delta \lambda / \lambda \quad \text{and} \quad \frac{\Delta L_2}{L_2} = \delta \lambda / \lambda \quad (2.27)$$

where $\Delta L_1$ and $\Delta L_2$ are the scan amplitudes of the plates having $L_1$ and $L_2$ spacing respectively. Equations 2.26 and equation 2.27 then lead to the condition:

$$\frac{L_1}{L_2} = \frac{\Delta L_1}{\Delta L_2} = \frac{m_1}{m_2} \quad (2.28)$$

The overlapping order problem can now be theoretically solved. However, designing a system, which has two Fabry-Perot interferometers with different spacings that must be kept parallel and dynamically synchronized through scans lasting an hour or longer (possible scanning time of a Brillouin study) was not an easy task. J. R. Sandercock overcame this difficulty when he developed the Tandem Fabry-Perot Interferometer[24] (see Figure 2.7).

**Figure 2.7[24]:** Top view of the Tandem Fabry-Perot interferometer design developed by Sandercock
The Tandem Fabry-Perot Interferometer consists of two plates mounted on a translation stage. The angle between the normals to the faces of the two plates is given by $\alpha = 20.4^\circ$. Two other plates are rigidly fixed in front of the ones on the translation stage to form the two Fabry-Perot interferometers. When the plate spacing for one of the two interferometers is set at $L$, the other spacing is automatically set to $L \cos(\alpha)$. When small oscillations are induced by the translation stage the spacings satisfy equation 2.28.

2.3 Experimental set-up

The experimental set-up for the Brillouin scattering experiments is illustrated in Figure 2.8.

![Figure 2.8: Experimental set-up for the experiments of this thesis.](image)
For the experiments of this thesis, a Kr+ laser at a wavelength of 647.1 nm (1.92 eV) was used. An intracavity etalon was used in the laser to assure single frequency operation. The laser light was then focused onto the sample with a camera lens to an approximate spot size of 50 microns. Scattered light was collected in backscattering geometry and focused into the Fabry-Perot apparatus through an entrance pinhole. The beam is then collimated and sent through the six-pass tandem Fabry-Perot interferometer. The transmitted light is then directed onto a silicon detector that sends information to a data acquisition system. The results are in the form of a graph of counts versus channel number. The number of registered counts is a measure of the intensity and the channel number can be transformed into a frequency shift that corresponds to the frequency of the excitation probed.

2.4 Light scattering from acoustic waves

It is now established that weakly scattered inelastic light signals can be separated and detected in the presence of strong, parasitic, elastic light signals. Why light should scatter inelastically from a material must now be addressed.

At a given temperature, atoms in a material will vibrate about their lowest energy positions. The motion of any one atom will have an effect on the motion of its neighbors. Collective motion of atoms throughout the sample becomes possible at certain frequencies. The associated normal modes lead to in-phase and out-of-phase excitations. The in-phase vibrational motion occurs at lower frequencies than the out-of-phase motion and these lower frequencies are called acoustic modes. The out-of-phase frequencies are called optic modes. Typically, in BLS, acoustic frequencies are studied.
Light is scattered from acoustic waves (or phonons) in two ways, either by elasto-optic scattering or by ripple scattering\[25\]. The mechanism, which is dominant, depends on whether the sample is transparent or opaque to the incident light. For a transparent sample, elasto-optic scattering is important. For an opaque material, where the penetration depth is less than the wavelength of the incident light, ripple scattering will dominate.

Elasto-optic scattering occurs because the phonons will perturb the dielectric function. As a result, the electromagnetic waves of the incoming light will interact with this perturbation and some photons will be scattered inelastically. Elasto-optic scattering occurs primarily with bulk phonons, but there can also be contributions from surface phonons.

Ripple scattering results from surface deformation by phonons. Phonons at a free surface or interface will corrugate or “ripple” the surface. As the phonons propagate, this ripple may be viewed as a moving grating that is capable of scattering incoming light.

The cross-sections for both elasto-optic and ripple scattering have been calculated using a Green’s function method\[26,27,28\] and by calculating the total scattered electric field\[25,29,30\]. Both methods, however, require knowledge of the elastic (C_{ij}), electric (\varepsilon_{ij}), and elasto-optic (k_{ij}) properties of the material being studied. The elasto-optic constants are, in general, not known. This makes calculating the cross-sections, and therefore peak intensities, difficult.

Typically the most crucial information to be extracted from a BLS measurement is the peak position, which depends only on the material properties. To determine how
the peak positions relate to the material's elastic constants, it is useful to start with the wave equation[31]:

$$\rho \frac{\partial^2 u_j}{\partial t^2} - c_{ijkl} \frac{\partial^2 u_k}{\partial x_i \partial x_j} = 0 \quad (2.29)$$

where \( \rho \) is the density of the medium and \( c_{ijkl} \) are elements of the elastic stiffness tensor. By applying appropriate boundary conditions the \( c_{ii} \)'s can be obtained. For the chalcogenide glass system, the scattering is from bulk phonons in an isotropic medium. The relations between the elastic properties of the solid and the peak frequencies then become[31]:

$$C_{11} = \rho v_1^2 \quad (2.30)$$

$$C_{44} = \rho v_t^2 \quad (2.31)$$

Where \( C_{11} \) is the elastic constant for longitudinal modes and \( C_{44} \) is the elastic constant for transverse modes. \( v_1 \) and \( v_t \) represent the longitudinal and transverse speeds of sound in the solid. The speed of the acoustic modes relates directly to the frequencies measured using the BLS system by \( v = \lambda f \), where \( \lambda \) is the wavelength of the phonon in the medium and \( f \) is the appropriate longitudinal or transverse mode frequency.

Conditions are different for the fcc cobalt sample. In this case, the modes being studied are surface ones for a soft film on a hard substrate (the criterion for considering the layer softer than the substrate is that the layer's transverse velocity is less than the substrate's transverse velocity). The wave equation is solved separately for the film and substrate[32]. Plane wave solutions are used as solutions to the wave equation and only
decaying solutions are allowed for the substrate because it is treated like a semi-infinite material. The boundary conditions required are continuity of the displacement and stress across the film/substrate interface and vanishing of the stress at the free surface of the film. Phase velocities of allowed modes can be found by satisfying the condition that the boundary condition determinant equals zero. The mode associated with the lowest phase velocity value is called the Rayleigh mode. The higher order solutions are also associated with Rayleigh modes, but they are frequently referred to as Sezawa modes. Elastic constants are obtained numerically in this situation.

Rayleigh waves in a layer supported by a substrate are dispersive[32]. Figure 2.9 shows a representative dispersion curve for a soft film (ZnO) on a hard substrate (Si). The x-axis is a plot of $hk$ where $h$ is the film thickness and $k$ is the wavevector. For $hk=0$, the Rayleigh mode has the Rayleigh velocity of the substrate. As $hk$ increases the Rayleigh mode velocity decreases asymptotically to the layer Rayleigh velocity. The higher order Rayleigh modes (or the Sezawa modes) require a minimum film thickness to propagate. Once this thickness is reached the modes begin with a velocity equal to the substrates transverse velocity and decrease asymptotically to the layer transverse velocity.

2.5 Summary

The technique of Brillouin light scattering consists of a detailed understanding of how the photons scattering from a sample can be manipulated by optical methods to reveal information about excitations within the sample. Multiple-beam interference is exploited to select certain frequencies. Once the frequency associated with an acoustic
Figure 2.9[32]: Dispersion curve for the first three Rayleigh modes from a ZnO film on a Si substrate.
mode excitation is obtained, it can be used to determine elastic properties of the sample. One goal of this thesis is to discover how the rigidity of $\text{Ge}_x\text{Se}_{1-x}$ changes with the addition of Ge (the motivation for this will be discussed in the following chapter). The rigidity of a sample relates directly to its elastic properties. A second goal is discovering the elastic constants for the fcc phase of cobalt. As has been shown in this chapter, the BLS technique is well suited for achieving both of these objectives because of its ability to extract frequency data that can be translated into elasticity information.
CHAPTER 3

CHALCOGENIDE GLASSES

3.1 Definition

The chalcogenide glasses get their name from the chalcogen elements in Group VI of the Periodic Table (e.g. O, S, Se, Te). These elements form covalent compounds with Group V (the pnictides) and Group IV elements. In general, elements from these groups obey the 8-N rule[33], which states that the number of covalent bonds the element has is given by 8-N, where N is the Group number. Therefore, a chalcogen element tends to form 2 covalent bonds, a pnictide 3, and a Group IV element 4. While this rule is a general trend, sometimes the number of bonds can deviate. When this occurs the atoms are referred to as coordination defects.

The term “glass” has been defined in several different ways. In common usage it is considered synonymous to “amorphous”, but some distinctions can be made. Generally, amorphous and glassy materials are distinguished as having none of the periodicity associated with a crystalline structure. A glass, however, can be further characterized as “an amorphous solid which exhibits a glass transition”[34]. A glass transition is a “phenomenon in which a solid exhibits a more or less abrupt change in
derivative thermodynamic properties (e.g. heat capacity or thermal expansivity) from crystal-like to liquid-like values with change of temperature"[34].

The specific chalcogenide glass that was investigated in this study is Ge$_x$Se$_{1-x}$, selenium being the 2-fold coordinated chalcogen element and germanium being a 4-fold coordinated Group IV element. Ge$_x$Se$_{1-x}$ is a good glass former in the composition range of x=0 to 0.42[35]. The analysis has concentrated in the region x=0.15 to x=0.33, a range in which the floppy to rigid transition has been predicted. The compound is semiconducting and in this range the energy gap is ~2eV[36].

3.2 Constraint Theory

Selenium, being 2-fold coordinated, tends to form chain and ring structures. Addition of 4-fold coordinated germanium leads to cross-linking of the Se chains (see Figure 3.1).

![Figure 3.1](image_url)

**Figure 3.1:** Cartoon representing the chain and ring structures formed by selenium (white circles) and the cross-linking of chains due to addition of germanium (black circles).
As more and more Ge is added to Se, the material becomes rigid. The amount of Ge necessary to transform the structure from a predominantly "floppy" Se matrix to a "rigid" Ge one can be found using contraint theory. J.C. Phillips first proposed a constraint counting argument[1] to determine the critical concentration of Ge required for rigidity. This idea was extended by M.F. Thorpe to develop a formal constraint theory [2]. It is Thorpe's constraint theory that will be referred to in this section.

Consider \( N \) atoms with \( n_r \) of them having \( r \) bonds. Therefore:

\[
\sum_r n_r = N
\]

For a covalent network of atoms, the primary constraints on the system come from bond stretching and angle bending. The potential due to these constraints can be written as:

\[
V = \frac{1}{2} \sum_{(i)} \alpha_{ij} (\Delta r_{ij})^2 + \frac{1}{2} \sum_{(ijk)} \beta_{ijk} (\Delta \theta_{ijk})^2
\]

Where \( \alpha_{ij}, \beta_{ijk} \) are force constants, \( \Delta r_{ij} \) is the change from equilibrium in nearest neighbor bond lengths, and \( \Delta \theta_{ijk} \) is the change from equilibrium in bond angle between adjacent bonds \( <ij> \) and \( <jk> \). Diagonalizing the dynamical matrix formed from the potential will give the number of constraints for the network. However, for the case of 3 dimensions, the bond stretching and angle bending constraints can be counted directly. For \( r \) bonds, the bond stretching constraints are \( r/2 \). The angle bending constraints are \( 2r-3 \).

