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A STUDY OF THERMAL DIFFUSE
X-RAY SCATTERING FROM LEAD

by

Sanford L. Schuster

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A THESIS

Presented to the Faculty of
The Graduate College in the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Doctor of Philosophy
Department of Physics

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Under the Supervision of Professor John W. Weymouth

Lincoln, Nebraska

June, 1969

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A STUDY OF THERMAL DIFFUSE
X-RAY SCATTERING FROM LEAD

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University of Nebraska, 1969

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ABSTRACT

A detailed study has been made of thermal diffuse x-ray scattering (TDS) from lead single crystals. The intensity of this scattering is compared with the expected intensity calculated by use of lead phonon dispersion curves determined by means of slow neutron scattering. This study was initiated in order to examine the extent to which x-rays, as distinct from neutrons, can be used to obtain reliable phonon dispersion curves in metals. For the few cases that exist in the literature where dispersion curves have been measured in metals with x-rays, the frequencies, as compared with those obtained by neutron scattering, often are lower by as much as 10% or more. In order to determine dispersion curves from scattered x-ray intensities, corrections must be made which depend on the dispersion curves, and for metals the approximations used for the curves have not been very good.

The TDS from lead was measured in the longitudinal and transverse branches along the [100] and [111] directions.

The crystals were acid polished, ion bombarded, carbon sputtered, and mounted in a vacuum chamber on a diffractometer. The intensity measurements were made by a scanning technique which incorporates a multiscaler. Amorphous scattering from lucite was used to determine both the normalization factor for the intensity and the correct polarization factor for the crystal pre-monochromator.

For the calculations of the expected TDS, 100°K dispersion curves obtained by neutrons and corrected to room temperature were used. The one phonon intensity was calculated directly from the $[100]$ and $[111]$ phonon data. The two phonon intensity was calculated by a method which expresses the cross section in terms of atomic force constants. The intensity of the higher order scattering was calculated by a method in which the Debye-Jauncey relation for TDS is expanded in powers of the Debye-Waller factor and the first two terms are subtracted. In addition, a very small Compton scattering contribution was calculated.

In comparing the measured intensity with the sum of all the calculated contributions it is observed that in all cases, except for some points along the $[111]$ transverse branch, the measured intensity is greater. The differences range from 10% to 60% or higher and have a periodic dependence on reciprocal lattice position. No satisfactory explanation for this discrepancy has been found.

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I. INTRODUCTION

I. a. The Use of Thermal Diffuse X-Ray Scattering to Determine Dispersion Curves in Crystals

Thermal diffuse x-ray scattering (TDS) is one of the tools used to determine the dispersion relations of lattice waves in a crystal. It provides an indirect approach, since the energy change of a photon in a photon-single phonon scattering process is too small to be measured. This energy change is $h\nu$, where h is Planck's constant and ν is the phonon frequency. The frequency versus wave vector characteristics of the lattice vibrations have to be determined from the intensity of the total scattering, and this includes not only photon-single phonon scattering events, but also photon-multiple phonon scattering events and Compton scattering. On the other hand, the inelastic scattering of slow neutrons provides a direct means for determining dispersion relations, since the energy change of a neutron in a neutron-phonon scattering process is of the same order of magnitude as the initial neutron energy.

Past investigations in which x-rays have been used to determine dispersion relations in metals^(1,2,3,4,5,6) yield curves which generally fall below the corresponding curves determined by means of neutron scattering. Figures 1, 2, and 3 show the dispersion relations obtained with neutrons and x-rays for Cu, Al, and Ni, respectively.

Figure 1. Cu Dispersion Curves

+—+ X-Rays⁽⁴⁾
 o—o Neutrons⁽⁷⁾

Figure 2. Al Dispersion Curves

+--+ X-Rays⁽⁵⁾
 o--o Neutrons⁽⁸⁾

Figure 3. Ni Dispersion Curves

+--+ X-Rays⁽⁶⁾
o--o Neutrons⁽⁹⁾

The frequencies are shown plotted against $a^2 q^2 / 2\pi$, where a is the appropriate lattice constant, and q is the wave vector magnitude associated with a vibrational state. These differences most likely occur because of the difficulties inherent in extracting the frequencies from the x-ray data. All contributions to the scattering other than the first order TDS must be subtracted from the measured intensity. Accurate calculations of the Compton scattering are available for this purpose,⁽¹⁰⁾ but if the multiple phonon contributions are to be accounted for, it is necessary that one assume a form for the dispersion relations in order to calculate such contributions. The best approximation used so far is that proposed by Walker,⁽⁵⁾ in which it is assumed that the crystal is elastically isotropic, and that the dispersion curve for any branch is given by the simple linear chain relation. This approach is not very good for most metals since the dispersion curves turn out to differ considerably from the linear chain relation. A second complication is the effect of the crystal surface on the scattering. As discussed in Appendix D, x-rays do not penetrate far below many surfaces because of high absorption. This means that any surface other than the perfectly flat surface, for which the calculations are made, may lead to incorrect dispersion relations, since the absorption depends on the shape of the surface. Any surface

contaminations will also have some effect. A third problem is the use of the correct polarization factor for the crystal monochromator used in the diffraction system. This is discussed in Appendix C.

The purpose of the present work is the measurement in the [100] and [111] directions of the TDS from lead single crystals, and comparison with the expected intensity calculated from the dispersion relations for lead determined by means of slow neutrons.^(11,12) The use of the known dispersion relations allows a calculation of the higher order scattering better than that due to Walker,⁽⁵⁾ and it is hoped that this comparison will help to clarify the nature of the problems involved in analyzing TDS from metals.

I. b. Kohn Anomalies

A secondary purpose of this investigation is the observation of possible Kohn anomalies, which show up as singularities in the slope of the dispersion curves. They arise from electron-phonon interactions and serve as an image of the Fermi surface in the dispersion curves. Stedman et al.⁽¹³⁾ actually have mapped out the lead Fermi surface by a detailed consideration of the suspected Kohn anomalies in their dispersion curve data.⁽¹²⁾ Since the first order TDS essentially is proportional to v^2 , it is hoped that the singularities can be confirmed in the x-ray data. The observation of Kohn anomalies with

x-rays is complicated by the fact that not all of the scattering is of the first order, and any small anomalies could be lost in the statistical scatter of the data. However, by far the greatest problem is the existence of small powder peaks, which makes it very difficult to select the true Kohn anomalies. One previous search for Kohn anomalies in lead by means of TDS was reported in 1962.⁽¹⁴⁾

I. c. Choice of Lead as the Sample

There are several reasons why lead was chosen as the metal to be examined. First, as is shown in Appendix J, the second and higher order TDS contributes significantly to the total scattering. Thus, the calculated second order, in particular, should correspond to an appreciable amount of the measured scattering. Since lead has a low, and now quite well established Debye temperature of about 85°K at room temperature, as discussed in Appendix F, and since the experiment is carried out at room temperature, it is possible to calculate the second order TDS using the approach due to Froman,⁽¹⁵⁾ in which it is assumed that the average energy per vibrational mode is kT . The problem would be complicated greatly if this were not the case. Another advantage of lead is that sample fluorescence is no problem when $CuK\alpha$ radiation is used. The $CuK\alpha$ line of 1.5405 Å falls well between the lead LIII and MI edges, the wavelengths of which are 0.9503 Å and

3.226 Å, respectively. Any fluorescence could be discriminated against easily by the single channel analyzer employed in the detection system, but none was ever observed. The high absorption coefficient of lead for the radiation employed is both an advantage and a disadvantage. It is an advantage if one desires to look at the role which surface effects play in the measured scattering, but it is certainly a disadvantage if one is attempting to investigate the lattice vibrations only. The immediate availability of oriented lead single crystals in our laboratory is another important reason for choosing lead as the sample.

II. DETAILS OF THE X-RAY APPROACH

II. a. Raw Data Accumulation

Although all components of the experimental apparatus are required for data collection, the parts which are involved either mechanically or electronically in the actual data acquisition are the diffractometer, the xenon-filled proportional tube and preamplifier package, an amplifier and single channel analyzer unit, and a 128 channel analyzer (MCA) with IBM typewriter for print-out. Each of these units is discussed individually in section III. The data is acquired in such a manner that variations in the incident beam intensity which are of several hours' duration have no effect on the shape of the data.⁽¹⁶⁾ With 2θ being the angle of scattering, the detector is made to scan back and forth over selected 2θ intervals in the $\phi - 2\theta$ scan mode, a mode in which the detector arm moves with twice the angular speed of the sample, while at the same time the MCA, operating in the multiscaling mode, is acquiring data corresponding to specific 2θ intervals in each of its channels. The signals which control the operation of the MCA are provided by switches on the diffractometer which are tripped at such times that the multiscaling operation of the MCA is synchronized with the 2θ scanning motion of the detector. This operation is discussed in detail in Appendix O. The signal is sent from the detector-

preamplifier package through the second amplifier, and then to the single channel analyzer, in which the window is set to encompass the peak associated with the 8.05 KeV $\text{CuK}\alpha$ line. The output of the single channel analyzer is then fed into the MCA. In actual operation the system would sometimes run continuously for four days, except for data prints taken about every twelve hours of running time. These prints were made in order not to lose data due to a later malfunction of the system, an occurrence which did happen occasionally.

The data accumulation procedure described above is that used for the $[100]$ L and $[111]$ L modes, for which the diffraction vector is maintained parallel to the direction being investigated. This amounts to maintaining the diffraction vector nearly perpendicular to the surface of the $[100]$ or $[111]$ oriented crystal under investigation. Data is acquired by hand when the $[100]$ T and $[111]$ T modes are investigated, for these require reciprocal space traversals approximately perpendicular to the crystal normal. Such traversals require changes not only in 2θ , but also in ω , the sample angular motion which is independent of 2θ and is in the diffraction plane. The experimental setup has no means by which these angular changes can be carried out automatically.

II. b. Amorphous Scattering

Scattering of x-rays from lucite, an amorphous

material, was used to determine the absolute intensity of the TDS from lead. The basis for this is discussed in detail in Appendix G. All of the contributions to the scattered intensity, whether it be from lead or lucite, are multiplied by a normalization factor B, and a polarization factor $P = \frac{1 + k \cos^2 2\theta}{1 + k}$, where k is characteristic of the monochromator crystal employed. B depends upon the divergences in the diffraction system, and it must be remeasured every time a slit size is changed. A comparison of the calculated lucite scattering with the measured scattering allows one to determine B and k. Most of the data of interest was taken with $B = 2.84 \times 10^{-21}$ cm²/sec and $k = 0.85$, but a small portion was taken with a larger exit horizontal divergence slit, for which $B = 3.99 \times 10^{-21}$ cm²/sec and $k = 0.86$. The difference in the two k values is not significant. The uncertainties in B and k are discussed in part VI.