To find the number of "zero frequency", or "floppy" modes (ways in which the network can be deformed with no cost in energy), the number of constraints must be subtracted from the total degrees of freedom for the system. For a 3 dimensional system the number of degrees of freedom is \( 3N \). Therefore the equation to find the number of zero-frequency modes \( M_0 \) is given by:
M₀ vanishes at the average coordination at which the system becomes rigid. This gives \( \bar{r} = r_c = 2.4 \), where \( \bar{r} \) is the average coordination number, and \( r_c \) is the critical coordination number for rigidity. When \( \bar{r} > r_c \) the network is rigid, and it is floppy when \( \bar{r} < r_c \).

### 3.3 Elastic Constants

As discussed in Chapter 2, BLS measurements relate directly to the elastic constants of a material. Thorpe and He[37], as well as Franzblau and Tersoff[38], performed numerical simulations to determine the elastic constants for a covalent glass system. In this section the work of Thorpe and He will be discussed and related to that of Franzblau and Tersoff.

Thorpe and co-workers began their simulation by selecting a potential similar in form to the one given in the previous section:

\[
V = \frac{1}{2} \sum_{ij} \alpha_{ij} [(u_i - u_j) \cdot r_{ij}] + \frac{1}{8} \sum_{ijk} \beta_{ijk} [(u_i - u_j) \cdot r_{ik} + (u_i - u_k) \cdot r_{ij}]^2
\]

Commencing from a diamond lattice, bonds were randomly removed. They allowed for two, three and four coordinated atoms, but did not permit formation of dangling bonds. To test whether the results might be dependent on parameters besides the average coordination, Thorpe and co-workers chose two normal bond distributions and one "extreme" distribution where the number of two coordinated sites was enhanced at the expense of the three coordinated sites (see Figure 3.2).
Figure 3.2[37]: Fraction of 3 coordinated sites as a function of mean coordination, $\langle r \rangle$.
Two typical distributions are shown by squares and triangles and one "extreme" distribution is shown by circles.

Using these three bond distributions, the number of floppy modes, $f$, the elastic constants $C_{11}$ and $C_{44}$, and the bulk modulus ($B$) were calculated. $f$ was calculated by counting the number of zero eigenvalues of the diagonalized dynamical matrix formed from the potential. Systems of 216-atom networks were used to find $f$. The expressions for the elastic moduli were those for the diamond lattice:

$$B = \frac{1}{3} (C_{11} + 2C_{12}) = \frac{1}{12a} (3\alpha + \beta)$$

$$C_{11} = \frac{1}{4a} (\alpha + 3\beta)$$

$$C_{44} = \frac{1}{a} \frac{\alpha \beta}{(\alpha + \beta)}$$

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512-atom networks were used to find the elastic moduli. \( \frac{\beta}{\alpha} \) was given a value of 0.2 and \( \frac{a}{\sqrt{3}} \) was used for the nearest neighbor distance. The results for \( f \) and \( C_{11} \) are shown in Figure 3.3, where the triangle and squares represent the "normal" distributions and the circles represent the "extreme" distribution.

Figure 3.3[37]: Elastic modulus \( C_{11} \) as a function of mean coordination for the three distributions shown in Figure 3.2. The inset shows the number of zero-frequency modes as a function of mean coordination for one of the "normal" bond distributions.

No significant variation was found between the three bonding distributions. Figure 3.4 illustrates the results for all three elastic moduli averaged over all three distributions.
Figure 3.4[37]: Elastic moduli $C_{11}$, $C_{44}$, and $B$ averaged over all three distributions as a function of mean coordination.

As is seen in Figures 3.3 and 3.4, the numerical simulations compare favorably with the mean-field theory predictions that the number of floppy modes should decrease to zero as the average coordination increases to 2.4 and that the elastic constants should go to zero as the average coordination is decreased to 2.4. The results of Thorpe and co-workers also show that the elastic moduli are governed by a power law dependence in average coordination with the critical exponent around 1.5. The solid lines in Figure 3.4 come from the equations:

$$C_{11} = 0.69(\alpha/4\alpha)(<\rho>-\rho_p)^{1.5}$$

$$B = C_{44} = 0.35(\alpha/4\alpha)(<\rho>-\rho_p)^{1.5}$$

where $<\rho>$ refers to the average coordination and $\rho_p$ is the critical concentration of 2.4.

Franzblau's results also show that the elastic constants vanish around an average coordination of 2.4. He too finds a power law behavior. Using a range of values for
\( \gamma = \beta / \alpha \) (where \( \gamma \) was given the value for diamond) from \( 10\gamma \) to \( \gamma/1000 \), he found the critical exponent to range from 1.35 to 1.89, respectively.

### 3.4 Evidence for the intermediate phase

Constraint theory originally predicted a solitary rigidity transition at \( x=0.20 \). However, both numerical simulations and experimental work exist to support the concept of an intermediate phase (IP) spanning a finite concentration range \( x_c(1) \) and \( x_c(2) \) that separates the rigid from the floppy in chalcogenide glasses.

#### 3.4.1 Theoretical evidence

Thorpe and colleagues\[8\] performed several numerical simulations that lead to the existence of an IP that could exist in chalcogenide glass systems. Their work rests on the foundation of Constraint Theory. Their system consisted of two, three, and four-fold coordinated atoms, for example \( \text{Ge}_x\text{As}_y\text{Se}_{1-x-y} \). Ge represents the 4-fold coordinated atom, As the 3-fold pnictide atom and Se the 2-fold chalcogen atom. Following Constraint Theory, this system would have an average coordination number, \( \bar{r} \), of \( 2+2x+y \) and would exhibit a single rigidity transition at \( \bar{r} = 2.4 \). Thorpe used a random bond model (RBM) to test this transition point. In this model atoms are positioned at random points on a plane, and connected with the proper number of bonds to each other (See Figure 3.5).
One important feature of the RBM is that there are no loops or rings; therefore, it gives a soluble approach to discover how the system would behave in the absence of rings. As bonds are added to the dilute system, rigidity will percolate in an "explosive-like" manner with the formation of an infinite rigid cluster. The RBM predicts this transition to occur at $\bar{\tau}_c = 2.3893$.

The RBM did not contain loops or rings. Thorpe's group wanted to determine how this transition might change if the number of small rings in the system was allowed to vary. A diamond lattice was a soluble system upon which they could vary the number of a given ring size. Thorpe chose to focus on eliminating small rings because small rings are those that first become nucleation sites for rigidity. To accomplish this, they started with a complete diamond lattice and selectively removed bonds that reduced the number of rings of a desired size. Once the target number of the selected ring size was reached, further bonds were removed at random. A diamond lattice has ring sizes of 6, 8, 10, and larger. Thorpe chose to eliminate the 6 and 8 size rings because rings larger than...
8 atoms would remain floppy and not contribute to rigidity nucleation. If one uses the number of floppy modes, \( f \), as a "free energy-like" quantity and the mean coordination number as a "temperature-like quantity" then the simulations showed that the rigidity transition tended to first order as the number of 6 and 8 size rings \( (n_{6,8}) \) was reduced (see Figure 3.6). The results of the simulation with zero 6 and 8-fold rings most closely resembled those of the RBM. Therefore, Thorpe and his colleagues suggest that the absence of small rings is what drives the rigidity transition in the RBM to first order.

![Figure 3.6](image)

**Figure 3.6**: Derivative of the fraction of floppy modes, \( f' \), versus the mean coordination number \( \langle r \rangle \). The number of six- and eight- fold rings is reduced for each curve as noted in the figure. The lines are only a guide to the eye.

One final step taken by Thorpe's group was to determine how self-organization may play a role in the rigidity transition[8]. They chose to start with a floppy network and add bonds, with the new criteria that a bond insertion only be allowed if it left the system unstressed. Thorpe defines unstressed as the condition where each bond and
angle can have its natural bond length and angle without being forced to change by its surround environment[8]. As each bond was added, the system was checked to see if the bond insertion created any stress. If it did, that insertion was not allowed and a new insertion was attempted. This process continued until it was no longer possible to add another bond without stressing the system. They found that the system became rigid while it was still stress free. The rigidity transition occurred at a mean coordination of 2.375±0.0015 (x=0.1875). Thorpe referred to this transition as the isostatic transition. However, there now existed a second transition. This second transition was from an unstressed rigid state to a stressed rigid state. This transition occurred at a mean coordination of 2.392 (x=0.1960) (see Figure 3.7), and was labeled the stress transition.

![Figure 3.7](image)

**Figure 3.7[8]:** Fraction of sites in the rigid and stressed percolating clusters. The circles are averages over the four simulations using 64,000 sites and the triangles are averages for simulations using 125,000 sites.

There are no redundant constraints below the stress transition, so the number of floppy modes is still linear in $\bar{r}$. This means that the isostatic transition will not appear in a plot
of floppy modes vs $\bar{r}$. The stress transition will appear on such a plot as a change in slope since Thorpe associated it with the first order transition due to the rapid increase in the number of sites (about $\frac{1}{2}$) in the stressed cluster after a few additional bonds are inserted at the stress transition (see Figure 3.8).

![Graph of Number of Floppy Modes vs Mean Coordination Number]

**Figure 3.8**: Number of floppy modes versus mean coordination number. The dashed line represents the constraint counting approach with the rigidity transition at 2.4 (open square). The dot-dash line represents the randomly diluted diamond lattice with a second order transition at 2.375 indicated by a solid circle. The self-organized model is shown by the solid line. It has a *second order* transition from a floppy to an unstressed rigid state at 2.375 (shown as an open circle) and a first order transition to a stressed rigid state at 2.392 (shown as an open triangle).

These two transitions create an intermediate phase consisting of an unstressed rigid region.
3.4.2 Experimental evidence

Experimental evidence for the existence of the intermediate phase in chalcogenide glasses has emerged in the recent past. Four classes of experiments have been performed by Dr. Punit Boolchand and his group at the University of Cincinnati on several glass systems providing evidence for the IP. These experiments[39] are Temperature-Modulated Differential Scanning Calorimetry (MDSC), Raman scattering measurements, molar volume measurements, and Mossbauer spectroscopy. The results of these experiments are summarized in the following paragraphs.

3.4.2.1 Differential scanning calorimetry

Conventional Differential Scanning Calorimetry (DSC) uses a linear ramp in temperature to search for endothermic heat flow signatures of glass softening by comparing the glass to an inert reference. MDSC varies from DSC by including a sinusoidal fluctuation to the applied temperature gradient. This allows for deconvolution of the results into a reversible heat flow (which follows the sinusoidal pattern) and non-reversible heat flow. MDSC measurements from the Cincinnati group on the Ge$_x$Se$_{1-x}$ glass system found that the non-reversing heat flow exhibited a minimum around the composition $x = 0.23$ (see Figure 3.9).
Figure 3.9(40]: Non-reversing heat flow versus Ge concentration showing a global minimum near x=0.225.

MDSC measurements were performed on other chalcogenide glass systems and intermediate phases were observed for the ternary systems of Ge<sub>x</sub>As<sub>x</sub>Se<sub>1-x</sub> and Ge<sub>0.25</sub>Se<sub>0.75</sub>I<sub>x</sub>[40].