II. c. Calculation of Expected Count Rates for X-Ray Scattering from Lead

The calculation of the total scattering requires separate calculations for the first order, second order, and higher order contributions to the TDS, and for the Compton scattering. As shown in Appendix A, the contributions to the TDS are given by the following:

$$I_1(\vec{s}) = \frac{B f^2 e^{-2M}}{2 \left(\frac{M}{P}\right) m^2} \left(\frac{1 + k \cos^2 2\theta}{1 + k} \right) \sum_j \frac{(\vec{s} \cdot \vec{e}_{qj})^2 \bar{E}_{qj}}{\omega_{qj}^2} \quad \vec{s} + \vec{q} = \vec{r} \quad (1)$$

$$I_2(\vec{S}) = \frac{8V_c f^2 e^{-2M}}{32\pi^3 \left(\frac{M}{\rho}\right) m^3} \left(\frac{1+k \cos^2 2\theta}{1+k} \right) \sum_{\vec{r}} \sum_{\substack{j,j' \\ \text{inter-} \\ \text{sections}}} \frac{(\vec{S} \cdot \vec{e}_{\vec{q}j})^2 (\vec{S} \cdot \vec{e}_{\vec{q}'j'})^2 \bar{E}_{\vec{q}j} \bar{E}_{\vec{q}'j'}}{\omega_{\vec{q}j}^2 \omega_{\vec{q}'j'}^2} d\nu_{\vec{q}} \quad (2)$$

$\vec{S} + \vec{q} + \vec{q}' = \vec{r}$

$$I_{\text{higher}}(\vec{S}) = \frac{8 f^2 e^{-2M}}{2 \left(\frac{M}{\rho}\right) m} \left(\frac{1+k \cos^2 2\theta}{1+k} \right) (e^{2M} - 1 - 2M - 2M^2) \quad (3)$$

The notation is completely defined in Appendix A. Some of the important quantities are $\omega_{\vec{q}j}$, the angular frequency of the vibrational mode specified by the wave vector $\vec{q}$ and polarization state j , $\bar{E}_{\vec{q}j}$, the average energy of the $\vec{q}j$ mode, $\vec{e}_{\vec{q}j}$, the polarization vector of the $\vec{q}j$ mode, $\vec{S}$, the diffraction vector, and $\vec{r}$, a reciprocal lattice vector. In the calculation of $I_1(\vec{S})$ the frequencies used are those due to Brockhouse et al.⁽¹¹⁾ but corrected to room temperature as discussed in Appendix I. The calculation of $I_2(\vec{S})$ follows a method briefly outlined by Froman,⁽¹⁵⁾ in which the average energy per mode is assumed to be kT , as mentioned above, and in which the integral is expressed in terms of atomic force constants instead of polarization vectors and frequencies. The atomic force constants used are those determined by Gilat⁽¹⁷⁾ for lead out to eight neighbors by making a least squares fit of the phonon dispersion curves obtained by Brockhouse et al.⁽¹¹⁾ at 100°K. The fact that the 100°K, instead of room temperature, force constants are used will be shown later to have little effect in the calculation of the second order TDS. The form which $I_2(\vec{S})$ takes in terms of the atomic force constants is discussed in detail in Appendix H. $I_{\text{higher}}(\vec{S})$

is calculated in a manner which has been used successfully by Eldridge in his x-ray investigation of sodium chloride⁽¹⁸⁾ and later of cesium iodide.⁽¹⁹⁾ The method is one in which the Debye-Jauncey expression for TDS⁽²⁰⁾ is expanded in powers of the Debye-Waller factor and the first two terms are subtracted. This presumably leaves only the third and higher order scattering contributions, for which the Debye expression should be a good approximation, as discussed in Appendix A.

The contribution of Compton scattering is discussed in Appendix B. It is shown there that

$$I_c(\vec{s}) = \frac{B}{m(\frac{\mu}{\rho} + \frac{\mu'}{\rho})} \left(\frac{1 + k \cos^2 2\theta}{1 + k} \right) i_c(\vec{s}) \quad (4)$$

where $\frac{\mu'}{\rho}$ is the mass absorption coefficient for the radiation scattered at an angle 2θ , and for lead $i_c(\vec{s})$ is the expression for the Compton scattering in electron units due to Heisenberg.⁽²¹⁾ This approach is based upon the Thomas-Fermi atomic model, and is assumed to be applicable to the heavy atoms.

Appendix J gives a detailed account of how these calculations are carried out.

II. d. Search for Kohn Anomalies

As mentioned in section I. b, the most difficult problem in the identification of Kohn anomalies is the elimination of powder peaks as anomaly candidates. Since the data is acquired in such a manner that the

same range of reduced wave vectors is scanned over in more than one zone, as, for example, from the (200) to (300) and (300) to (400) reciprocal lattice points, the first criterion that something be identified as a Kohn anomaly will be that it appear at least twice in scan positions corresponding to the same reduced wave vector. The positions of the bumps so selected are then compared with the positions of possible powder lines, and those bumps with which several powder lines may be associated are considered very doubtful as anomaly candidates. This is particularly true of bumps which appear in the TDS from the [100] and [111] oriented crystals, and which can be associated with the same powder lines. Any sets of candidates which remain, where each set is associated with a particular reduced wave vector, will be considered possibly to be associated with Kohn anomalies.

III. EXPERIMENTAL APPARATUS

III. a. X-Ray Generator and Tube

A Picker number 816 constant potential generator and control was used to supply voltage and current to a Dunlee high intensity copper anode x-ray tube. The generator output is regulated with a Zener diode feedback system, and the system is claimed to have a drift of less than 60 volts at an output of 40 KV. The x-ray tube is constructed with beryllium windows and has a 16 mm by 1.6 mm focal spot. The spot focus was used throughout, and except for periods during which it was desired to eliminate the half wavelength radiation passed by the monochromator, the tube was operated at 40 KV and 24 ma.

A very important consideration is the stability of the x-ray beam. If possible, it is desired that the beam intensity be limited to variations which are due to statistics only. This system is very good in this respect, and Ashby⁽²²⁾ has found that intensity variations can be accounted for by making corrections for variations in air absorption due to atmospheric pressure and temperature changes. As discussed in Appendix M, it was found in this work that an additional correction was necessary to account for variations in the efficiency of the detection system caused by temperature variations. Figure 4 shows a fixed-time monitor of the x-ray beam as reflected off the monochromator crystal. The tube was run at

Counts for 1000 Seconds

Figure 4. X-Ray Beam Stability

- Average
- 95% Confidence Interval for Poisson Distribution
- 95% Confidence Interval from Sample Scatter

40 KV and 24 ma, and each count was conducted for 1000 seconds. There appears to be a very slight rise in the count rate over the two day period. This corresponded to a quite steady temperature and pressure. The scatter is a little larger than that expected from a Poisson distribution. This monitor was taken after the tube had been in operation for several days. A cold tube was usually warmed up overnight at 40 KV and 24 ma before any data was taken.

III. b. Diffractometer

A vertical axis Picker diffractometer was used in this investigation. The diffractometer, x-ray tube, monochromator, goniostat, vacuum chamber, slit system, and detector are shown in their operating configuration in Figure 5. Figure K-2 shows a top view of the system without the monochromator shield in place. The function of the diffractometer is to define the directions of the incoming and scattered radiation with respect to the sample for any given detector position. The diffractometer may be operated in one of two modes. It is usually operated in the $\theta - 2\theta$ scan mode, in which the detector arm is moved about the vertical axis with an angular speed twice the rotational speed of the sample about the same axis. This motion allows one to change the length of the diffraction vector, while maintaining a constant direction

Figure 5. Diffraction System in Operating Configuration

relative to the sample surface. In the second mode the sample can be rotated about the vertical axis while the detector remains fixed. This is known as the ω motion of the sample. Both the ω and $\theta - 2\theta$ motions are motor driven and can be step scanned, scanned, or oscillated between fixed limits.

III. c. Goniostat

The goniostat employed is a copy of that used by Costello⁽²³⁾ in his work on the same apparatus. He describes in detail the construction of the device, so that discussion will not be repeated here. The goniostat is used to translate the sample into the beam, and to orient it for desired reciprocal space traversals. It is shown from the front in Figure 5 and from the top in Figure K-2. The large wheel provides the angular degree of freedom designated by χ , and it corresponds to a rotation about an axis perpendicular to the diffractometer axis. The smaller wheel upon which the sample chamber is mounted provides an angular degree of freedom designated by ϕ , and corresponds to a rotation about an axis perpendicular to the χ axis. The relationships between ω , ϕ , and χ are shown in Figure 6. Axis 3 is the diffractometer axis, while axes 1, 2, and 4 are mutually perpendicular. The sample chamber mount has the capability of being translated parallel to

Figure 6. Angles Used in Crystal Orientation

the ϕ axis over a $3/8$ inch range. This is necessary for proper sample alignment. The χ and ϕ motions have scales which can be read to 0.01° . The angular orientation of a sample cannot be carried out with this precision, however, because of backlash in the gear system, but the precision is probably better than the 0.1° which Costello⁽²³⁾ states, because the goniostat used here has less backlash than that which he used. The base of the goniostat is that which was used previously, and it is maintained in the same alignment by reference marks on its base and on the diffractometer.

III. d. Vacuum Chamber

The vacuum chamber employed can be seen mounted in Figures 5 and K-2, and disassembled in Figure 7. It was designed and built by Dr. John Eldridge. Before the vacuum is established the chamber is held against the O ring by means of an outer threaded ring which is screwed onto the supporting back plate. The window, which is about two inches from the sample, is a piece of fifty mil mylar glued with Elmer's glue onto the brass surface of the chamber. During this work the vacuum was maintained in the range of about 100 to 300 microns, and the supporting bars seen in the chamber window are necessary in order that vertical kinks formed in the mylar at this pressure can be eliminated. There are actually

Figure 7. Diffraction System with Vacuum Chamber
Dismounted

two vacuum chambers, one with the vertical support bars placed as shown, and a second with the supports shifted by $22\frac{1}{2}^\circ$, so that all 2θ values may be investigated with no interference from the supports.

III. e. Pre-Monochromator

The pre-monochromator is discussed in detail in Appendix K. It is shown as part of the diffraction system in Figure 5, where its lead shielding is in place, and in Figure 7, where the lead shielding is removed. The lithium fluoride monochromator crystal is clearly visible in the top view shown in Figure K-2. This monochromator, including the rotatable x-ray tube mount, was designed by S. Schuster and built by E. Brooks. The crystal is doubly bent into a form described by Warren⁽²⁴⁾ and Chipman⁽²⁵⁾ in order to reduce the vertical divergence in the beam incident upon the sample. The monochromator utilizes the (200) reflection from lithium fluoride, and the scattering angle is 45° for $\text{CuK}\alpha$ radiation, which is at 8.05 KeV. Since the x-ray tube is normally operated at 40 KV, the monochromator also passes the second, third, and fourth multiples of the 8.05 KeV line. The half wavelength contribution turns out to be the only important one, and it must be accounted for at those reciprocal space positions for which half wavelength Bragg reflections from the sample occur. If the

monochromator crystal were bent uniformly, the incident beam cross section would be uniform. Figure K-6 indicates that this is not the case, and this must be considered when the resolution in reciprocal space is calculated.