3.4.2.2 Raman measurements

Raman measurements[40] taken on the Ge<sub>x</sub>Se<sub>1-x</sub> glass system show an increase in peak intensity associated with corner-sharing (CS) tetrahedra (200cm<sup>-1</sup>) and edge-sharing (ES) Ge(Se<sub>1/2</sub>)<sub>4</sub> tetrahedra (215cm<sup>-1</sup>), while the intensity of the Se-Se stretch mode (CM) of Se<sub>n</sub>-chains (250cm<sup>-1</sup>) decreases as the Ge concentration is increased (see Figure 3.10). A graph (see Figure 3.11) of the frequency of the CS and ES modes with Ge concentration reveals three regions. The first region is linear with
Figure 3.10[40]: Macro-Raman plots for various Ge concentrations, $x$. The three dominant features are the corner-sharing mode (CS), the edge-sharing mode (ES), and the Se$_n$-chain mode (CM).
Figure 3.11[40]: (a) Corner-sharing (CS) and (b) edge-sharing (ES) mode frequency variation with Ge composition.
concentration and corresponds to the floppy regime. The third region obeys a power law behavior as predicted for the rigid phase by Franzblau, Tersoff [38], Thorpe, and He [37]. The region connecting the floppy and rigid regions corresponds to the intermediate phase. From the Raman experiments Boolchand et. al. placed the intermediate phase between 20%-26% Ge concentration.

3.4.2.3 Molar volumes

Molar volume measurements on glasses "provide a means to establish compactness of the network backbone or the available free volume" [39]. Feltz et al. [41] first discovered that the molar volume of Ge$_x$Se$_{1-x}$ displayed a minimum around $\bar{r} = 2.44$. Boolchand repeated these measurements and found a minimum at $\bar{r} = 2.46$ (see Figure 3.12).

3.4.2.4 Mossbauer spectroscopy

The last set of experiments to show evidence of an IP is from Mossbauer spectroscopy. Here a description is given of the $^{129}\text{I}$ Mossbauer emission spectroscopy performed by Boolchand [39]. In $^{129}\text{I}$ spectroscopy, $^{129}\text{mTe}$ is used as a dopant in the Ge$_x$Se$_{1-x}$ system. Te has a covalent radius of 1.36Å. This is larger than the covalent radius for Se (1.16Å). The consequence of the Te atom's larger size leads to substitution for Se atoms that have surrounding free volume available or where the local bonding structure can be distorted with little or no strain energy. The daughter $^{129}\text{I}$ sites resulting
Figure 3.12[39]: Variation of molar volume with Ge composition showing a global minimum.
from the Te atoms will then give bonding information because the nuclear quadrupole couplings of an I-Ge bond (-890MHz) is distinguishable from the I-Se bond (-1385MHz) [42]. Boolchand refers to the I-Ge bond as an A site and an I-Se bond as a B site[39]. A random network model predicts a monotonic decrease in B sites compared to A sites[43] (shown as a dashed line in Figure 3.13). The results of the spectroscopy, however, show a peak centered at 23% Ge concentration. Boolchand suggests that the peak reflects the “largest surface to volume ratio of the rigid fragments”[39]. Instead of allowing large stressed rigid structures the network prefers to disperse the rigid fragments to keep itself stress free. Small rigid volumes force Te atoms to remain at B sites longer than if large rigid structures were present.
Figure 3.13[39]: Variation in site intensity ratio $I_B/I_A$ from $^{129}$I Mossbauer measurements on Ge$_x$(Se$_{0.99}$Te$_{0.01}$)$_{1-x}$ glasses versus $x$ (smooth line). The broken line represents the site intensity ratio for a chemically ordered continuous random Ge$_x$Se$_{1-x}$ network.
CHAPTER 4

OBSERVATION OF PHOTO-INDUCED FLUIDITY IN A CHALCOGENIDE GLASS

4.1 Introduction

In this Chapter, Brillouin light scattering (BLS) measurements are presented for Ge_xSe_{1-x} glasses taken primarily with 647.1nm radiation from a Kr^+ -ion laser as the probe beam. At this excitation energy, the samples are quasi-transparent to the incident radiation and therefore bulk, and not surface, properties of the glasses are being probed. In these backscattering measurements, we excite the longitudinal acoustic (LA) mode, and find that the mode frequency, \( v_{LA}(x, P) \), softens (red shifts) and concomitantly broadens strikingly as a function of probe power \( P_r \). Evidence of onset of the mode softening first appears as \( P_r \) is increased from 2mW to 3mW revealing a shallow minimum with \( \Delta v_{LA} / v_{LA} \approx 8\% \) within the glass compositions \( 0.15 < x < 0.25 \). With rising \( P_r \) (4-6mW), a progressively increasing \( \Delta v_{LA}(x) \) is observed from \( x \sim 0.15 \), leading up to a gigantic 25% reduction in \( v_{LA}(x) \) near the critical value \( \tilde{r} = 2.38(2) \) (\( x = 0.19 \)).

For \( x > 0.20 \) these photo driven self- energy changes begin to rapidly diminish and are completely suppressed even at the highest laser power \( P_r = 6mW \) beyond \( x \sim 0.24 \). These observations constitute evidence for light-induced melting of the network when the
\( \beta \) constraints are weakened allowing for pliancy of the bond angles. The curbing of these photon-induced phonon self-energy changes at concentrations beyond \( x \sim 0.19 \) arise from the percolation of rigidity due to cross-linking and the eventual onset of stressed rigidity. In contrast to the Raman measurements [6], the long wavelength nature of the vibrational excitation probed in the BLS measurements, permits one to directly establish the global photo-melting of the network at a given probe power level \( P_r \).

Data taken with 514.5nm and 488nm is also presented to highlight the differences between excitation with near or sub bandgap, as opposed to super bandgap, radiation. For both of these wavelengths it is shown that the LA mode frequency still softens and the peak broadens reversibly with increasing laser power; however there is no longer a local minimum to the softening nor a maximum to the broadening as a function of \( x \). Instead, the extent of the softening and broadening increases monotonically with decreasing Ge concentration. The difference in the response to exciting photon wavelength is accounted for by the increasing opacity of the samples as the wavelength decreases and the resulting thermal effects (discussed in section 4.4).

### 4.2 Sample preparation

The samples used in these experiments were prepared at the University of Cincinnati in Professor Punit Boolchand's research group. The desired molar ratio of 99.9999\% pure elemental Ge and Se was sealed in an evacuated (<5x10\(^{-7}\) Torr) silica ampoule. The melt was homogenized at 1000\(^\circ\)C for at least 48 hours and then equilibrated at about 50\(^\circ\)C for another 24 hours before being water quenched. To precisely determine the glass composition, the glass transition temperature was measured.

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for each sample. Their results (along with data for Ge$_x$S$_{1-x}$) are shown in Figure 4.1. These data reflect the monotonic increase of $T_g$ with $x$.

![Figure 4.1](image)

**Figure 4.1**: Glass transition temperatures for the binary compounds Ge$_x$S$_{1-x}$ (open circles) and Ge$_x$Se$_{1-x}$ (solid circles).

### 4.3 Experiment

The BLS measurements were performed with a tandem six-pass Fabry-Perot interferometer [24] using a probe beam focused to a 50μm spot, and spectra recorded as a function of laser power in the $2\text{mW} \leq P_r \leq 9\text{mW}$ range, and glass compositions in the $0.15 < x < 1/3$ range. Excitation wavelengths used were 647.1nm, 514.5nm and 488nm. The local temperature due to laser heating was estimated for several values of $P_r$ through Raman Stokes/ anti-Stokes measurements at various compositions. For all samples, $T$-
dependent Brillouin measurements were also undertaken to separate thermal effects from the photo-induced contributions to the observed softening. BLS data were recorded at low, constant, laser power ($P_r = 3$ mW) at various temperatures up to 20°C above the glass transition temperature $T_g$ for each composition. The $\text{Ge}_x\text{Se}_{1-x}$ glass samples used in the present work were the same samples used in the earlier [6,7] Raman scattering measurements. The glass transition temperatures, $T_g(x)$, and the $\Delta H_{nr}$ heat-flow term were established [6,7] by Temperature-Modulated Differential Scanning Calorimetry (MDSC).

During the course of the experiments, it became clear that there are three predominant power regimes associated with the $\text{Ge}_x\text{Se}_{1-x}$ samples. These regimes are classified as low power ($P \leq 3$ mW), intermediate power ($4$ mW $< P < 6$ mW) and high power ($P > 6$ mW). Trends in the Brillouin spectra are quantitatively different within these regimes. The experiments on $\text{Ge}_x\text{Se}_{1-x}$ in this thesis focus on the low and intermediate power regimes. Preliminary results from the high power regime will be presented in Appendix A.

Figure 4.2 displays the observed Brillouin lineshapes at several glass compositions, all recorded at a low probe power of $P_r = 2$ mW (subscript for power refers to excitation wavelength: $r$=red (647.1nm), $g$=green (514.5nm) and $b$=blue (488nm)). Each spectrum was acquired for an average time period of two to three minutes. Here one observes the LA-mode frequency, $v_{LA}(x)$, to systematically blue-shift with increasing $x$. Figure 4.3 and Figure 4.4 show the observed Brillouin lineshape for glass samples at $x = 0.33$ and $x = 0.22$ respectively, this time studied as a function of probe laser power ($P_r$). For these experiments the recorded power levels, $P_r$, did not extend
Figure 4.2: Observed Brillouin lineshapes in Ge$_x$Se$_{1-x}$ glasses at indicated compositions $x$ showing a blue-shift of the LA-mode with $x$. 

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Figure 4.3: Observed Brillouin line shapes in Ge$_{0.33}$Se$_{0.67}$ glass taken sequentially (bottom to top) as a function of indicated 647.1 nm probe power, $P_r$, showing essentially no change of LA mode with $P_r$. 

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Figure 4.4: Observed Brillouin line shapes in Ge$_{0.22}$Se$_{0.78}$ glass taken sequentially (bottom to top) as a function of indicated 647.1nm probe power, $P_r$, showing reversibility of LA mode softening with $P_r$. 

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beyond the intermediate power range (i.e. \( P_r \leq 6 \text{mW} \)). Spectra from the \( x = 0.33 \) sample exhibited no change as \( P_r \) increased to \( 6 \text{mW} \). In contrast, the \( x=0.22 \) spectra reveal the LA-mode frequency (\( \nu_{LA} \)) to red-shift and the mode width (\( \Gamma_{LA} \)) to concomitantly broaden as \( P_r \) increases to \( 6 \text{mW} \). Furthermore, upon decreasing the power \( P_r \) back to its initial value of \( 2 \text{mW} \), one recovers the original lineshape (\( \nu_{LA}, \Gamma_{LA} \)) underscoring that changes in the observed Brillouin lineshape up to \( P_r = 6 \text{mW} \) are reversible. Parallel observations taken in close vicinity to \( x = 0.19 \), show the mode-softening and broadening effect with \( P_r \) to be spectacularly large (\( 25\% \)), as revealed by the global summary of the present Brillouin results appearing in Fig. 4.5.