III. f. Resolution

The resolution in reciprocal space is determined by the angular divergences allowed by the four-way adjustable slit immediately after the monochromator, the width of the beam focus at the sample, and the four-way adjustable slit just before the detector. An aluminum collimator, which is adjustable in length, extends from the detector slit to the vacuum chamber window, at which point a four-way slit is opened sufficiently far that the detector sees the entire beam focus at all 2θ angles. The function of the collimator is to stop any extraneous scattering from reaching the detector. The slit mountings are displayed clearly in Figures 5 and 7. The resolution is considered in detail in Appendix L. There it is shown that the incident horizontal divergence is $1^{\circ} 35'$, the incident vertical divergence is $12'$, the exit horizontal divergence is $52'$, and the exit vertical divergence is 1° . These divergences are the worst possible allowed by the slit and focus sizes, but it turns out that, due to structure in the incident beam, the resolution in reciprocal space is smaller than that which is predicted

by these numbers. Table L-1 gives the reciprocal space resolution for three different 2θ angles characteristic of the experiment. These resolutions, which are given in terms of a dimensionless reciprocal space, range from 0.040 at $2\theta = 46.00^\circ$ to 0.025 at $2\theta = 107.90^\circ$ for the resolution in the direction parallel to the diffraction vector, and from 0.017 to 0.036 for the direction perpendicular to the diffraction vector. These numbers include the effect of the 2θ sweep motion and the channel dwell time of the MCA, but they do not include the effect of mosaic spread in the sample crystals.

III. g. Detection System

The detector used is a xenon-filled proportional counter and preamplifier assembly supplied by Picker. We also had on hand a Hamner proportional counter which is more efficient at eliminating the effects of the half wavelength radiation passed by the monochromator; but it was found to undergo breakdowns in counting efficiency after a few hours' operation. Thus, this counter system, although initially preferred, had to be eliminated. The pulse height analyzer window was set wide enough so that it encompassed the 8.05 KeV CuK_α peak and allowed for some drift of the peak. For example, for most of the data runs the peak occurred at about 6.00 on the base line scale, and the window was set at 3.80 and 9.00. This window allowed not only for peak drift, but also

was small enough so that the 8.05 KeV escape peak was eliminated. The peak drift originates from two sources. First, as the detector tube is used, the peak position drifts downward very slowly. Except in the earliest data runs, the peak position was checked once a day, and the detector voltage increased, if necessary, to keep the peak centered within the window. The peak position also is a function of the count rate being monitored. In one investigation, for example, an integrated count rate taken with the base line at 1.00 yielded a count rate of about 13 per second, and the 8.05 KeV peak was centered at 8.00 with a half width of 15%. An integrated count rate of 1400 per second coincided with a peak position of about 7.20 with a half width of about 22%.

This Picker detector has some half wavelength contamination in the window settings employed. It is due to iron fluorescence from the back wall of the counter tube. As mentioned above in the monochromater discussion, this contamination is important in those reciprocal space regions where a half wavelength Bragg reflection occurs, and a full wavelength reflection does not. A method of correcting for this has been given by Costello and Weymouth⁽²⁶⁾ in which the fraction, f , the ratio of the half wavelength contamination in the window to the half wavelength intensity above the window, is measured. Knowing f , one then determines the half wavelength

contamination in regions where it is important by measuring the integrated count rate with the base line set at the upper window level, and then multiplying by f . This method was used in some of the early data runs and proved successful; but when it was found that the peak was beginning to decline at a noticeable rate, it was no longer used, since f depends on the window settings with respect to the peak position. Instead, a method was employed whereby the half wavelength was eliminated by running the x-ray tube at 14 KV and 32 ma, and then normalizing the data to that obtained at 40 KV and 24 ma.

III. h. Multichannel Analyzer

The MCA used is a 128 channel Nuclear Data Model 110. The data accumulation procedure has already been discussed briefly in section II. a, and some typical external control switch settings are described in detail in Appendix O. In the multiscaling operation, the channel dwell time of 8.33 seconds is produced by externally placing counts into the control channel, channel zero, by full wave rectification and proper shaping of the 60 cycle per second line voltage. Thus, 120 counts per second are inserted into channel zero, and when 1000 counts are accumulated, the system is advanced to the next higher channel. The accumulated data is printed out by an IBM Selectric typewriter equipped with an Autofinger attachment. The noise inherent in the entire

detection system, including the analyzer, is found to be 0.16 ± 0.02 counts per second. This is obtained by running the system with the x-ray tube port shut. The uncertainty corresponds to a 95% confidence interval.

IV. SAMPLES

IV. a. Preparation

The lucite sample which was used for the amorphous scattering measurements is approximately a 1" x 1" x $\frac{1}{2}$ " block cut from a $\frac{1}{2}$ " thick sheet which was on hand in the laboratory shop. The most highly polished and scratch-free surface of the sample was chosen as the scattering surface.

The lead crystal samples were grown from the melt in our laboratory. The lead used was of 99.999% purity, and was obtained from American Smelting and Refining Company of South Plainfield, N. J. The [111] oriented lead crystal was chosen from among several grown by J. Danke⁽²⁷⁾ in a study which he made concerning the preferred orientation of crystals grown from the melt. This sample did not have to be cut, as it was grown with the desired orientation. It was about $\frac{3}{16}$ " thick and about $\frac{7}{8}$ " in diameter. The [100] oriented crystal was grown by J. Beaver and P. Schulze, and it had to be rough cut with a jeweler's saw and then acid polished in order to achieve the desired orientation. This sample was about $\frac{1}{4}$ " thick, and had an oval-shaped surface area somewhat smaller than the area of the [111] sample. Each of the samples was found to have a rocking curve half width of about 12'.

Initially each sample was coated with an oxide surface layer which had to be removed. To do this, the crystals were mounted, in turn, on a goniometer head attached to a steel shaft, oriented, and then acid polished. Each crystal was oriented to within about 1° by means of Laue back reflection photographs such that the appropriate symmetry direction was parallel to the shaft. Then the shaft with the particular mounted crystal was placed into an acid polisher⁽²⁸⁾ in which the polishing surface is perpendicular to the axis of the shaft. In this polisher the polishing wheel is covered with two thicknesses of cotton bed-sheeting, and the outer edge of the wheel is in constant contact with an acid bath so that the cloth becomes soaked with the etching solution. The crystal and the wheel rotate in the same direction so that piling up of etching solution on the sample will be at a minimum. To get the polishing process started, the sample is slowly moved toward the wheel until light contact is made, at which time it is drawn back slightly so that there is a film of solution between the polishing cloth and the sample.

Different etches, etch procedures, and follow-up surface preparations were used during the course of the experiment. The [111] crystal was initially prepared with an etch consisting of two parts glacial acetic acid and one part 30% hydrogen peroxide (H_2O_2). It was polished for about five minutes, washed in distilled water, dried

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A second polish was carried out for ten minutes in an etch consisting of six parts glacial acetic acid, one part 30% H_2O_2 , and one part distilled water. This process removed the sticky residue mentioned above. The polishing process was followed by a rinse in distilled water in order to remove the etching solution, and then by a vigorous rinse in kerosene in order to replace the water layer with a kerosene layer. The kerosene protects the sample from oxidation during transfer from the acid polisher to the sputtering apparatus. Once either sample was inside the sputtering apparatus the system was pumped down to .002 microns for about twenty-four hours. This causes the removal of the kerosene surface layer. Next the sample was ion bombarded for five to ten minutes, sputtered for eight hours, ion bombarded again for $1\frac{1}{2}$ hours, and again sputtered for eight hours. The second ion bombardment was necessary because the short bombardment did not remove the oxide layer.

After the preparation just described, the surface of the [100] crystal was very shiny and somewhat wavy, but not so much as was the surface of the [111] crystal after the initial preparation described first in this section. When the [111] crystal was prepared according to the etch and ion bombardment procedure, its surface was not as bright as that of the [100] crystal prepared in the same manner, and it was not as bright as it was

after its own initial preparation. This diminished brightness was a result of using the same etches as were used in the preparation of the [100] crystal. The etches were weakened because of the [100] crystal preparation, and the [111] surface prepared with it was not as bright because of a finer surface roughness produced with the weaker etch.

The data acquired in this experiment is from the [100] and [111] crystals prepared according to the double etch, ion bombardment, and sputtering procedure, and from the [111] crystal prepared according to the initial single etch procedure. Since the [111] surface has a different character in each case, a comparison of the data should give information concerning surface effects on the TDS.

IV. b. Alignment

The alignment procedure for the lead samples is straightforward, but tedious. First, alignment for a longitudinal scan is described, and then that for a transverse scan. Each sample was mounted on a lucite base with silastic, and fixed by means of set screws onto the back plate of the vacuum chamber. Such a mounting can be seen in Figure 7 with a crystal for which the surface was not yet prepared. In the latter stages of this work the bases were modified so as to allow trans-

lation of a sample perpendicular to the base axis. This allowed investigation of any portion of the sample surface.

The crystal first had to be translated into the beam at the point where the incoming beam intersected the path defined by the detector's collimation system. This was accomplished by inserting a slotted lead plug into the end of the collimator at the chamber window. When the sample was moved into the intersection of the incoming beam with the path defined by the slot and the detector slit, it was in such a position that a Bragg reflection would fall at approximately the correct 2θ value. This approximate position was found by running the x-ray tube at 40 KV and 24 ma, moving the crystal into the beam, and finding when the TDS count rate was a maximum. The dial which controls this motion provides a translation of 1/96 inch per turn. When this step was accomplished, the lead plug was removed, the x-ray tube was turned down to 12 KV and 2 ma, and the detector was set at a 2θ value corresponding to a Bragg reflection. For example, for the [111] crystal, $2\theta_{111} = 31.27^\circ$ and $2\theta_{222} = 65.23^\circ$ are the angles of interest. The detector was first set at $2\theta_{111}$, and χ , ω , and d , the distance into the beam, were varied until the reflection was found and maximized. The (222) reflection was then found and maximized. This was done alternately between the two reflections several times until χ , ω , and d values were found which maximized both reflections at the proper 2θ values. The

system was considered aligned whenever either the center of the half width or the maximum value of each peak fell within $0.1^\circ 2\theta$ of the desired value. The alignment so far described is for an arbitrary ϕ value. Some of the data was taken with arbitrary ϕ , and some with a ϕ value for which the plane defined by the ϕ axis and the symmetry direction was perpendicular to the diffraction plane. The data taken in the latter case was practically identical with that in the arbitrary case for both crystals. This fact indicates that in both samples the symmetry direction is close enough to the crystal normal that no absorption correction needs to be made for the angle of incidence not being equal to the angle of reflection, as measured with respect to the crystal surface. To carry out this kind of alignment, the crystal was aligned for various values of ϕ until that value was found for which realignment at $\phi + 180^\circ$ required only a change in χ , and not ω . Had the crystal normal in each case coincided with the ϕ axis, the above procedure would have left the crystal normal and the symmetry direction in a plane perpendicular to the diffraction plane, thus eliminating completely the already mentioned absorption correction. However, the normals to the mounted crystals did not coincide with the ϕ axis because each sample was a little thicker on one edge than the opposite. This alignment did serve to define the zero position for the

ω motion as far as the lucite sample was concerned, since it was of much more uniform thickness and, hence, its normal much closer to the ϕ axis. For both the $[111]$ and $[100]$ crystals ω_0 was found to be 1.2° .