In Fig. 4.5, the variation of \( \nu_{LA}(x,P_r) \) and \( \Gamma_{LA}(x,P_r) \) is plotted in panels (a) and (b), while the non-reversing heat-flow term, \( \Delta H_{nr}(x) \) deduced from the Temperature-Modulated Differential Scanning Calorimetry (MDSC) data [6,7] is provided in panel (c). The central result of the present work (Fig. 4.5) is the giant, reversible, softening and broadening of the LA-mode in the mildly floppy network \( (0.15 < x < 0.19) \) and its subsequent recovery as rigidity percolates through the lattice. These behaviors appear to be correlated to the nonreversible heat flow in MDSC measurements. In particular \( \Delta H_{nr} \) displays a local minimum at \( x_c(1) \) which coincides with the concentrations where the largest light induced changes in \( \nu_{LA}(x,P_r) \) and \( \Gamma_{LA}(x,P_r) \) occur. In addition to the local minimum, a more pronounced global minimum in \( \Delta H_{nr} \) occurs at \( x_c(2) \). Thermal contributions to the softening do not quantitatively change the position of the minimum observed in Figure 4.5(a), however they do qualitatively change the shape of the curves at
Figure 4.5: Brillouin light scattering results in Ge\textsubscript{x}Se\textsubscript{1-x} glasses. (a) LA mode frequency, \(v_{LA}\), and (b) mode width, \(\Gamma_{LA}\), variation with glass composition, x, studied at various probe power levels, \(P_r\). squares – 2mW; circles – 3mW, triangles – 4mW; inverted triangles – 5mW, diamonds – 6 mW. (c) Non-reversing heat-flow, \(\Delta H_{nr}(x)\) deduced from MDSC taken from ref. 6. Solid lines are a guide to the eye. Temperature corrected data shown in Fig 4.12
low Ge concentration. The thermal effects will be discussed in detail in the following section.

Figure 4.6 shows the observed Brillouin lineshape for glass samples at \( x = 0.22 \), this time for an excitation wavelength of 514.5nm (instead of 647.1nm related to Figure 4.5). The peak behaviors are qualitatively similar to those in Figures 4.4 recorded for 647.1nm light. Reversible frequency softening and linewidth broadening are evident. In general the Brillouin signal intensity was weaker for the peaks excited at this wavelength compared to data recorded at 647.1nm. Each spectrum was acquired for an average time of ten minutes. Another difference is evident upon examining the linewidth. Peaks excited with 514.5nm photons were much broader than those excited in the red. Figure 4.7 summarizes results similar to those of Figure 4.5, except the excitation wavelength is now 514.5 nm. As seen, the extent of the softening increases monotonically with decreasing Ge concentration.

This differing behavior between Figures 4.5 and 4.7 can be traced to the penetration depth of the light. The approximate penetration depths for various Ge concentrations are given in Table 4.1 for both \( \lambda=647.1\text{nm} \) and \( \lambda=514.5\text{nm} \). As the excitation energy is increased, the absorption coefficient for each sample increases dramatically\[35,44-46\]. The resulting absorption leads to greater confinement of the photon energy to the vicinity of the sample surface. Therefore, for a given focused spot size, a lower wavelength photon beam will deposit its energy in a smaller volume...
Figure 4.6: Observed Brillouin line shapes in Ge_{0.22}Se_{0.78} glass taken sequentially (bottom to top) as a function of indicated 514.5nm probe power, P_g, showing reversibility of LA mode softening with P_g.

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Figure 4.7: Frequency and linewidth data for all Ge concentrations. The excitation wavelength is 514.5nm.
Table 4.1: Penetration depth of \( \lambda = 647.1 \text{nm} \) and \( \lambda = 514.5 \text{nm} \) laser radiation in Ge\(_x\)Se\(_{1-x}\) at various Ge concentrations.

than photons of a higher wavelength. This will enhance the extent of local heating for a given Ge concentration, which will be discussed in further detail in section 4.4.

Pump-probe BLS measurements on the present glasses were also performed at glass compositions of \( x = 0.15, 0.22 \) and \( 1/3 \), keeping the narrowly focused probe beam (\( \lambda = 514.5 \text{nm} \)) power \( P_g \) fixed at 4mW and the loosely focused pump beam (\( \lambda = 488 \text{nm} \)) power \( P_b \) variable in the \( 3.5 \text{mW} < P_b < 166 \text{mW} \) range. This range of \( P_b \) yields a similar photon flux as in the probe-only experiments. With increasing \( P_b \), the LA-mode frequency softened by about 25\% for the \( x = 0.22 \) sample and for the \( x = 0.15 \) sample, and by a negligible amount for the \( x = 1/3 \) sample. Figure 4.8 displays the results for the \( x=22\% \) sample up to \( P_b = 84 \text{mW} \). Because of irregular sample shape and difficulty in realizing an accurate measure of the expanded pump beam spot diameter, direct

<table>
<thead>
<tr>
<th>Ge conc.</th>
<th>( \lambda = 647.1 \text{nm} )</th>
<th>( \lambda = 514.5 \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>15%</td>
<td>( 20 \mu\text{m}^a )</td>
<td>( 0.27 \mu\text{m}^d )</td>
</tr>
<tr>
<td>20%</td>
<td>( 40^a )</td>
<td></td>
</tr>
<tr>
<td>25%</td>
<td>( 120^c )</td>
<td>( 1.2^d )</td>
</tr>
<tr>
<td>30%</td>
<td>( 290^a )</td>
<td>( 1.02^b )</td>
</tr>
<tr>
<td>33%</td>
<td>( 1300^a )</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.8: Observed Brillouin line shapes in Ge$_{0.22}$Se$_{0.78}$ glass taken sequentially (bottom to top) with 2.7mW of 514.5nm probe power, $P_g$, and varying the loosely focused 488nm pump power, $P_b$, as indicated. Mode softening and reversibility are evident.
comparisons between pump power levels and probe-only power levels are not reliable. However, the monotonic increase in the degree of softening with decreasing Ge concentration is in harmony with the trends of Fig. 4.7. Furthermore, the softening and broadening of the LA-mode in these experiments were found to be reversible in the pump power $P_b$.

The central results from experiments performed on Ge$_x$Se$_{1-x}$ in the low and intermediate power regimes ($P\leq6$mW) are the softening and broadening of the longitudinal acoustic mode. For all three excitation wavelengths (647.1nm, 514.5nm, and 488nm) used the softening and broadening were reversible. For the 647.1nm wavelength, the softening exhibited a frequency minimum at a germanium concentration ($x=0.19$). This concentration in fact coincides with the concentration found in Raman results for the breaking of the Se bond bending constraint [6].

4.4 Temperature dependence

Undoubtedly some part of the observed mode softening with $P_r$ (Fig. 4.5a) is of a thermal nature, which can be established from the T-dependent BLS measurements. Indeed, since the $T_g$'s of the glasses [6] rapidly increase from 42°C at $x = 0$ to 425°C at $x = 1/3$, one expects the thermally induced softening to be the largest for the very soft pure Se glass and to be the smallest for the rigid GeSe$_2$ glass. Hence if temperature effects were significant to the observations related to softening they should reveal, contrary to the results summarized in figure 4.5(a) and 4.5(b), a monotonic variation of the mode softening and broadening as a function of $x$ (as in the case of the results for 514.5 excitation). Our T-dependent Brillouin measurements in the $23°C < T < 450°C$ range
taken with 647.1nm light and a fixed probe power $P_r = 3$mW, at glass compositions of $x = 0.15, 0.21, 0.23, 0.29$ and $1/3$ are summarized in Figure 4.9 and 4.10. For each composition, the sample was heated to a temperature of $20^\circ C$ beyond $T_g$. For the glass at $x = 0.21$ for instance, $V_{LA}$ is found to decrease from its ambient temperature value by about 9% when the temperature was raised to $215^\circ C$ ($T_g = 195^\circ C$). While it is improbable that heating by a mere 6 mW of laser power could produce a local sample temperature as high as $215^\circ C$, even the full extent of this temperature related contribution to $\Delta V_{LA}(x = 0.21, P_r = 3$mW) is vastly inadequate to account for the observed 22% softening (Fig. 4.5). Further, the $x = 1/3$ glass shows virtually no thermal softening until $450^\circ C$, while the $x = 0.15$ glass shows a 12% softening, fixing in essence the extent of thermally induced softening. Given the steady increase of the $T_g$’s with $x$ and the minimal changes to the band gap for compositions $0.15 < x < 0.30$, it is clear that thermal contributions to the observed softening at $P_r = 3$ mW will be at most 12% for the entire compositions ranging from 0.15 to 0.30. Thus thermal effects do not account for the dramatic changes in $V_{LA}(x,P_r)$ and $\Gamma_{LA}(x,P_r)$ observed near $x = x_c(1)$ with increasing 647.1nm laser power. In Figure 4.5(a) the increased slope of the baseline on which the giant softening in $V_{LA}(x)$ resides as a function of $P_r$ most likely has a small thermal component in addition to a network connectivity related contribution, which will be discussed in the following paragraph.
Figure 4.9: Temperature dependence of $v_{LA}(x)$ mode frequency in indicated glasses studied at a fixed probe power, $P_r = 3$ mW. The compositions of the $\text{Ge}_x\text{Se}_{1-x}$ glasses were $x = 0.15, 0.21, 0.23, 0.29, 0.33$. 

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Figure 4.10: Temperature dependence of $\Gamma_{LA}(x)$ mode linewidth in indicated glasses studied at a fixed probe power, $P_r = 3\text{mW}$. 

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In order to determine the extent of local heating due to the $\lambda=647.1\text{nm}$ laser spot, Raman stokes/antistokes temperature measurements were performed. Four samples (x=15%, 20%, 26%, and 33%) were analyzed at laser powers from 1mW to 7mW. The temperature increase was determined for each. Fits to the data were performed using Microcal Origin version 4.0. A representative fit to the Raman spectra for the 20% sample at a laser power of $\sim 1\text{mW}$ is shown in Figure 4.11. Three Gaussian peaks were used in the fit and the stokes/antistokes intensity ratios were calculated for the peak at $\sim 194\text{cm}^{-1}$. The maximum temperature rise for the 15% sample was estimated to be 125°C. Similarly, temperature increases for the 20%, 26% and 33% samples were 91°C, 82°C and 10°C respectively. The amount of thermal frequency softening was extracted from these local temperature changes by using the frequency shift versus temperature information from Figure 4.9. Figure 4.12 displays the frequency shift and linewidth versus Ge concentration information of Figure 4.5(a) and (b) now corrected for thermal effects.

The longitudinal bulk elastic constant $C_{11}(x)$ was calculated from the frequency data in Figure 4.12(a). The results are plotted in Figure 4.13. Here the relation $C_{11} = \left[\{\rho(x)\lambda^2v_{LA}^2/4n(x)^2\}\right]$ was used to obtain the elastic constant; $\lambda$, is taken as 647.1nm, $n(x)$ represents the refractive index [47], and $\rho(x)$ the specific gravity of these Ge$_x$Se$_{1-x}$ glasses [39]. The present BLS results are in quantitative accord with the $C_{11}(x)$ results on these glasses reported earlier [48] in ultrasonic measurements by several groups. And even though $C_{11}(x)$ becomes super-linear in the rigid phase ($x > 0.26$), the rigidity transitions at $x_c(1)$ and $x_c(2)$ are generally smeared in these bulk measurements due to presence of background forces such as dihedral-angle and van der Waals forces. The
Figure 4.11: Representative fit to the Raman spectra. This spectrum is from the 20% Ge concentration sample. The laser power was ~1mW. Three peaks were used in the fit and the stokes/antistokes intensity ratios were calculated for the peak at ~194cm⁻¹.
Figure 4.12: Brillouin light scattering results in Ge$_x$Se$_{1-x}$ glasses, where figures (a) and (b) are now adjusted for thermal effects. (a) LA mode frequency, $v_{LA}$, and (b) mode width, $\Gamma_{LA}$, variation with glass composition, $x$, studied at various probe power levels, $P_r$. (c) Non-reversing heat-flow, $\Delta H_{nr}(x)$ deduced from MDSC taken from ref. 7. Solid lines are a guide to the eye.
Figure 4.13: Longitudinal elastic constant, $C_{11}(\bar{r})$ variation with mean-coordination number, $\bar{r}$, in Ge$_x$Se$_{1-x}$ glasses studied as a function of indicated pump power $P_r$. 