Alignment for the transverse mode scan required first an alignment along the direction for the longitudinal mode, and then an alignment for the transverse traversal. The $[111]$ transverse data was acquired in a traversal between the (333) and (224) reciprocal lattice points, while that for the $[100]$ direction was acquired between the (420) and $(4\bar{2}0)$ reciprocal lattice points. The (333) to (224) orientation, for example, was accomplished by changing 2θ and ω a calculated amount from the (333) reflection, and then rotating about the ϕ axis until the (224) reflection appeared. Then the (333) and (224) peaks were maximized by varying χ and ω at (333) and ϕ and ω at (224) . The (224) reflection was found to have three-fold symmetry about the $[111]$ direction, as expected. The $[100]$ crystal was oriented in a similar manner, except that it had the advantage of four-fold symmetry. This allowed an additional fine alignment in which the TDS intensity on one side of (400) was placed by ω adjustment in the proper ratio to the TDS at the corresponding point on the other side of (400) . The two intensities are not equal because of the $\left[1 + \frac{\sin(\theta + \Delta\omega)}{\sin(\theta - \Delta\omega)}\right]^{-1}$ absorption factor, which varies in opposite directions on opposite sides of the (400) peak. This factor is discussed in Appendix D.

The alignment of the lucite sample was accomplished by setting ω at 0.00° , and χ such that the sample surface was approximately perpendicular to the diffraction plane. The χ setting is not critical, since the absorption factor does not depend on χ . With the slotted plug in the collimator, the sample was brought into the beam until the measured intensity was maximized, and the sample was aligned. As mentioned above, an ω value of 1.2° should have been used. However, a sample calculation shows that $\omega = 0.00^\circ$ leads to an error in the BP values discussed in Appendix G of, at most, a negative one percent. As discussed later, this is of no concern.

V. RESULTS OF EXPERIMENT AND CALCULATION

V. a. Experimental Data and Results Expected from Calculation

All of the experimental data and relevant calculations are shown in Figures 8 through 12. In each instance the count rate is plotted against the dimensionless, reduced wave vector $aq/2\pi$, where, as mentioned before, a is the lattice constant, and q is the wave vector magnitude for a vibrational state. The reciprocal space position is given by the coordinates of the reciprocal lattice vectors along the direction in question, and the coordinates collectively are designated by τ . In all cases any error bars shown correspond to 68% confidence intervals. In the longitudinal data the reciprocal space resolution ranges from about ± 0.020 to about ± 0.013 in units of $aq/2\pi$ as one moves away from the reciprocal space origin. In the transverse data the resolution is about ± 0.018 in units of $aq/2\pi$. Any expected count rates which are plotted are obtained from the calculated I/BP values given in Appendix J, and from B and k values of 2.84×10^{-21} cm²/sec and 0.85, respectively. The pressure and temperature corrections described in Appendix M have been applied only to the data of Figure 10. At a maximum these corrections were found to be only 0.3%.

In Figure 8 the data collected between the (200)

and (600) reciprocal lattice points is displayed along with that expected from calculations. This data is described as longitudinal data, since the diffraction vector lies along the [100] symmetry direction, and since the polarization vectors of the vibrational modes are parallel and perpendicular to the symmetry direction. Equation (1) shows that in this case the first order TDS is associated with the longitudinal phonons. The same comment applies to Figures 10 and 11, where the diffraction vector is parallel to the [111] direction. This data was taken with the [100] sample prepared according to the ion bombardment and sputtering method described in section IV. a. The first plot in Figure 9 is higher statistical resolution data taken between the (200) and (400) reciprocal lattice points in order to search for Kohn anomalies. It is skewed slightly with respect to the corresponding data in Figure 8, and the contamination due to the half wavelength (600) reflection, which falls at the Brillouin zone boundary between (200) and (400), has not been removed. The contamination has been eliminated in Figure 8 by running the x-ray tube at 11 kV and 32 ma to remove the half wavelength contribution, and then normalizing the data to that obtained at 40 kV and 24 ma. There was no half wavelength contamination at the zone boundary between the (400) and (600) reciprocal lattice points. The second half of Figure 9 shows the data acquired between

the (400) and (420) reciprocal lattice points. In this traversal the diffraction vector was nearly perpendicular to a [100] symmetry direction. Almost all of the first order data then corresponds to transverse phonons. This data was obtained by changing ω and 2θ so as to make traversals between (400) and (420), and between (400) and (4 $\bar{2}$ 0). To go from (400) to (4 $\bar{2}$ 0), the ω changes are opposite to those in going from (400) to (420). The absorption decreases in going from (400) to (4 $\bar{2}$ 0), and increases in going from (400) to (420). The high count rate and low count rate data displayed is the measured data in these two directions corrected for such absorption effects. No half wavelength correction was applied to this transverse data.

The [100] data is skewed downward with respect to the calculated points in a direction in each instance which corresponds to increasing 2θ . It definitely has the shape which is predicted, but it is everywhere considerably higher than expected from the calculations. The points calculated with reduced force constants are explained in a later section. Paskin and Weiss⁽¹⁴⁾ also have measured the TDS from lead in this direction, but their data flattens out at the bottom and does not show the expected rise at the zone boundary. They did not make any calculations such as those done in this investigation.

Figures 10, 11, and 12 present the results for the $[111]$ direction. Figures 10 and 11 both correspond to traversals between the (111) and (333) reciprocal lattice points, but the data of Figure 10 is of higher statistical resolution, and it was taken with a wider horizontal divergence exit slit. It is included to be used in the search for Kohn anomalies. The Figure 10 data is the original data taken after the crystal was acid polished and placed into the vacuum chamber with no ion bombardment and sputtering. It is seen in Figure 10 that the data for different runs does not coincide at the zone boundaries. This was found to be due to the slow downward drift of the CuK_α peak with respect to the pulse height analyzer window. The drift was accounted for when the data of Figures 8, 9, 11, and 12 was acquired, and it is seen that it poses no problem in these cases. The half wavelength correction due to Costello and Weymouth⁽²⁶⁾ was applied to the data of Figure 10, while in Figure 11 the data was corrected by the method of reducing the x-ray tube voltage. Although they are not shown in Figure 10, calculations of the scattering expected with the wider exit slit were made, and the lead $[111]$ L frequencies were extracted. This is done in Appendix N, and it is found there that the frequencies are low, as are those for other metals investigated with x-rays, and that they are not consistent from one zone to the next. The same

[111] sample was used to obtain the data of Figures 11 and 12, but the surface was prepared by the ion bombardment and sputtering method, and it appeared rougher, as has been mentioned in section IV. a. The same B and k values as in Figures 8 and 9 apply to Figures 11 and 12. Figure 12 displays the [111] T data obtained by a traversal between the (333) and (224) reciprocal lattice points. It has been corrected downward to account for decreased absorption caused by changes in the ω values. No half wavelength correction was applied to this data.

As with the [100] data, the [111] data is skewed downward with respect to the calculated points in a direction in each instance which corresponds to increasing 2θ . Except for a portion of the [111] T data, it is everywhere considerably higher than that expected from calculations. The data of Figures 10 and 11 are very similar in shape, although the crystal surface was prepared differently in each case, and the exit horizontal divergence was different in each case. The [111] L data is very similar to that acquired by Paskin and Weiss,⁽¹⁴⁾ particularly as far as the asymmetry and the bump about 0.75 units from the (111) reciprocal lattice point are concerned.

In each direction there are several possible Kohn anomalies. The Kohn anomaly analysis is carried out in the subsequent analysis of the experimental results.

Figure 8. [100] Longitudinal Data

- Experimental Points
- Calculated Points for 100°K Force Constants
- x Calculated Points for Reduced Force Constants

Figure 9. [100] Transverse and High Resolution Longitudinal Data

- Experimental Points (Includes High Count Rate Transverse Data)
- + Experimental Low Count Rate Transverse Data
- Calculated Points for 100°K Force Constants

Figure 10. High Resolution Longitudinal Data

Figure 11. [111] Longitudinal Data

- Experimental Points
- Calculated Points for 100°K Force Constants
- × Calculated Points for Reduced Force Constants

Figure 12. [111] Transverse Data
 • Experimental Points
 • Calculated Points for 100° K
 Force Constants

V. b. Differences Between Experiment and Calculation

As has been seen in Figures 8 through 12, the measured count rates are higher than the calculated count rates in all regions investigated, except for a portion of the $[111]$ T data. Figures 13 through 15 display the absolute and percent differences between the measured and calculated count rates. Figure 13 shows the differences for the $[100]$ L data, Figure 14 that for the $[100]$ T and $[111]$ T data, and Figure 15 that for the $[111]$ L data.

The most striking feature of these plots is the way in which the measured data is skewed with respect to the calculated points. As already mentioned, it is skewed downward in the direction of increasing 2θ . The effect appears to be more multiplicative in nature than additive, and it has a periodic dependence on reciprocal lattice position. The greatest effect occurs in the $[111]$ L data, where the difference is greater than 100% near the (111) reciprocal lattice point. As a whole, the percent differences cover the range from about 10% to 60%. The $[111]$ T data difference has a shape different from that for the other data, and, as mentioned above, it is the only case which is negative over part of its reciprocal space interval.

Count Rate Excess

Absolute (sec⁻¹)

Figure 13. Asymmetry of [100] Longitudinal Data With Respect to Calculations

- Referred to Calculations for 100°K Force Constants
- x Referred to Calculations for Reduced Force Constants

Count Rate Excess

Figure 14. Asymmetry of [100] and [111] Transverse Data With Respect to Calculations

- [100] High Count Rate Data and [111] Data Referred to Calculations for 100°K Force Constants
- + [100] Low Count Rate Data Referred to Calculations for 100°K Force Constants

Count Rate Excess

Absolute (sec⁻¹)

Figure 15. Asymmetry of [111] Longitudinal Data With Respect to Calculations

- Referred to Calculations for 100°K Force Constants
- * Referred to Calculations for Reduced Force Constants

V. c. Summary of Results

The intensity of x-rays scattered from lead single crystals is of the order of magnitude predicted by calculations of the TDS, but, except for a portion of the [111] T data, most of the data is in the range from 10% to 60% higher than that predicted. The experimental data is skewed downward with respect to the calculations in the direction of increasing 2θ , and the skewness displays a periodic dependence on reciprocal space position. The shape of the [100] data agrees well with that predicted by the calculations, but it disagrees with the shape of the corresponding data of Paskin and Weiss.⁽¹⁴⁾ The shape of the [111] data does not conform as well with that expected from calculations, but it is similar to the shape of the [111] data acquired by Paskin and Weiss.⁽¹⁴⁾ There are several possible Kohn anomalies present in the data.

VI. DISCUSSION AND CONCLUSIONS

VI. a. Deviations of Experimental Results from Calculations.

In this section several possible sources for the difference between experiment and calculations are considered.