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dihedral angle is formed between four bonded atoms A-X-Y-B and is defined by the angle between the planes containing atoms AXY and XYB [49]. The dihedral angle force is a restoring force that opposes any change to the equilibrium value of the dihedral angle.

For the case of 514.5nm and 488nm light the amount of heating should be much higher. This is because there is a larger difference between the band gap for Ge_xSe_1-x and the energy delivered by a shorter wavelength photon than a longer one. This, in turn, increases the absorption for shorter wavelength photons. The penetration depths shown in Table 4.1 support this idea. The amount of heat produced by the 514.5nm light will be restricted to a volume on the order of 100 times less than the volume for 647.1nm light. This should lead to higher temperatures and, therefore, larger thermal components of the softening. The monotonic increase in the softening with decreasing Ge concentration provides further evidence that the thermal component washes out the athermal one because it follows the trend in T_g's.

4.5 Summary

At low probe-power (P_t < 3mW), the observed \( v_{\text{LA}}(x) \) increase with \( x \) reflects the intrinsic variation (Figure 4.13) of the longitudinal bulk elastic constant \( C_{11}(x) \) in the glasses with connectivity (\( \bar{\tau} \)). With increasing probe-power \( P(\geq 4 \text{ mW}) \) glasses in the composition range \( 0.15 \leq x \leq 0.24 \) soften as reflected in a general reduction of \( C_{11} \) (photo-softening, Figure 4.13), with the largest softening occurring for the \( x = 0.19 \) concentration.
In conclusion, Brillouin light scattering measurements on Ge$_x$Se$_{1-x}$ glasses provide direct evidence for a giant, reversible, light-induced softening and broadening of the LA mode that steadily increases from $x = 0.15$ and is most pronounced at $x = 0.19(1)$ before recovering beyond $x = 0.20$. While the photo-driven response of the network is traced to photomelting of the glass (to be discussed in the following chapter) due to weakening broken bond angle constraints, the reversal and eventual restoration of the intrinsic phonon self-energy at concentrations beyond $x \approx 0.24$ is due to the structure transforming, via cross-linkage, to a stressed rigid (over constrained) network. Brillouin scattering has been shown to be a powerful optical probe to manipulate the broken bond constraints and reversibly photo-melt glassy networks. The ability to photo-create and erase elastic signatures over a relatively narrow compositional window is an unusual, previously unexplored, feature of the photo-response of glasses.
CHAPTER 5

THEORY AND DISCUSSION FOR CHALCOGENIDE GLASSES

Experiments reported here are the first to observe light induced effects in the chalcogenide glasses using Brillouin Light Scattering. However, a wide variety of other light induced phenomena have already been reported for these materials. Included in this list are photofluidity [50], photocontraction/expansion [51,52], photodarkening/bleaching [46,53], photoconductivity[54], as well as photoinduced anisotropy[55,56]. Experimental work on photo-induced effects on chalcogenide glasses was reported as early as 1968[57]. In this section, the current theoretical basis for photo-induced fluidity is presented and the experiment of Hisakuni and Tanaka[50], which gives evidence for athermal, macroscopic photoinduced structural change in a chalcogenide glass, is discussed.

5.1 Photo-induced fluidity: Valence Alternation Pair (VAP) theory

To explain the photo-induced phenomena mentioned in the preceding paragraph, examination of the electronic properties of chalcogenide glasses is necessary. Typical qualities of materials that exhibit photo-induced structural and chemical changes include

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low average coordination and steric hindrance of atoms or large internal free volume. The low photoluminescence efficiency of chalcogenide glasses (not more than 10-20\%[58]) indicates that recombination processes occur nonradiatively[58]. Strong electron-phonon coupling is proposed as the catalyst for these nonradiative processes[58].

To determine how electron-phonon coupling can account for nonradiative recombination and lead to photo-induced structural changes, examination of the energy associated with various bonding configurations is presented. The approach follows the method of Kastner et. al.[59]. There are four p level electrons in the outer shell of a chalcogen element. In the ground state, two of these electrons form a lone pair. The other two form covalent bonds with neighboring atoms, and hence lead to local two-fold coordination. Kastner[60] argues that the lone pair states are responsible for localized states in the gap of chalcogenide semiconductors. Interactions of these states with surrounding atoms then allow deviations from normal bonding configurations. We will follow the labeling convention of Kastner, Adler, and Fritzsche[59] and refer to the ground state configuration as \( \text{C}_2^0 \), where the subscript represent the number of bonds and the superscript represents the charge of the atom. Kastner et. al.[59] propose five alternative configurations from the ground state for the chalcogen atom. All the configurations and the energy associated with each are shown in Figure 5.1.
As is shown in Figure 5.1, the lone pair (LP) states are assigned zero energy. Each bond is given \(-E_b\) energy. An antibonding state is slightly higher in energy from the LP state than the bonding state is lower, so it is given energy \(E_b + \Delta\). For additional electrons added to the antibonding states an energy \(U_o^*\) is required which is less than the energy, \(U_{LP}\), required to place an extra electron in a single localized lone pair orbital. \(U_o^*, U_{LP}\), and \(\Delta\) are considered small compared to \(E_b\).

According to Kastner\[59\], the lowest-energy neutral defect from the configurations given is \(C_3^0\). However, \(C_3^0\) can follow an exothermic reaction to become \(C_3^+ + C_1^-\). A visualization of this change is shown in Figure 5.2.
Figure 5.2[61]: Visualization of elementary atomic steps. The atoms are chalcogens (represented by C). a shows the atomic configuration before excitation, b is after the formation of a valence alternation pair (VAP), and c is a possible configuration after recombination.

The process begins with \(2C_3^0 \rightarrow C_3^+ + C_3^-\), which costs \(U_{\alpha}^-\) in energy. Now \(C_3^-\) can react with a ground state atom to become a ground state atom and a \(C_2^+\) atom: \(C_3^- + C_2^0 \rightarrow C_2^0 + C_1^+\). This process is exothermic if \(2\Delta - (U_{LP} - U_{\alpha}^-) > 0\). With these steps the \(C_3^+ + C_3^-\) pair, called a valence alternation pair (VAP) [59] can be formed. It is important to note that the average coordination of the network during this process remains the same even though the local coordination can vary. Kastner estimates a formation energy of 0.8eV for the VAP, which is significantly lower than the gap energy for Se of 2eV[59].
are $10^{17}$-$10^{18}$ native VAPs in chalcogenide glasses [62]. Photo-induced densities of VAPs reach $10^{18}$-$10^{20}\text{cm}^{-1}$ depending on the material, illumination energy and time[63].

The fact that the VAP energy is less than the gap energy allows the VAP to be a metastable state for excitations in the system. An exciton, or bound electron-hole pair, can be formed by supplying energy on the order of the band gap. As described by Street [58], this exciton can recombine in two ways. The first way is to simply return to its original ground state. The second way is for the exciton to self-trap by forming a $C_3^+$, $C_1^-$ pair. These possibilities are shown graphically in Figure 5.3 (Street refers to the pair as $D^+$ and $D^-$).

![Figure 5.3](image_url)

Figure 5.3[58]: Configuration coordinate diagram for a chalcogen element. Two recombination paths are shown: one directly to the ground state and another where a metastable VAP is created.

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It is at this point, after the exciton is formed, that the electron-phonon coupling becomes important. There is an energy barrier to self-trapping and also one for a VAP to recombine to the ground state. Street proposes that the exciton is responsible for the formation of high-energy defects that relax via phonon emissions to the VAP described by Kastner et al. [58]. Because the energy for the VAP (0.8eV) is much lower than the gap energy (2.0eV, also the energy for exciton formation), the energy barrier to transfer from an exciton to a VAP is small. More phonon emissions are then required to recombine the metastable VAP back to the ground state.

Fritzsche noted that the VAP had the ability to produce structural changes by recombining into a bonding arrangement that differed from the original [61]. His visualization of these "elementary steps" is extended to Ge$_x$Se$_{1-x}$ in Figure 5.4.

Figure 5.4[61]: Visualization of elementary atomic steps for Ge$_x$Se$_{1-x}$. The white circles represent the chalcogen Se atoms. The black circles represent the group IV Ge atoms. The middle figure shows the VAP pair formed during illumination and the side figures are before illumination (left) and after illumination (right).
We propose that the bandgap light introduced during Brillouin Light experiments provides the energy necessary to allow these elementary photostructural steps to occur. The structural rearrangement continues as long as the sample remains exposed to light. As the laser power is increased, more photons are available to interact with the atoms; therefore, further steps can occur. Eventually the area being exposed will exhibit a "fluid-like" nature, as more and more atoms are able to participate in the dynamic structural and bonding rearrangement. The resulting photo-induced fluidity is evident in our BLS spectra as a decrease in the phonon frequency and decrease in the lifetime evident as broadening of the BLS peaks. As laser power is decreased, fewer bond rearrangements can occur, the fluidity is diminished, and the phonon frequency increases. Why this softening begins to occur at x=0.15 is related to the reduction of network stress associated with the breaking of the Se bond bending constraint. These ideas are discussed in more detail in the next section.

5.2 Discussion

Two distinct factors underlie the dramatic changes in the phonon self-energies illustrated in figures 4.12a and 4.12b and the dependence of C_{11}(x) on P_r (figure 4.13). The first is related to the network structure and the effectiveness of bond constraints as the Ge concentration (x) is tuned. As melts are quenched to form these Ge_xSe_{1-x} glasses, structural arrest occurs at the glass transition temperature T_g when, in fact, T_g of a network forming solid can be viewed to be an intimate reflection of its global connectivity [7]. At very low x (x ~ 0), T_g is low (~ 40°C) and all constraints are in tact because the network stress energy associated with Se bond bending forces overwhelms
thermal energies ($kT_g$) when the structure is frozen in. However, as $x$ increases $T_g$ rises and we expect at some concentration near $x = 0.15$ ($T_g = 125°C$), $kT_g$ becomes comparable to the network stress energies associated with Se-bond bending forces. As a result, for Ge$_x$Se$_{1-x}$ glasses of composition $x \geq 0.15$, the Se-bond bending force ceases to act as a *complete* constraint; the Se-Se-Se bond angle can therefore spread more from its mean value in these glasses. This weakening of the $\beta$ constraint contributes to the unmistakable softening observed below $x \sim 0.19$. While $T_g$'s continue to rise as $x$ increases beyond $x=0.15$, the progressive breaking of the $\beta$ constraint beyond $x \sim 0.19$ is however suppressed due to the onset of percolation of rigidity near $x = 0.20$. The accompanying increased network stiffness in this concentration regime ($x \geq 0.20$) begins to gradually lock the Se-Se-Se linkages and thereby restrain the continued weakening of the bond bending constraint. If, in fact, all constraints were intact, then the isostatically rigid fragments begin to percolate and lead to the floppy to rigid transition at $x = 0.20$.