VI. a. 1. Spurious Instrumental Scatter. The slit system was designed so that only scattering from the target area on the crystal sample would be received. This is verified by the fact that with this system TDS from cesium iodide single crystals agrees well with that expected from calculations.⁽¹⁹⁾ Also, the shape of the scattering in the [111] direction has been found to be the same with other experimental arrangements.^(14,29) One of the setups was the system used in this work, except that a post monochromater instead of premonochromater was used.⁽²⁹⁾

VI. a. 2. Atomic Scattering Factor. The scattering factor, f , which was used in equations (1), (2), and (3), is the best calculated factor available for lead.⁽³⁰⁾ As discussed in Appendix E, it is calculated from Dirac-Slater wave functions,⁽³¹⁾ which include relativistic and exchange effects. Since the CuK_α line falls between the lead LIII and MI edges, a dispersion correction was applied. This dispersion correction was calculated

from the same Dirac-Slater wave functions.⁽³²⁾ The scattering factor is that for a rigid, un-ionized, free atom, but it is used here with reference to atoms in a single crystal. Since in a metal the outer electrons are not strictly associated with a single atom, one might expect that the scattering factor would be altered with respect to that for a free atom. In lead the outer three electrons are considered to be conduction electrons, and their wave functions are not at all localized. Thus, their contribution to the scattering factor will be negligible except for very small values of $\sin\theta/\lambda$. Strictly speaking, the scattering factor for Pb^{+3} would have been a better choice, but calculations of the Pb^{+2} and Pb^{+4} atomic scattering factors by means of Dirac-Slater wave functions⁽³¹⁾ indicates that the difference between the Pb and Pb^{+3} scattering factors is negligible for the $\sin\theta/\lambda$ region covered. The periodic variations in the percent differences are similar to those observed in alkali halides,⁽³³⁾ except that with the alkali halides the differences usually are negative once the zone boundary is passed. These variations are explained by effects on the scattering factor which arise from considering an atom to be deformable instead of rigid. Since the percent differences are periodic in shape in reciprocal space, it is possible that one must consider the atoms to be deformable, but since the differences are positive, except for a small portion of the $[111]$ T branch, there

must be some other contribution to the excess scattering.

VI. a. 3. Debye-Waller Factor. As discussed in Appendix F, The lead room temperature Debye temperature of about 85°K is now well established. In the primary reference⁽³⁴⁾ it is given as $85^{\circ} \pm 6^{\circ}\text{K}$. The complete calculations have been made using a Debye-Waller factor, e^{-2M} , corresponding to the 85°K Debye temperature. Several sample calculations for the [111] L and [100] L data have been made using Debye-Waller factors corresponding to 91°K and 79°K. These calculations vary from the 85°K calculations by only about 2%. Thus, the Debye-Waller factor is not the source of the difference between the measured data and the calculations.

VI. a. 4. Normalization and Polarization Factors. In equations (1), (2), (3), and (4) the correct normalization factor, B, and the correct monochromator polarization factor, k, must be used. B and k were determined from x-ray scattering by lucite, and the small errors in B and k of 0.7% and 1.2%, respectively, stated in Appendix G arise from the uncertainty of the straight line fit to the data. However, these errors were arrived at under the assumption that the uncertainties in factors involved in calculating the expected scattering were negligible. This is not really the case, as the uncertainties in the mass absorption coefficients used are possibly as large as $\pm 5\%$.⁽³⁵⁾ When this uncertainty is

considered, it is found that the straight line fit to the data falls in a range of about $\pm 4\%$ of its location when no error in mass absorption coefficients is allowed. Since the entire line is shifted, there is an effect on the uncertainty in B, but none on that in k, as k turns out to be the ratio of the slope of the line to its intercept. The result is that B is known to within about $\pm 4\%$.

In one trial run in which paraffin, in addition to lucite, was used, the paraffin B value was only 1.3% higher than that with lucite, and the paraffin k value was about 6% lower. However, the paraffin data did not fit a straight line as well as did that for the lucite.

The $\pm 4\%$ uncertainty in the B value used is not enough to account for the differences between experiment and calculation. In addition, when the paraffin B and k values were used in calculations in the [111] direction, there was practically no difference between these calculations and those in which the lucite values were used, particularly between the (111) and (222) reciprocal lattice points, where the difference between experiment and calculation is the largest. The normalization and polarization factors do not appear to be the source of the problem.

VI. a. 5. Second and Higher Order Calculations. As noted in Appendix H, the force constants used in the second order calculation were obtained by a least squares fit⁽¹⁷⁾

to the 100°K phonon dispersion curves of lead, as determined by neutron scattering.⁽¹¹⁾ There is uncertainty in the force constants from the standpoint that the fit has a mean deviation of 4% from the observed frequencies. There is uncertainty in the second order calculation due to the fact that the phonon frequency distribution calculated by Gilat⁽¹⁷⁾ from these force constants does not agree well with that measured experimentally by Stedman et al.⁽³⁶⁾ although the general features are the same. This means that the force constants determined from the fit of symmetry direction frequencies do not yield the correct frequencies and polarization vectors in non-symmetry directions. Since the non-symmetry directions are summed over in the second order calculation, there is probably an error introduced. It is hoped that the result is not much different from a correct calculation, since one essentially is averaging, over the first Brillouin zone, the scattering associated with pairs of wave vectors. The only way by which one could determine the error is by carrying through the second order calculation using the correct frequencies and polarization vectors throughout the first zone. Although they give non-symmetry frequencies, Stedman et al.⁽³⁶⁾ do not give the corresponding polarization vectors.

Since the force constants correspond to 100°K data, there is some error incurred due to the fact that the present work was done at room temperature. As discussed

in Appendix I, the room temperature dispersion curves generally are lower than the curves at 100°K . To estimate the effect on the second order calculation, the 100°K dispersion curves for lead determined by Stedman et al.⁽¹²⁾ were compared with the corresponding data which he acquired at room temperature. The average percentage shift from the values at 100°K for all frequencies determined at room temperature was about -4%. For a simple linear restoring force the percent change in the force constant is twice the percent change in the frequency. In order to make a calculation it was then assumed that each atomic force constant is reduced in magnitude by 8% at room temperature. The effect on the calculated total scattering of using the reduced force constants in the second order calculation can be seen in Figures 8, 11, 13, and 15. This causes a change in the calculated values in the correct direction, but the change is very small with respect to the difference between measured data and calculations.

The higher order scattering has been calculated by a method applied successfully by Eldridge to sodium chloride,⁽¹⁸⁾ and later to cesium iodide.⁽¹⁹⁾ If the differences between measurements and calculations originated in the higher order calculation, the difference should decrease as one moves toward the origin of reciprocal space, since the higher order scattering decreases in this direction. As seen in Figures 13 and 15, just

the opposite is true.

Thus, if the problem is associated with one of these calculations, it would probably be due to having used the incorrect frequencies and polarization vectors throughout the Brillouin zone in the second order calculation. However, as can be seen in Figures J-4, 5, 6, and 7, the second order calculations do have the expected shape with their peaking at the reciprocal lattice points. This shape would have to be skewed considerably, and the magnitude increased, in order to account for the differences between calculations and measurements. However, the second order calculations cannot be skewed any more than they are, at least in the $[111]L$ and $[100]L$ calculations, for the integral involved is symmetric with respect to a Brillouin zone boundary for these directions. Any skewness depends only on the factors which multiply the integral. Thus, use of correct frequencies and eigenvectors in the integration could increase the second order calculation, but it would not help to explain the periodicity evident in the difference plots.

VI. a. 6. Surface Modes. The frequencies of waves at a crystal surface should be different from those of the bulk waves, since the environment of an atom at the surface is different from that in the interior. Gazis et al.⁽³⁷⁾ have investigated the propagation of surface elastic waves in cubic crystals, and Wallis and Mara-

dudin(38) have developed a theory concerning surface effects on the TDS from crystal lattices. For lead, Gazis predicts waves which attenuate rather quickly with respect to the penetration depths discussed in Appendix D. Wallis indicates that the surface waves should affect the TDS, but he finds no way to separate the surface phonon from the bulk phonon contribution. However, since the surface waves attenuate quickly, one would suspect that they do not contribute much to the TDS when compared with the bulk waves. This is found to be the case with cesium iodide,⁽¹⁹⁾ for which the expected TDS agrees quite well with the measurements. Cesium has a larger absorption coefficient than does lead, so the effect of surface waves can be ruled out as the source of the difference between experiment and calculations.

VI. a. 7. Surface Contamination. Any residual surface oxides and the sputtered carbon layer should have some effect on the measured scattering. The presence of oxide powder layers is made known by small peaks which show up in the data. All peaks and sharp slope changes were analyzed in the search for Kohn anomalies, and a few of them were identified as probable powder peaks, although there doesn't seem to be any recognizable pattern occurring among them. It does seem that any surface oxide would cause some absorption of the incoming and outgoing beam, and thus cause a reduction, with respect to the calcula-

tions, of the scattering by bulk phonons. Surface oxide diffuse scattering would be present to some extent, but it cannot explain the periodic character of the extra scattering.

A surface layer of amorphous carbon similarly would cause a small reduction in the bulk phonon scattering because of absorption, and there would also be present a contribution from the amorphous scattering. This amorphous scattering would be additive in nature, and it would decrease slowly as one moves away from the origin of reciprocal space. The fact that, from an additive standpoint, the extra scattering rises rapidly on either side of a reciprocal lattice point seems to rule out amorphous surface layer scattering as the source of the problem, particularly as far as the periodicity in reciprocal space of the extra scattering is concerned. This is also evident from the [111] data in which there was no sputtered surface layer. Extra scattering with the periodic effect was still present. Thus, the surface layer may contribute some extra scattering, although not much, and it does not explain the periodic nature of the observed extra scattering.

VI. a. 8. Surface Roughness. The absorption correction is applied in expressions (1), (2), (3), and (4) under the assumption that the sample surface is flat. Microscopic examination shows, however, that the sample surfaces

are rough. As discussed previously, this roughness depends on the etch procedure which was used in the preparation. A general theoretical treatment of surface roughness is extremely complicated. The specific case treated in Appendix D shows a decrease in the expected scattering, instead of the increase measured. In the general case of random surface roughness, one would expect the effect of the roughness to be averaged out, unless the distances characteristic of the roughness are not negligible with respect to the size of the beam focus.

The example treated in Appendix D is for the case of $2\theta = 90^\circ$. As 2θ increases one would expect the effect of surface roughness to decrease, since at $2\theta = 180^\circ$ there should be no effect. However, the decrease in the effect would probably be smooth in character, unlike the periodic nature of the percent differences between experiment and calculations shown in Figures 13, 14, and 15. The [111] data of Figures 10 and 11 are similar in shape, although the sample, as has been discussed, had a different appearing surface roughness in each case. Thus, from the above arguments, it does not seem that crystal surface roughness is the source of the extra scattering.

VI. a. 9. Divergence Corrections. One problem which usually is considered in x-ray scattering work is that of divergence corrections. These are corrections which must be applied to the measured data if the scattering

cross-section varies appreciably over the reciprocal volume element. This will be the case when one approaches a reciprocal lattice point, because the first order TDS will then increase very rapidly. The work on cesium iodide,⁽¹⁹⁾ which was carried out on the same apparatus with the same divergence conditions, indicates that small divergence corrections are necessary only near reciprocal lattice points. Quite large corrections would be necessary in the present data, and they would have to be applied not only near reciprocal lattice points, but throughout the region between such points. Rough calculations have indicated that angular divergences much larger than those employed in this work would be necessary to account for the magnitude of the difference between experiment and calculations. Thus, both other experimental work, and rough divergence calculations indicate that divergence is not the problem.

VI. a. 10. Summary of Possible Sources of the Extra Scattering. The above considerations do not pinpoint a source for the observed extra scattering. The periodic variations in reciprocal space of the percent difference between the measurements and calculations may be due to the effect of deformable atoms on the atomic scattering factor. The magnitude of the extra scattering might be connected with the second order calculation, even though the calculation displays the characteristics ex-

pected of it. Scattering from the amorphous carbon layer probably gives a little extra scattering, but it certainly does not explain the periodic character of the scattering. The other effects considered are thought to be negligible.

VI. b. Kohn Anomalies

The criteria for identifying a Kohn anomaly is discussed in section II. d. Since the Kohn anomaly search is a secondary purpose of this work, only the results, and not the details, of the search are described.

From the analysis by Stedman et al.⁽¹³⁾ Kohn anomalies should occur in all of the data presented in this work. Slope changes are found in many positions, some of which are expected. In most cases it is impossible to make identification of a Kohn anomaly because of the multitude of lead oxide powder lines which are possible. The best possibilities were found in the $[111]$ T data in the reduced wave vector ranges 0.51-0.53, 0.61-0.63, and 0.68-0.71. For the $[111]$ T branch Stedman et al.⁽¹³⁾ list an anomaly at 0.47 ± 0.02 , and one at 0.68 or 0.72. Both of these and something between may be showing up in the present data. However, in the analysis there were powder lines which could have been associated with either the lower slope change or the middle one, but not both. If the correspondence with the Stedman analysis is correct, the middle slope change is likely due to powder contamination.

VI. c. Conclusions

This study was initiated in an effort to clarify the reasons why dispersion curves for metals determined by x-ray methods generally fall below the corresponding curves determined with neutrons. The feeling was that an improved calculation of the second order TDS might remove the disagreement between the x-ray and neutron results. The experimental results obtained show that this is not the case. Calculation of the $[111]$ L dispersion curve from the data gives not one curve, but several, depending upon the region of reciprocal space with which each curve is associated. As shown in Appendix N, all of the curves fall below the corresponding curve obtained with neutrons.

It can safely be assumed that the scattering observed is associated with phonons, since the predicted order of magnitude of the TDS is the same as that measured, and since characteristics of the dispersion curves are evident in the x-ray scattering, particularly in the $[100]$ direction. The source of the extra scattering is not at all clear. A possible explanation of the periodic variation in the difference between measured and calculated scattering might be that of a deformable ion effect on the scattering factor. However, since the measurements are almost always greater than the calculations, there must be some additional scattering, such as scattering

from an amorphous surface layer. The assumption of additional scattering can be made if the calculated second order scattering is correct. It is possible that this calculation might be higher when correct frequencies and polarization vectors are used, although it would require a large change to account for the magnitude of the difference between experiment and calculations. An increase in the second order calculation could not, however, explain the periodic nature displayed by the difference plots.

Two Kohn anomalies observed with neutrons⁽¹³⁾ in the $[111]$ T mode likely have been identified in the x-ray data. It is possible that others are seen, but due to their coincidence with lead oxide powder line positions, one cannot make a positive identification.

Appendix A. Thermal Diffuse Scattering of X-Rays by Monatomic Crystals--Kinematic Approach

This problem has been treated thoroughly in the literature, but for completeness it will be considered here in some detail. The discussion through equation (A.23) is taken from James. (39)

Consider the case of x-rays incident upon a crystal having one atom per unit cell with no thermal motion. Compared to scattering by a single electron, and under the assumption that the wave is scattered only once by each atom, the scattered amplitude is

$$A(\vec{s}) = f \sum_{n=1}^N e^{i\vec{s} \cdot \vec{r}_n} \quad (\text{A.1})$$

where f is the atomic scattering factor

$\vec{s}$ is the diffraction vector

$|\vec{s}|$ is $4\pi \sin\theta/\lambda$

$\vec{r}_n$ is the position of n^{th} atom

N is the total number of atoms involved

Suppose at time t the n^{th} atom is displaced by an amount $\vec{u}_n(t)$ from its equilibrium position defined by $\vec{r}_n$. Then

$$A(\vec{s}, t) = f \sum_{n=1}^N e^{i\vec{s} \cdot [\vec{r}_n + \vec{u}_n(t)]} \quad (\text{A.2})$$

The quantity of interest is the intensity, $I(\vec{s}, t)$, of the scattered wave.

$$I(\vec{s}, t) = AA^* = f^2 \sum_{n,m=1}^N e^{i\vec{s} \cdot (\vec{r}_n - \vec{r}_m)} e^{i\vec{s} \cdot [\vec{u}_n(t) - \vec{u}_m(t)]} \quad (\text{A.3})$$

(A.3) gives the intensity of the scattered wave at time t if the period of vibration of the atoms is much greater than the period of the incident radiation, which is the case with x-rays. This means that the incoming radiation essentially sees a static lattice. But observations are made over many lattice vibrational periods, so that one must take the time average of (A.3) in order to get the observed intensity.

Only the second exponential in (A.3) is time averaged. Let us define

$$P_{nm} = \bar{S} \cdot [\bar{u}_n(t) - \bar{u}_m(t)] \quad (\text{A.4})$$

$$\overline{e^{iP}} = 1 + i\bar{P} - \frac{\bar{P}^2}{2!} - \frac{i\bar{P}^3}{3!} + \frac{\bar{P}^4}{4!} + \dots = 1 - \frac{\bar{P}^2}{2} + \frac{\bar{P}^4}{24} + \dots \quad (\text{A.5})$$

since the odd power terms' time averages are zero. That is, positive and negative values of P_{nm} are taken to be equally likely.

$$\overline{e^{iP}} \approx e^{-\frac{1}{2} \bar{P}^2} \quad (\text{A.6})$$

This was rigorously proved by Ott⁽⁴⁰⁾ in 1935.

To evaluate $\bar{P}_{nm}^2$, assume that the lattice displacements $\bar{u}_n(t)$ can be expressed as a sum of harmonic elastic waves. These are the normal modes of the crystal lattice. In the actual crystal lattice the phases of these waves are assumed to vary rapidly and arbitrarily with time because of the damping that must occur. The picture is that of each wave continually being stopped and started anew with an arbitrary phase, after a time absolutely

very short, but long enough to contain many periods of vibration of the wave. This has to be assumed, for it would not make sense to talk about a wave if its lifetime were about the same as its period of vibration. The harmonic approach does not allow for thermal expansion, so it is an approximation from the standpoint that anharmonic contributions to the potential are neglected.

There are $3K$ harmonic waves in a monatomic crystal, where K is the number of atoms in the crystal. These waves are specified by K $\vec{q}$ values, and three polarizations for each $\vec{q}$ value.

Let

$$\vec{u}_n(t) = \sum_{\vec{q},j} \vec{e}_{\vec{q},j} a_{\vec{q},j} \cos(\omega_{\vec{q},j}t - \vec{q} \cdot \vec{r}_n + \delta_{\vec{q},j}) \quad (\text{A.7})$$

where $\vec{q}$ is the wave vector

$\vec{e}_{\vec{q},j}$ is the unit vector for one of the three independent modes associated with the wave vector $\vec{q}$

$\omega_{\vec{q},j}$ is the angular frequency of mode $\vec{q},j$

$\delta_{\vec{q},j}$ is the arbitrary phase which changes many times over the time of observation, but is constant over many oscillations of a given wave

$a_{\vec{q},j}$ is the wave amplitude which ultimately is determined by thermal equilibrium conditions.

$$P_{nm} = \vec{S} \cdot \sum_{\vec{q},j} \vec{e}_{\vec{q},j} a_{\vec{q},j} [\cos(\omega_{\vec{q},j}t - \vec{q} \cdot \vec{r}_n + \delta_{\vec{q},j}) - \cos(\omega_{\vec{q},j}t - \vec{q} \cdot \vec{r}_m + \delta_{\vec{q},j})] \quad (\text{A.8})$$

$$P_{nm}^2 = \sum_{\vec{q}_j} \sum_{\vec{q}'_{j'}} (\vec{S} \cdot \vec{e}_{\vec{q}_j}) (\vec{S} \cdot \vec{e}_{\vec{q}'_{j'}}) (a_{\vec{q}_j} a_{\vec{q}'_{j'}}) \times \quad (A.9)$$

$$\left[\begin{aligned} & \cos(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_n + \delta_{\vec{q}_j}) \cos(\omega_{\vec{q}'_{j'}} t - \vec{q}' \cdot \vec{r}_n + \delta_{\vec{q}'_{j'}}) \\ & - \cos(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_m + \delta_{\vec{q}_j}) \cos(\omega_{\vec{q}'_{j'}} t - \vec{q}' \cdot \vec{r}_n + \delta_{\vec{q}'_{j'}}) \\ & - \cos(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_n + \delta_{\vec{q}_j}) \cos(\omega_{\vec{q}'_{j'}} t - \vec{q}' \cdot \vec{r}_m + \delta_{\vec{q}'_{j'}}) \\ & + \cos(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_m + \delta_{\vec{q}_j}) \cos(\omega_{\vec{q}'_{j'}} t - \vec{q}' \cdot \vec{r}_m + \delta_{\vec{q}'_{j'}}) \end{aligned} \right]$$

In (A.9) only those terms for which $j'=j$ and $\vec{q}'=\vec{q}$ will survive when the time average is taken, since the factors in the other terms have phases which are completely independent of each other. Thus, the average of the product equals the product of the averages for such terms and they vanish.

Therefore

$$\begin{aligned} \overline{P_{nm}^2} &= \sum_{\vec{q}_j} (\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \overline{(a_{\vec{q}_j})^2} \left[\cos^2(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_n + \delta_{\vec{q}_j}) + \cos^2(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_m + \delta_{\vec{q}_j}) \right. \\ &\quad \left. - 2 \cos(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_m + \delta_{\vec{q}_j}) \cos(\omega_{\vec{q}_j} t - \vec{q} \cdot \vec{r}_n + \delta_{\vec{q}_j}) \right] \\ &= \sum_{\vec{q}_j} (\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \overline{(a_{\vec{q}_j})^2} \left[1 - \cos(2\omega_{\vec{q}_j} t - \vec{q} \cdot (\vec{r}_m + \vec{r}_n) + 2\delta_{\vec{q}_j}) - \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m) \right] \\ \frac{1}{2} \overline{P_{nm}^2} &= \frac{1}{2} \sum_{\vec{q}_j} (\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \overline{a_{\vec{q}_j}^2} \left[1 - \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m) \right] \end{aligned} \quad (A.10)$$

$\overline{a_{\vec{q}_j}^2}$ is the mean square amplitude determined by time averaging, but it will be assumed to be the same as that determined from thermal equilibrium conditions.