The second factor responsible for the dramatic self-energy changes in figures 4.12a and 4.12b as well as the behavior of $C_{11}(x, P_r)$ (Figure 4.13), is that pair-producing light selectively interacts with the mildly floppy network ($0.15 < x < 0.19$) with the weakened $\beta$ constraints by a mechanism that can be described as follows. The near-band gap probe beam ($\lambda = 647.1$nm or $E_{ph} = 1.92$ eV $\sim E_g$ (bandgap) $\sim 2$ eV) creates self-trapped excitons. The excitons recombine *non-radiatively* by forming a VAP leading nearest-neighbor covalent bonds in the network to *switch* as 2 eV of photon energy becomes locally available per event (see Figure 5.4). We suppose the switched state of the glass is also stress-free since Ge and Se continue to be 4- and 2-fold coordinated, and for that reason additional light-induced *bond-switching* can rapidly ensue resulting in
photomelting. In the chalcogenides, bond-switching intrinsically derives [64] from the metastability of lone-pair electrons on Se, and is driven, in our case, by an optical pump. Finally, in under- and over-coordinated glasses, the optically driven bond-switching is energetically suppressed because of network stress build up, as reflected in the increasing value of $\Delta H_m$ in the glasses (Figure 4.5c). In chalcogenides, a light-induced bond-switching mechanism will lead to a photomelted state as the pump power is increased most favorably when the network is globally stress free. The photomelted state can be viewed as an optically excited state of the glass network, which reverts back to the self-organized ground state of the system when the optical pump power is decreased. The envisaged mechanism provides in a natural fashion for the reversibility of the light-induced effects observed in the present BLS experiments because as the power is decreased, fewer photons are available to excite the system, therefore, less of the region will be in a photomelted state. The photomelted region will decrease as the power is decreased until the beginning state is reached at the original power level. The related [50] observation of photofluidity in As$_2$S$_3$ glass fibers (as discussed in the following section), and the present photomelting observed in a $\text{Ge}_{0.22}\text{Se}_{0.78}$ glass probably share a common microscopic origin illustrated by the VAP theory.

### 5.3 Experimental evidence for photo-induced fluidity

Our results of Chapter 4 provide evidence of macroscopic photo-induced softening in the Ge$_x$Se$_{1-x}$ chalcogenide system. Although photo-induced effects in chalcogenide glasses have been seen in a variety of experiments microscopically, Hisakuni and Tanaka[50] were the first to exhibit macroscopic photo-induced fluidity.
They used a flake of $\text{As}_2\text{Se}_3$ and applied a force to bend it. Without light exposure the flake bent elastically, returning to its previous state, after the stress was removed. Bending during illumination with locally focused light caused permanent deformation at the focus position. They also applied an elongation force to an $\text{As}_2\text{Se}_3$ optical fiber and flake. The region of the fiber exposed to the focused light constricted under elongation. The effects of elongation on the flake are presented in Figure 5.5. Elongation of the flake occurred only while the flake was being illuminated.

![Figure 5.5](image.png)

Figure 5.5[50]: Elongation of an $\text{As}_2\text{Se}_3$ flake with and without illumination.

To test whether the fluidity was thermally induced, they repeated the elongation measurements on the $\text{As}_2\text{Se}_3$ flake at several temperatures (see Figure 5.6). The fluidity of the sample while not illuminated increased with increasing temperature. The fluidity of the illuminated flake, however, decreased when the temperature was increased from room temperature. Hisakuni and Tanaka claim that this contrast between the temperature dependence of the illuminated and unilluminated sample shows that the fluidity of the illuminated state is not thermally driven, but is an athermal, light-induced effect.

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Figure 5.6[50]: Results of temperature dependence for experiments of Figure 5.5. In the dark, the viscosity of the samples could not be measured ($>10^{14}$ poise). The results with illumination are represented by open triangles. High temperature data is shown with black triangles.
CHAPTER 6

ELASTIC CONSTANTS OF FACE-CENTERED-CUBIC COBALT

6.1 Introduction

In this chapter Brillouin light scattering measurement of the independent elastic constants and moduli of fcc cobalt stabilized at room temperature are presented. These elastic parameters are important because they are central to determining the volume and shear strain energies that control the critical film thickness in their epitaxial growth. Moreover, while providing a direct and reliable test of the validity of total-energy calculations, the $C_{ij}$'s also determine magneto-elastic energies recognized to be important to the reported tendency of the magnetization of Co to display thickness and orientational dependence in laminar and superlattice geometries.[65-68] The elastic constants determined in our epitaxial fcc Co films at room temperature show that they are, within experimental error, the same as those measured around 700 K from the high temperature stable fcc phase of cobalt.[69] This agreement in the individual $C_{ij}$'s for the high temperature fcc phase and the epitaxial strain-stabilized fcc structure is remarkable and highlights the importance and progress made in synthesizing meta-stable crystal structures. Moreover, the bulk modulus measured at room temperature is found to be $\sim 25\%$ smaller than theoretical estimates based on total energy calculations for fcc
Co,[17,70,71] and confirms previous evidence of this discrepancy.[71]

6.2 Experiment

The fcc cobalt was grown by sputter epitaxy in a system described elsewhere[72] on a sequence of designed seed layers (10Å Pt layer followed by a 220Å Cu buffer layer) that were deposited on a (100) MgO substrate. The Co epilayer was deposited as a wedge of gradient 28.5Å/mm with a film thickness (h) that varied continuously from zero to a maximum value of 1140Å. The fcc structure of the Co film and the (100) film orientation were confirmed by x-ray diffraction scans as shown in Figure 6.1. Both the fcc Co (200) and the fcc Cu (200) reflections measured at a Co thickness of 500Å are clearly evident as is the (200) reflection from the MgO substrate. The [100] direction was in the film plane parallel to the steepest wedge incline. The Brillouin light scattering (BLS) measurements were performed in a back scattering geometry at room temperature with a tandem Fabry-Perot interferometer operated in a sequential six-pass configuration.[24,73] Approximately 100 mW of p-polarized λ=514.5 nm laser radiation was used to record the p-polarized spectra for seven different film thicknesses at a typical recording time of 15 minutes for each spectrum. The dispersion of the phonon velocities was measured by varying the magnitude of \( qh \), the product between the in-plane wave vector \( q \) and film thickness, through tuning the angles of incidence \( \theta \) between 40° and 80° as well as probing the wedge at different epilayer thicknesses. In order to study the effects of structural anisotropy on the acoustic waves in the cubic films, the BLS spectra
Figure 6.1: X-ray diffraction scan showing the (100) Co film orientation for a cobalt film thickness of 500Å. The x-ray wavelength was \( \sim 1.541 \text{Å} \) (a superposition of Cu K\( \alpha_1 \) and K\( \alpha_2 \) wavelengths). The inset schematically illustrates (not to scale) the structure of the wedge-shaped sample.
were also recorded for each direction of \( q \) as the propagation direction was tuned from the \([100]\) direction in steps of 2\(^\circ\) through a total in-plane angle of 200\(^\circ\). As discussed below, these in-plane variations in the surface wave velocity confirmed the four-fold symmetry of the cubic cobalt epilayer.

### 6.3 Results and Discussion

Figure 6.2 shows typical Brillouin spectra from the fcc Co wedge at a thickness of 1000\(\text{Å} \) for an angle of incidence \( \theta = 45^\circ, 50^\circ, 60^\circ \) and \( 70^\circ \). In addition to the principal Rayleigh mode labeled \( R \), higher-order localized Sezawa modes identified as \( S_1 \) and \( S_2 \) are evident in each spectrum as weaker peaks. Figure 6.3 shows spectra from three different thickness regions (1000\(\text{Å}, 640\text{Å}, 360\text{Å} \)) all at the same angle of incidence. At the lowest film thickness probed (360\(\text{Å} \)), only the modes corresponding to \( R \) and \( S_1 \) were clearly observed; with increasing \( h \) the number of observable excitations increased, with up to four modes evident around 1000\(\text{Å} \) (as seen at lower angles in Figure 6.2). The phase velocities \( V_s \) of the phonons were obtained by dividing the measured Brillouin shifts by \( q = (4\pi/\lambda) \sin\theta \). Results for \( V_s \) for several values of \( \theta \) are summarized in figure 6.4 as a function of \( q h \), the normalized film thickness. Figure 6.5 shows the variation of the Rayleigh velocity in the film plane and establishes a difference of approximately 200 m/s in the velocity as the wave propagation direction is varied from \([100]\) to \([110]\). The four-fold symmetry evident in figure 6.5 also confirms conclusions reached from the x-ray analysis that, despite the lattice mismatch strain in fcc Co, conversion to the stable bulk room-temperature hcp phase has not occurred.
Figure 6.2: Brillouin spectra taken at a cobalt thickness of 1000Å for θ = 70°, 60°, 50°, and 45°. The Rayleigh (R) and higher order Sezawa modes (S1 and S2) are labeled.
Figure 6.3: Sample spectra from three different sample thickness positions (1000Å, 640Å, 360Å) all taken with the same angle of incidence (60°).
Figure 6.4: Dispersion curves showing mode velocity vs qh for $\theta = 70^\circ$, $60^\circ$, $50^\circ$ and $45^\circ$. The transverse sound velocity of MgO is shown. The Rayleigh (R) and higher order Sezawa modes (S1 and S2) are labeled.
Figure 6.5: Variation of the Rayleigh velocity with in-plane propagation direction on Co film. A difference of $\approx 200\text{m/s}$ is found as propagation is varied from [110] to [100]. The Co thickness is 1000Å and the angle of incidence is 70°.
The wedge geometry utilized in this study has no significant impact on the measured elastic mode dispersion curves. For instance this is reflected by the fact that the velocities determined for in-plane propagation directions where the wave vector q is either up or down along the steepest incline of the wedge are identical within the accuracy of the measurements. This was confirmed for the smallest (h=360Å) and the largest (h=1000Å) Co film thickness probed. Moreover, with the laser beam focused to a spot of ~20μm in diameter and a thickness gradient of 28.5Å/mm, for the Co film, the wedge structure has minimal effect on the measurements at a specific film thickness.

For the (100) fcc Co film investigated, the acoustic modes with q along [100] consist of a linear combination of partial waves with displacements polarized in the sagittal plane. The principal mode in this case is the Rayleigh wave, while higher order modes polarized in the sagittal plane are Sezawa modes. The velocities of the modes can be calculated by taking into account the mechanical boundary conditions at the interfaces.[32] Due to the Cu seed layer, we model the sample as a three-layer (Co-Cu-MgO) structure. The 10Å Pt buffer layer was neglected for simplicity. There are, in general, six partial waves in each of the thin layers (Co, Cu) which satisfy the equations of motion while three outgoing partial waves characterize the waves in the substrate. These partial waves are combined linearly with weighting factors chosen to satisfy conditions related to the continuity of stress and displacement at each interface. In solving numerically for the wave dispersion, fixed values of the in-plane wave vector q = ω/Vs, are assumed and solutions for Vs, the wave velocity, are searched to make the determinant associated with the boundary condition matrix vanish. The phase velocities were also confirmed by finding the resonances in the elastodynamic Green's tensor.
calculating the elastodynamic Green's tensor we followed the method of Every et. al.[74]
Briefly this method consists in solving the wave equation in each medium subject to the
usual boundary conditions and to the presence of a delta force acting on the free surface.
The desired phase velocities are found by locating the peaks in the transverse component
of the Greens tensor. Comparisons between the theoretical and actual Brillouin spectra
are shown in Figure 6.6 for various thicknesses at an angle of incidence of 60°. If the
phase velocity lies above the bulk transverse shear velocity of the substrate, the acoustic
modes do not localize in the epilayer. Instead, at least one of the partial waves describing
these "leaky" modes has an oscillatory component normal to the interface. The dashed
lines in Figure 6.4 identify this cutoff velocity associated with the MgO substrate.

Based on elastic continuum theory for the cubic Co film, Cu seed layer and
substrate, we calculate the best fits to the measured velocity dispersions. The fits are
shown in Figure 6.3 as solid lines. The three independent elastic constants as well as the
densities of bulk MgO and fcc Cu listed in Table 6.1[75,76] were used as input
parameters. While the dispersion of the Rayleigh and higher order modes provide
constraints on the fitting parameters, fits to the in-plane anisotropy in the Rayleigh
velocity $V_R$ placed additional restrictions, particularly on the values of $C_{11}$ and $C_{12}$. As
expected the magnitude of $V_R$ at large $q_h$, was mainly determined by $C_{44}$ of the Co layer.
We note that the Rayleigh velocity for $q_h << 0.5$ tends to 4100 m/s, well below $V_R =
5513$ m/s of the MgO substrate. This reduction in the Rayleigh speed in our films at small
$q_h$ arises directly from the presence of the Cu seed layer. Due to the limited thickness
(220Å) of this intermediate soft layer, $V_R$ is suppressed only by $\sim$1400 m/s from that of
Figure 6.6: Comparison between actual data (top) and theoretical calculations (bottom) for the mode spectra at indicated sample thickness and an incident angle of 60°. The x axis is frequency shift in GHz.
Table 6.1: Elastic constants and density parameters for MgO and Cu.

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}$ (GPa)</td>
<td>294</td>
<td>169</td>
</tr>
<tr>
<td>$c_{12}$ (GPa)</td>
<td>93</td>
<td>122</td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>155</td>
<td>75.3</td>
</tr>
<tr>
<td>$\rho$ (g/cm$^3$)</td>
<td>3.58</td>
<td>8.94</td>
</tr>
</tbody>
</table>


MgO; at large Cu film thicknesses, $V_R$ would approach the low Rayleigh velocity (2012 m/s) of bulk Cu as $q_h$ tends to zero. In contrast to the influence of $C_{44}$ on the Rayleigh wave velocity, $C_{11}$ was found to have the biggest effect on the first Sezawa mode, while $C_{12}$ tended to offset these effects in the cubic lattice, thus revealing that the quantity ($C_{11} - C_{12}$), is a relevant parameter in the fits. Specific values for $C_{11}$ and $C_{12}$ of the Co layer were narrowed through fits to the four-fold symmetry associated with in-plane Rayleigh wave propagation on the cubic lattice as evident in Figure 6.4.

Our results for the $C_{ij}$'s of fcc Co are summarized in Table 6.2, together with findings from two previous measurements.[69,77] It is noted that although, as evident in figure 6.5, the Rayleigh velocity is determined to the accuracy of 1%, the uncertainty associated with $C_{44}$ in Table 6.2 is higher. This larger error is derived from the quality of the fits to the Rayleigh wave dispersion as those in Figure 6.3. In particular, at small $q_h$, $V_R$ is dominated by the elastic properties and thickness of the thin Cu seed layer and, therefore, the influence of $C_{44}$ of the Co film on the mode velocities in this range is weaker leading to the larger uncertainty. Similarly, the Sezawa waves primarily lead to the determination of $C_{11}$ and are also affected by the seed layer properties leading to the higher error margins indicated in Table 6.2.

We have also provided, for completeness, the measured elastic constants of the hcp[78] and bcc[79] phases. It is possible to directly compare the elastic constants of the hcp phase to those of the fcc polymorph through transformations outlined in Ref. 80. The results in column 2 of Table 6.2 are from neutron scattering measurements carried out at
<table>
<thead>
<tr>
<th>$c_{ij}$ (GPa)</th>
<th>fcc measured $^a$</th>
<th>fcc measured $^b$</th>
<th>fcc measured $^c$</th>
<th>bcc measured $^d$</th>
<th>hcp measured $^e$</th>
<th>fcc calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}$</td>
<td>225 (± 25)</td>
<td>223 (± 13)</td>
<td>238</td>
<td>193</td>
<td>307</td>
<td></td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>160 (± 20)</td>
<td>186 (± 15)</td>
<td>158</td>
<td>170</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>92 (± 15)</td>
<td>110 (± 4)</td>
<td>128</td>
<td>48</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>182 (± 12)</td>
<td>198</td>
<td>185</td>
<td>177</td>
<td>193</td>
<td>235 $^f$ 269 $^g$ 242 $^h$</td>
</tr>
</tbody>
</table>

a. This work.

Table 6.2: Measured elastic constants $C_{ij}$ and bulk modulus ($B$) for fcc, bcc, and hcp cobalt and theoretical estimates for the bulk modulus ($B$) of fcc Co.
elevated temperature (710K) where fcc Co is the stable phase.[69] Column 3 in Table 6.2 includes the fcc Co elastic constants deduced from ultrasonic data by extrapolating to 0% Ni and Al content from the fcc stabilized Co(Al,Ni) alloy.[77] It is evident that $C_{11}$ and $C_{12}$ as well as the modulus $B = (C_{11} + C_{12})/3$ for fcc Co, measured by the three different methods agree to within $\pm 5\%$. Moreover, the values for $C_{44}$ deduced in the present study (92$\pm$15 GPa) and that derived from the high temperature phase via neutron scattering (110$\pm$4 GPa) are in agreement within the error margin. The agreement of the elastic constants determined at low and high temperatures from fcc Co is interesting. It confirms that, despite the 2.8% lattice mismatch between the Co film and the Cu seed layer, the room temperature pseudo-morphic fcc structure and the high temperature (710K) fcc lattice attained via transformation from the hcp phase are both governed by linear elastic theory and lie within the elastic limit.

The bulk modulus, $B$, which is derived from the second derivative of the total energy – volume curve at the minimum, is a sensitive measure of the relative accuracy of total energies. In fact $B$ is a better indicator of the accuracy of first principles total-energy calculations than the lattice constants. On the other hand the independent elastic constants impose stricter constraints on the theory than the bulk modulus $B$, which is determined from symmetry conserving volume modifications. For instance, the augmented spherical wave approximation does not include a full potential and hence while reliable for bulk moduli of crystals with atoms in cubic environments, it is not as dependable for the shear $C_{44}$ coefficient.[81] In the case of first principle calculations, i.e. a calculation with no adjustable parameters, the results provide a check on the effectiveness of empirical potentials far from the structural ground state as in forced registry epilayer films and the
applicability of linear elastic theory. Results for the modulus based on local-spin density and atomic-sphere approximations in cubic structures are in excellent agreement with experiment for most of the non-magnetic, ferromagnetic, and anti-ferromagnetic 3d and 4d elements.[71] The biggest discrepancy however is the 25% higher theoretical values of B for the ferromagnetic metals Fe, Co and Ni.[71] Other calculations[17,70] of B for fcc Co also show similar disagreements for fcc Co in comparison to the measured values and thus, in view of the agreement amongst the various experimental results, this discrepancy is likely a consequence of approximations made in the theoretical estimates.
CHAPTER 7

CONCLUSIONS

The results of this BLS study provide evidence for photo-induced fluidity in the Ge_xSe_{1-x} chalcogenide glass system. This evidence was obtained from the dependence of the LA phonon self-energy on the power of the incident probe beam. At low probe-power (P < 3 mW), the observed LA mode frequency increase with x reflects the intrinsic variation of the longitudinal bulk elastic constant C_{11}(x) in the glasses with connectivity (r). With increasing probe-power P(≥ 3 mW) glasses in the composition range 0.15 ≤ x ≤ 0.24 soften as reflected in a general reduction of C_{11} (photo-softening, Figure 4.13), with the largest softening occurring for the x ~ 0.19 concentration. This softening becomes possible because of the decrease of internal stress in the sample due to the breaking of the Se bond bending constraint. The softening is reversible with power up to 6 mW.

The reversible softening and broadening is the result of photo-induced fluidity associated with bond switching. Bonds between the chalcogen Se atoms can switch because of excited states available due to lone pair electrons. The switching mechanism is driven by an optical pump that creates excitons that self-trap, forming over- and under-coordinated valence alternation pairs (VAPs). The VAPs can return to normal coordination with an accompanying change in atomic positions. The formation and
relaxation of VAPs can continue as long as the sample is exposed to light. When the light is removed the bond switching will cease.

For the metastable fcc cobalt film grown as a wedge structure, we have measured the elastic constants by Brillouin scattering. The Rayleigh and higher order modes are well described by elastic continuum theory and the three independent $C_{ij}$ constants deduced in this study are in good agreement with those determined by inelastic neutron scattering on the high temperature fcc phase of Co. These finding hence illustrate in a striking manner the stabilizing of a metastable phase via epitaxy which, in this case, allows for the structural and elastic properties of a high temperature ferromagnetic phase to be retained at ambient temperatures. Our study confirms that despite excellent agreement between theoretical and experimental values for $B$ for most of the 3d elements, there remains a discrepancy of about a 25% over estimate in the calculated bulk moduli for the ferromagnetic cubic phases of Co.
CHAPTER 8

FUTURE WORK

8.1 Future work for on glasses

A number of interesting future experiments still remain to be performed on the Ge$_x$Se$_{1-x}$ chalcogenide glass system with BLS. The high power regime along with the unusual time dependence should be more thoroughly investigated. A preliminary amount of work has already been performed and that data is reported in Appendix A. An extension of the temperature dependence can be made by using a cryostat system to cool the sample while the BLS measurements are taken. Taking data at low temperature would allow for the removal of any thermal softening effects. Pressure dependence measurements may be possible using a diamond anvil cell. Exposing the sample to high pressures may induce stress and reduce the effect of the stress reduction caused by the broken Se bond constraint. However, the Brillouin signal from a methanol/ethanol pressure medium in the diamond anvil cell will overlap with the glass peaks, so another pressure medium should be used.
The measurements performed in this thesis and those suggested in the above paragraph can be extended to any other chalcogenide glass system. Both other binary systems and ternary systems have already been created and can be obtained for analysis. Variations in bandgap energy and sample reactivity will determine how amenable to BLS a new glass will be, but several possibilities exist (e.g. Si$_x$Se$_{1-x}$ and P$_x$Se$_{1-x}$).