From (A.3)

$$\begin{aligned} \overline{I(\vec{S})} &= f^2 \sum_{n,m=1}^N e^{i\vec{S} \cdot (\vec{r}_n - \vec{r}_m)} e^{-\frac{1}{2} \sum_{\vec{q}_j} (\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \overline{a_{\vec{q}_j}^2} [1 - \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m)]} \\ &= f^2 e^{-\frac{1}{2} \sum_{\vec{q}_j} (\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \overline{a_{\vec{q}_j}^2}} \sum_{n,m=1}^N e^{i\vec{S} \cdot (\vec{r}_n - \vec{r}_m)} e^{\frac{1}{2} \sum_{\vec{q}_j} (\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \overline{a_{\vec{q}_j}^2} \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \end{aligned} \quad (A.11)$$

Define

$$2M = \frac{1}{2} \sum_{\vec{q}_j} (\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \overline{a_{\vec{q}_j}^2} = \sum_{\vec{q}_j} G_{\vec{q}_j} \quad (A.12)$$

$$G_{\vec{q}j} = \frac{1}{2} (\vec{S} \cdot \vec{e}_{\vec{q}j})^2 \bar{a}_{\vec{q}j}^2 \quad (\text{A.13})$$

Therefore
$$\bar{I}(\vec{S}) = f^2 e^{-2M} \sum_{n,m=1}^N e^{i\vec{S} \cdot (\vec{r}_n - \vec{r}_m)} e^{\sum_{\vec{q}j} G_{\vec{q}j} \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \quad (\text{A.14})$$

$(\vec{S} \cdot \vec{e}_{\vec{q}j})^2 \frac{\bar{a}_{\vec{q}j}^2}{2}$ is just $|\vec{S}|^2$ times the mean square displacement of an atom along $\vec{S}$ due to the $\vec{q}j$ mode. Since the modes are independent, the sum over all $\vec{q}j$ gives $|\vec{S}|^2$ times the net mean square displacement of the atom along $\vec{S}$.

Since $|\vec{S}| = 4\pi \sin \theta / \lambda$

$$G_{\vec{q}j} = (\vec{S} \cdot \vec{e}_{\vec{q}j})^2 \frac{\bar{a}_{\vec{q}j}^2}{2} \equiv 16\pi^2 (\sin \theta / \lambda)^2 \bar{U}_{\vec{q}j}^2(\vec{S})$$

$$2M = \sum_{\vec{q}j} G_{\vec{q}j} = 16\pi^2 (\sin \theta / \lambda)^2 \sum_{\vec{q}j} \bar{U}_{\vec{q}j}^2(\vec{S}) = 16\pi^2 (\sin \theta / \lambda)^2 \bar{U}^2(\vec{S}) \quad (\text{A.15})$$

e^{-2M} is the Debye-Waller factor, and one can show that it is independent of the direction of $\vec{S}$ for a cubic material.

Now determine $G_{\vec{q}j}$ in terms of the average number of phonons associated with the $\vec{q}j$ mode. From (A.14) then consider the contributions to $\bar{I}(\vec{S})$ from scattering events involving one phonon, two phonons, and so on. Classically the total lattice KE is

$$E_{\text{kin}} = \frac{1}{2} \sum_{n=1}^K m |\dot{\vec{u}}_n|^2$$

Therefore
$$\bar{E}_{\text{kin}} = \frac{1}{2} m \sum_{n=1}^K \overline{|\dot{\vec{u}}_n|^2} \quad (\text{A.16})$$

From (A.7) $\dot{\vec{u}}_n(t) = - \sum_{\vec{q}_j} \vec{e}_{\vec{q}_j} a_{\vec{q}_j} \omega_{\vec{q}_j} \sin(\omega_{\vec{q}_j} t - \vec{q}_j \cdot \vec{r}_n + \delta_{\vec{q}_j})$ (A.17)

$$|\dot{\vec{u}}_n|^2 = \sum_{\vec{q}_j} \sum_{\vec{q}'_j} (\vec{e}_{\vec{q}_j} \cdot \vec{e}_{\vec{q}'_j}) a_{\vec{q}_j} a_{\vec{q}'_j} \omega_{\vec{q}_j} \omega_{\vec{q}'_j} \sin(\omega_{\vec{q}_j} t - \vec{q}_j \cdot \vec{r}_n + \delta_{\vec{q}_j}) \sin(\omega_{\vec{q}'_j} t - \vec{q}'_j \cdot \vec{r}_n + \delta_{\vec{q}'_j})$$

$$\overline{|\dot{\vec{u}}_n|^2} = \frac{1}{2} \sum_{\vec{q}_j} \overline{a_{\vec{q}_j}^2} \omega_{\vec{q}_j}^2 \quad (\text{A.18})$$

Therefore

$$\overline{E}_{\text{kin}} = \frac{m}{4} \sum_{\vec{q}_j} \overline{a_{\vec{q}_j}^2} \omega_{\vec{q}_j}^2 = \frac{mK}{4} \sum_{\vec{q}_j} \overline{a_{\vec{q}_j}^2} \omega_{\vec{q}_j}^2$$

Mean total energy $\equiv \overline{E} = 2 \overline{E}_{\text{kin}}$. (A.19)

$$\overline{E} = \frac{mK}{2} \sum_{\vec{q}_j} \overline{a_{\vec{q}_j}^2} \omega_{\vec{q}_j}^2 \equiv \sum_{\vec{q}_j} \overline{E}_{\vec{q}_j}$$

where $\overline{E}_{\vec{q}_j}$ is the average energy associated with the mode $\vec{q}_j$.

Therefore $\overline{a_{\vec{q}_j}^2} = \frac{2 \overline{E}_{\vec{q}_j}}{mK \omega_{\vec{q}_j}^2}$ (A.20)

But one can show quantum mechanically that

$$\overline{E}_{\vec{q}_j} = (\overline{n}_{\vec{q}_j} + \frac{1}{2}) \hbar \omega_{\vec{q}_j}$$

where $\overline{n}_{\vec{q}_j} = \frac{1}{e^{\frac{\hbar \omega_{\vec{q}_j}}{kT}} - 1}$ = average number of phonons in the mode $\vec{q}_j$. (A.21)

$$G_{\vec{q}_j} = \frac{1}{2} (\vec{s} \cdot \vec{e}_{\vec{q}_j})^2 \overline{a_{\vec{q}_j}^2} = \frac{(\vec{s} \cdot \vec{e}_{\vec{q}_j})^2 \overline{E}_{\vec{q}_j}}{mK \omega_{\vec{q}_j}^2} \quad (\text{A.22})$$

Consider equation (A.14).

$$\bar{I}(\vec{s}) = f^2 e^{-2M} \sum_{n,m=1}^N e^{i\vec{s} \cdot (\vec{r}_n - \vec{r}_m)} e^{\sum_{\vec{q}} G_{\vec{q}} \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \quad (\text{A.14})$$

Let $\mathcal{I}_0 = \sum_{n,m=1}^N e^{i\vec{s} \cdot (\vec{r}_n - \vec{r}_m)}$. This is the interference function for a static monatomic lattice, and it has a non-zero value only when $\vec{s} = \vec{\tau}$, a reciprocal lattice vector.

The second exponential in (A.14) will now be expanded, and it will be found that succeeding terms in the expansion correspond to scattering events in which zero, one, two, three, ---, etc. phonons are involved. When $2M$ is small, the exponent of the second exponential is small, and one can cut the expansion off after a few terms.

$$\bar{I}(\vec{s}) = f^2 e^{-2M} \sum_{n,m=1}^N e^{i\vec{s} \cdot (\vec{r}_n - \vec{r}_m)} \left[\begin{aligned} &1 + \sum_{\vec{q}} G_{\vec{q}} \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m) \\ &+ \frac{1}{2} \sum_{\vec{q}} \sum_{\vec{q}'} G_{\vec{q}} G_{\vec{q}'} \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m) \cos \vec{q}' \cdot (\vec{r}_n - \vec{r}_m) \\ &+ \frac{1}{6} \sum_{\vec{q}} \sum_{\vec{q}'} \sum_{\vec{q}''} G_{\vec{q}} G_{\vec{q}'} G_{\vec{q}''} \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m) \cos \vec{q}' \cdot (\vec{r}_n - \vec{r}_m) \cos \vec{q}'' \cdot (\vec{r}_n - \vec{r}_m) \\ &+ \dots \end{aligned} \right] \quad (\text{A.23})$$

$$\bar{I}(\vec{s}) = I_0(\vec{s}) + I_1(\vec{s}) + I_2(\vec{s}) + I_3(\vec{s}) + \dots \quad (\text{A.24})$$

$$I_0(\vec{s}) = f^2 e^{-2M} \sum_{n,m=1}^N e^{i\vec{s} \cdot (\vec{r}_n - \vec{r}_m)} = f^2 e^{-2M} \mathcal{I}_0(\vec{s}) \quad (\text{A.25})$$

$$I_1(\vec{s}) = f^2 e^{-2M} \sum_{\vec{q}} G_{\vec{q}} \sum_{n,m} e^{i\vec{s} \cdot (\vec{r}_n - \vec{r}_m)} \cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m) \quad (\text{A.26})$$

$$\cos \vec{q} \cdot (\vec{r}_n - \vec{r}_m) = \frac{1}{2} \left[e^{i\vec{q} \cdot (\vec{r}_n - \vec{r}_m)} + e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_m)} \right] \quad (\text{A.27})$$

$$\begin{aligned}
I_1(\vec{s}) &= \frac{1}{2} f^2 e^{-2M} \sum_{\vec{q}, j} G_{\vec{q}, j} \left[\sum_{n, m} e^{i(\vec{s} + \vec{q}) \cdot (\vec{r}_n - \vec{r}_m)} + \sum_{n, m} e^{i(\vec{s} - \vec{q}) \cdot (\vec{r}_n - \vec{r}_m)} \right] \\
&= \frac{1}{2} f^2 e^{-2M} \sum_{\vec{q}, j} G_{\vec{q}, j} \left[\psi_0(\vec{s} + \vec{q}) + \psi_0(\vec{s} - \vec{q}) \right]
\end{aligned} \tag{A.28}$$

Treating I_2 and I_3 in the same manner, one obtains

$$\begin{aligned}
\bar{I}(\vec{s}) &= f^2 e^{-2M} \psi_0(\vec{s}) + \frac{1}{2} f^2 e^{-2M} \sum_{\vec{q}, j} G_{\vec{q}, j} \left[\psi_0(\vec{s} + \vec{q}) + \psi_0(\vec{s} - \vec{q}) \right] \\
&\quad + \frac{1}{8} f^2 e^{-2M} \sum_{\vec{q}, j} \sum_{\vec{q}', j'} G_{\vec{q}, j} G_{\vec{q}', j'} \left[\psi_0(\vec{s} + \vec{q} + \vec{q}') + \psi_0(\vec{s} + \vec{q} - \vec{q}') + \psi_0(\vec{s} - \vec{q} + \vec{q}') + \psi_0(\vec{s} - \vec{q} - \vec{q}') \right] \\
&\quad + \frac{1}{48} f^2 e^{-2M} \sum_{\vec{q}, j} \sum_{\vec{q}', j'} \sum_{\vec{q}'', j''} G_{\vec{q}, j} G_{\vec{q}', j'} G_{\vec{q}'', j''} \left[\begin{aligned} &\psi_0(\vec{s} + \vec{q} + \vec{q}' + \vec{q}'') + \psi_0(\vec{s} + \vec{q} + \vec{q}' - \vec{q}'') + \psi_0(\vec{s} + \vec{q} - \vec{q}' + \vec{q}'') \\ &+ \psi_0(\vec{s} + \vec{q} - \vec{q}' - \vec{q}'') + \psi_0(\vec{s} - \vec{q} + \vec{q}' + \vec{q}'') + \psi_0(\vec{s} - \vec{q} + \vec{q}' - \vec{q}'') \\ &+ \psi_0(\vec{s} - \vec{q} - \vec{q}' + \vec{q}'') + \psi_0(\vec{s} - \vec{q} - \vec{q}' - \vec{q}'') \end{aligned} \right] \\
&\quad + \dots
\end{aligned} \tag{A.29}$$

When a strictly quantum mechanical approach is taken with this problem, it is found that I_1 is a contribution to the scattered intensity which corresponds to the creation or destruction of a phonon by the photon that is scattered. I_2 corresponds to a two phonon interaction, I_3 to a three phonon interaction, and so on. The photons involved in such scatterings undergo energy changes, but this has been neglected in the above treatment since the changes are well below the limits of observation.