8.2 Future work on metastable phases

As the technique of molecular beam epitaxy improves, metastable phases may be attainable for other transition metals. The results from this thesis on fcc cobalt have shown that Brillouin light scattering is an effective tool for characterizing these new phases.
APPENDIX A

PRELIMINARY HIGH POWER AND TIME DEPENDENT MEASUREMENTS ON Ge\textsubscript{x}Se\textsubscript{1-x}

A.1 High power regime (P>6mW)

One of the central themes of this thesis focuses on the reversible softening and broadening of the LA mode revealed in the low and intermediate power range (P≤6mW). However, some high power (P>6mW) measurements were performed and for completeness will be included here. A thorough examination of this region is left for future work. Figure A.1 displays spectra recorded at 647.1nm from Ge\textsubscript{0.17}Se\textsubscript{0.83} where the power levels extend into the high power regime (P>6mW). The power is increased from 2mW by steps of 1mW. At 2mW only one peak is evident. By 9mW two peaks are evident. The peak at the higher (lower) frequency will be classified as the “outer” (“inner”) peak. At 9mW the outer peak is more well defined and narrower than the inner one. The frequency of the outer peak in the 9mW spectrum corresponds closely to the position of the single peak in the low power (2mW) spectrum. Upon decreasing the power form 9mW back to 8mW, the outer peak intensity weakens, while the inner mode becomes the stronger spectral feature with a narrowed linewidth. By 5mW only the inner peak is visible and it has increased in frequency and decreased in linewidth. The decrease in power to 5mW also shows that the peak no longer returns to the same
Figure A.1: Spectra of Ge$_{0.17}$Se$_{0.83}$ where the power levels were allowed to extend into the high power regime.
frequency and linewidth it had at the corresponding power when \( P_r \) was being increased from 2mW. This shows that the process is no longer reversible once the high power regime (\( P > 6 \) mW) is reached. As the power is decreased back to 2mW from 9mW, the spectral features eventually recover to the same form \( (v, \Gamma) \) as at the original excitation power of 2mW. Other experiments at low \( (x < 0.19) \) and intermediate \( (0.19 < x < 0.24) \) Ge concentrations display similar results. On the other hand, at high \( (x > 0.24) \) Ge concentrations, a well-formed outer peak did not appear beyond 6mW; however the single peak in the spectra usually developed an asymmetry that appeared as an increase in linewidth on the low frequency side of the peak (see Figure A.2).

"High" power measurements were also performed using 514.5nm photons. The presence of two Brillouin peaks was again observed with low and intermediate Ge concentrations \( (x < 24\%) \) as was the case for \( \lambda = 647.1 \) nm excitation. For high Ge concentration samples \( (x \geq 24\%) \), the 514.5nm photons could produce extra features at lower frequencies, but the original peak appearing at 2mW would remain essentially unchanged with power.

Due to the fact that spectra were acquired by increments of 1mW and that each spectrum was acquired for an average of three (ten) minutes with 647.1nm (514.5nm) excitation wavelength, the total time of illumination must increase for experiments extending into the high power regime. Therefore, the differences between the low/intermediate power and the high power experiments are possibly related to the time of exposure to illumination and not just the increase in power. This possibility prompted experiments to determine the effect of photon exposure time, which will be discussed in the following section.
Figure A.2: Spectra of Ge$_{0.26}$Se$_{0.74}$ where the power levels were allowed to extend into the high power regime.
A.2 Time dependence

To determine what effect the time of exposure had on the results, several experiments were performed at a fixed laser power of 2.7mW for 647.1nm photon excitation with spectra taken at regular time intervals (ΔT) of 1000s each. At the end of the interval (ΔT) the spectrum was saved with the appropriate time interval label (ΔT_j). A new spectrum was then reinitialized and acquired for the next 1000s. Figure A.3 shows representative sets of spectra for the time dependent measurements (bottom panel) on the 18% Ge sample with 647.1nm light as well as a power dependent measurements (top panel) showing “splitting” at 7mW. As seen in the time dependent plot, even after the first 1000s time interval two peaks are evident. The higher frequency peak (the outer peak) corresponds to a frequency close to that recorded with 3mW for about 60s during the power dependence measurements. The lower frequency peak (the inner peak) corresponds to the value typical of that recorded with 4mW for short time. As time progresses, the outer peak generally becomes relatively stronger and the entire spectrum less intense.

Figure A.4 is a time dependent experiment on a sample (Ge_{0.33}Se_{0.67}) lying well into the rigid region. For this rigid sample there is no evidence for the formation of a second peak with time for excitation at λ=647.1nm. This behavior is representative of the other samples with Ge concentrations (x>0.24) placing them in the rigid region.

Similar time dependent measurements were performed using the 514.5nm excitation wavelength. Figures A.5 and A.6 summarize two observed results for Ge_{0.18}Se_{0.82} and Figure A.7 show results for Ge_{0.33}Se_{0.67}. For the 18% Ge sample (and other low concentrations) excited with 514.5nm photons two distinct types of splitting...
Figure A.3: (a) Comparison of high power data ($\Delta T$ refers to total scan time at indicated power level) and (b) time dependent Brillouin spectra for Ge$_{0.18}$Se$_{0.82}$ ($\Delta T$ refers to time interval blocks of 1000s) recorded at $\lambda=647.1$nm.
Figure A.4: Time dependence measurements for Ge$_{0.33}$Se$_{0.67}$. Each time interval is 1000s. The power remained fixed at 4mW and the laser light used was 647.1nm. The first few spectra were decreased in size by the amounts shown.
Figure A.5: Time dependence measurement for $\text{Ge}_{0.18}\text{Se}_{0.82}$ using 514.5nm light. A constant power of 4mW was used and spectra taken at $\Delta T=1000$s intervals.
Figure A.6: Time dependence measurement for Ge$_{0.18}$Se$_{0.82}$ using 514.5nm light. A constant power of 4mW was used and spectra taken at $\Delta T = 1000s$ intervals for intervals 1-4. The light was blocked for 1hr and 20min prior to recording spectrum $\Delta T_5$ and again for 45min prior to recording spectrum $\Delta T_6$. 

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Figure A.7: Time dependence measurement for Ge\textsubscript{0.33}Se\textsubscript{0.67} using 514.5nm light. A constant power of 4mW was used and spectra taken at 1000s intervals.
were observed. In Figure A.5, the single peak appearing in time interval five ($\Delta T_5$) splits into two peaks by $\Delta T_8$ that remain centered about the peak positions of the spectra recorded in $\Delta T_5$. The higher frequency, outer peak is at the peak position recorded with 2mW during the power dependent measurements. The lower frequency, inner peak is at a lower frequency than the peak position recorded with 4mW during the power dependent measurements. At $\Delta T_7$ the inner peak is clearly evident, but the outer peak has not yet formed. By $\Delta T_{10}$ both peaks are well evolved and distinct.

A different time dependence behavior for the 18% Ge sample (still with 514.5nm photon excitation) is illustrated in Figure A.6. During $\Delta T_1$, only one peak is evident and its position corresponds to that for the 4mW peak of 18% from the power dependence measurements. By $\Delta T_3$, two peaks are evident. The high frequency, outer peak is located at a position for the 2mW peak from the power dependent scan. The low frequency inner peak, however, remained at the same location as the single peak from $\Delta T_1$. By $\Delta T_4$ the high frequency outer peak became stronger relative to the inner peak.

During this experiment it was attempted to determine whether the time dependent effects could be reversed if the light was blocked. After $\Delta T_4$ the light was blocked for 1 hour and 20 minutes ($5.16\Delta T$), then another spectrum was taken for 1000s. Before $\Delta T_6$ spectrum was acquired, the light was again blocked, this time for 45 minutes ($2.7\Delta T$). It is evident from the $\Delta T_5$ and $\Delta T_6$ spectra that blocking the light did in fact reduce the relative intensity of the higher frequency peak. In essence, the outer peak could be erased if the light were blocked for a long enough time period.
The 33% Ge sample (Figure A.7) excited with 514.5nm photons showed no change in the location of the peak with time. This behavior is similar to the results for 647.1nm. There was a slight increase in peak width by AT₃. Some additional features appeared at lower frequencies beyond AT₆, that are not shown in Figure A.7.

It is clear from figures A.3, A.5 and A.6 that time dependence measurements for the 647.1nm and the 514.5nm light could produce extra peaks in the BLS spectra. However, for the 514.5nm light second peaks did not appear to be as predictable as for 647.1nm light. For example, with 647.1nm photon excitation, the high (x>0.24%) Ge concentration samples did not produce clear second peaks within the time interval allowed. At most, there may have been a slight asymmetry to the peak width. Some of the lower Ge concentrations did not produce evidence for a second peak within the allotted time for 514.5nm excitation. Some of the variation in formation of the second peak between the different wavelengths may be accounted for by examining linewidth differences. The 647.1nm peaks were much narrower than the 514.5nm samples, therefore, evidence of splitting would be easier to find with the 647.1nm light.

It is important to note that the results of the time dependence experiments for both wavelengths show no evidence for a continuous change in frequency of the peak positions. This means that the mode softening cannot be induced by time alone. The softening phenomenon is dependent on an increase in power. The time dependence measurements do, however, give insight into the high power results of the power dependent experiments (Figures A.1 and A.3a). The appearance of an additional peak at high power may be linked to the fact that the total time the sample has been under illumination increases for high power measurements. The total time increases because
during an experiment the power is increased by steps of 1mW and a scan is taken at each power level. Going to a higher maximum power level is then associated with a longer total time for the experiment.

All of the time dependent results shown in the figures are for a fixed power of 4mW. Experiments were also performed where the power still remained fixed, but was set at a different level. If the power was increased, the number of time intervals before splitting occurred decreased. If the power was decreased, the number of time intervals before splitting occurred increased. These results reveal that the photon flux, rather than time of exposure alone, is crucial to understanding of the high power results.

A.3 Summary

In summary, at high power (>6mW), the spectra show evidence of new excitations in the form of an additional peak. In producing this peak, there appears to be a delicate interplay between the power incident on the sample and the total time that the sample has been exposed to light. Increasing the power on the sample allows peaks in the specified concentration range to decrease in frequency. At high powers (P>6mW) the peak may “split” into two peaks. For exciting radiation of 647.1nm the second peaks in all concentration regimes tends to disappear when the power is reduced back to 2mW, but the original peak will return to a slightly higher frequency than the one at which it started. For exciting radiation of 514.5nm the second peak may reduce in intensity with decreasing power, but it will often remain even at 2mW. However, both the original and new peak will increase their frequencies upon a decrease in power.
A clue as to why these new peaks form at high power comes from the time dependent experiments. Given enough time, a new peak may form even though the power remains constant. What constitutes enough time of exposure seems to vary depending on the Ge concentration and the power level of the incident light. For samples that have shown evidence of a second peak with time, increasing the power decreases the amount of time before the second peak appears. This emphasizes that the formation of a second peak is related to the photon flux rather than just power or time separately. However, in no instance did the exposure time produce continuous shifting of the peak position. Instead, the exposure time allowed for a new peak to appear in the BLS spectra. The softening effect seems to be strictly related to the change in power. Therefore, the appearance of an extra peak is likely related to the photo-excited state reaching some metastable state with time. A regular increase in power will allow more and more atoms to participate in the photo-melted state (hence the softening), but it will also decrease the time for a metastable state to be reached for any one power level (as evidenced by the decrease in time necessary for a new peak to form if a higher constant power is used as opposed to a lower one). With a higher power level more atoms are free to explore new energy configurations and possibly find a more stable one than the one that they previously occupied.
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