Consider the one phonon term and note that $G_{\vec{q}, j} = G_{-\vec{q}, j}$.

$$I_1(\vec{s}) = \frac{1}{2} f^2 e^{-2M} \sum_{\vec{q}, j} G_{\vec{q}, j} \left[\psi_0(\vec{s} + \vec{q}) + \psi_0(\vec{s} - \vec{q}) \right] \tag{A.28}$$

φ_0 has an appreciable value only when $\vec{s} + \vec{q} = \vec{r}$, a reciprocal lattice vector. Suppose that $\vec{s} + \vec{k} = \vec{r}$. Then $\vec{s} - \vec{k} = \vec{r}$. In the first sum $\varphi_0(\vec{s} + \vec{k}) \neq 0$, while all other terms are zero. In the second sum $\varphi_0[\vec{s} - (\vec{r} - \vec{k})] \neq 0$, while all other terms are zero. Since $G_{\vec{q}j} = G_{-\vec{q}j}$

$$I_1(\vec{s}) = f^2 e^{-2M} \sum_j G_{\vec{q}j} \varphi_0(\vec{s} + \vec{q}) \quad \vec{s} + \vec{q} = \vec{r} \quad (\text{A.30})$$

Because of detection limitations it is the integrated intensity which is required. I_1 will continue to denote the first order scattering throughout the discussion, although the actual quantity referred to will vary because of consideration of integrated intensities. Let $\vec{s}$ vary such that $\vec{s} + \vec{q}$ covers the entire peak of φ_0 at $\vec{r}$. Guinier⁽⁴¹⁾ shows that

$$\int \varphi_0(\vec{s}) dV_s = 8\pi^3 \frac{V}{V_c} \quad (\text{A.31})$$

where V_c is the volume of the primitive unit cell in the monatomic crystal and V is the diffracting volume.

$$I_1(\vec{s}) = 8\pi^3 \frac{V}{V_c} f^2 e^{-2M} \sum_j G_{\vec{q}j} \quad \vec{s} + \vec{q} = \vec{r} \quad (\text{A.32})$$

Using (A.22) one has

$$I_1(\vec{s}) = \frac{8\pi^3}{mK} \frac{V}{V_c} f^2 e^{-2M} \sum_j \frac{(\vec{s} \cdot \vec{e}_{\vec{q}j})^2 \bar{E}_{\vec{q}j}}{\omega_{\vec{q}j}^2} = \frac{8\pi^3 f^2 e^{-2M}}{m V_c} \left(\frac{N}{K}\right) \sum_j \frac{(\vec{s} \cdot \vec{e}_{\vec{q}j})^2 \bar{E}_{\vec{q}j}}{\omega_{\vec{q}j}^2} \quad \vec{s} + \vec{q} = \vec{r} \quad (\text{A.33})$$

since $\frac{V}{V_c} = N$, the number of atoms involved in the scattering. However, it is most likely that the reciprocal volume

element around $\vec{S}$ is large enough to contain many points $\vec{q}$, all of which will then contribute to the scattered intensity.

The K points $\vec{q}$ are distributed over a volume of reciprocal space equal to $\frac{8\pi^3}{V_c}$. Therefore, the number of $\vec{q}$ values per unit volume of reciprocal space is $\frac{KV_c}{8\pi^3} = \frac{V_0}{8\pi^3}$, where V_0 is the crystal volume. Let ΔW be the reciprocal volume element. ΔW contains $\frac{V_0}{8\pi^3} \Delta W$ points $\vec{q}$.

$$I_1(\vec{S}) = \frac{(\Delta W) f^2 e^{-2M}}{m} \frac{NV_0}{KV_c} \sum_j \frac{(\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \bar{E}_{\vec{q}_j}}{\omega_{\vec{q}_j}^2} = \frac{(\Delta W) N f^2 e^{-2M}}{m} \sum_j \frac{(\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \bar{E}_{\vec{q}_j}}{\omega_{\vec{q}_j}^2}$$

Therefore, in electron units per unit volume of reciprocal space

$$I_1(\vec{S}) = \frac{N f^2 e^{-2M}}{m} \sum_j \frac{(\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \bar{E}_{\vec{q}_j}}{\omega_{\vec{q}_j}^2} \quad (\text{A.34})$$

Consider the two phonon term.

$$I_2(\vec{S}) = \frac{1}{8} f^2 e^{-2M} \sum_{\vec{q}_j} \sum_{\vec{q}'_j} G_{\vec{q}_j} G_{\vec{q}'_j} \left[\begin{aligned} &\psi_0(\vec{S} + \vec{q} + \vec{q}') + \psi_0(\vec{S} + \vec{q} - \vec{q}') \\ &+ \psi_0(\vec{S} - \vec{q} + \vec{q}') + \psi_0(\vec{S} - \vec{q} - \vec{q}') \end{aligned} \right] \quad (\text{A.35})$$

ψ_0 is non-zero only when its argument is a reciprocal lattice vector. Suppose that for a given $\vec{S}$ and $\vec{a}$, $\vec{S} + \vec{a} + \vec{b} = \vec{\tau}$, where $\vec{a}$ and $\vec{b}$ are vectors in the first Brillouin zone. For each term in the brackets pick out that value of $\vec{q}$ in the sum over $\vec{q}$ for which the argument is of the form $\vec{S} + \vec{a} + \vec{q}'$. Then sum over $\vec{q}'$.

$$\psi_0(\vec{S} + \vec{q} + \vec{q}') = \psi_0(\vec{S} + \vec{a} + \vec{q}') \neq 0 \quad \text{for } \vec{q} = \vec{a} \text{ only when } \vec{q}' = \vec{b}.$$

$$\psi_0(\vec{S} + \vec{q} - \vec{q}') = \psi_0(\vec{S} + \vec{a} - \vec{q}') \neq 0 \quad \text{for } \vec{q} = \vec{a} \text{ only when } \vec{q}' = -\vec{b}.$$

$$\psi_0(\vec{S}-\vec{q}+\vec{q}') = \psi_0(\vec{S}+\vec{a}+\vec{q}') \neq 0 \quad \text{for } \vec{q} = -\vec{a} \text{ only when } \vec{q}' = \vec{b}.$$

$$\psi_0(\vec{S}-\vec{q}-\vec{q}') = \psi_0(\vec{S}+\vec{a}-\vec{q}') \neq 0 \quad \text{for } \vec{q} = -\vec{a} \text{ only when } \vec{q}' = -\vec{b}.$$

Since $G_{\vec{q}j} = G_{-\vec{q}j}$, each term is going to give the same contribution when the appropriate $\vec{q}$ is chosen and the sum over $\vec{q}'$ is carried out. Thus, the four terms in the brackets can be reduced to one of the form $4\psi_0(\vec{S}+\vec{q}+\vec{q}')$.

$$I_2(\vec{S}) = \frac{1}{2} f^2 e^{-2M} \sum_{\vec{q}jj'} G_{\vec{q}j} G_{\vec{q}'j'} \psi_0(\vec{S}+\vec{q}+\vec{q}') \quad (\text{A.36})$$

$$\text{where } \vec{S}+\vec{q}+\vec{q}' = \vec{r}$$

But, again, it is the integrated intensity which is of interest.

$$\int \psi_0(\vec{S}) dV_S = 8\pi^3 \frac{V}{V_c} = 8\pi^3 \frac{N}{V_c} \quad (\text{A.31})$$

$$I_2(\vec{S}) = \frac{1}{2} \frac{8\pi^3 N}{V_c} f^2 e^{-2M} \sum_{\vec{q}jj'} G_{\vec{q}j} G_{\vec{q}'j'} \quad (\text{A.37})$$

$$\vec{q}' = \vec{r} - \vec{S} - \vec{q}$$

If the reciprocal volume element is ΔW , there are $\frac{V_0}{8\pi^3} \Delta W$ points in ΔW upon which the double scattering process can start.

$$I_2(\vec{S}) = \frac{1}{2} (\Delta W) N K f^2 e^{-2M} \sum_{\vec{q}jj'} G_{\vec{q}j} G_{\vec{q}'j'} \quad (\text{A.38})$$

$$\vec{q}' = \vec{r} - \vec{S} - \vec{q}$$

The sum over $\vec{q}$ is now replaced by an integral over $\vec{q}$. The integral is over all values of $\vec{q}$ lying in the intersections of a first Brillouin zone surrounding $\vec{S}$ with first zones surrounding reciprocal lattice points. Each

$\vec{q}$ value connected with $\vec{S}$ lies in one such intersection region only. Rewrite (A.38) to include the different $\vec{r}$.

$$I_2(\vec{S}) = \frac{1}{2} (\Delta W) N K f^2 e^{-2M} \sum_{\vec{r}} \sum_{\vec{q}, \vec{q}'} [G_{\vec{q}, j} G_{\vec{q}', j'}] \vec{S} + \vec{q} + \vec{q}' = \vec{r} \quad (\text{A.39})$$

$$\sum_{\vec{q}} \rightarrow \frac{V_0}{8\pi^3} dV_{\vec{q}} = \frac{K V_c}{8\pi^3} dV_{\vec{q}} \quad (\text{A.40})$$

$$I_2(\vec{S}) = \frac{(\Delta W)}{16\pi^3} N K^2 V_c f^2 e^{-2M} \sum_{\vec{r}} \int \sum_{\substack{j, j' \\ \text{inter-} \\ \text{sections}}} [G_{\vec{q}, j} G_{\vec{q}', j'}] \vec{q}' = \vec{r} - \vec{S} - \vec{q} dV_{\vec{q}}$$

Per unit volume of reciprocal space, one has

$$I_2(\vec{S}) = \frac{N V_c}{16\pi^3 m^2} f^2 e^{-2M} \sum_{\vec{r}} \int \sum_{\substack{j, j' \\ \text{inter-} \\ \text{sections}}} \frac{(\vec{S} \cdot \vec{e}_{\vec{q}, j})^2 (\vec{S} \cdot \vec{e}_{\vec{q}', j'})^2 \vec{E}_{\vec{q}, j} \vec{E}_{\vec{q}', j'}}{\omega_{\vec{q}, j}^2 \omega_{\vec{q}', j'}^2} dV_{\vec{q}} \quad (\text{A.41})$$

$\vec{q}' = \vec{r} - \vec{S} - \vec{q}$

The expressions for each of the higher order scattering terms progressively become more complicated, and it is necessary to use an approximation for their combined effect. In his first calculation of thermal diffuse scattering from a monatomic solid, Debye⁽²⁰⁾ used equations (A.3) and (A.6), and assumed that the atomic displacements are independent of one another. His result was that

$$I_{TDS}(\vec{S}) = N f^2 (1 - e^{-2M}) = N f^2 e^{-2M} (e^{2M} - 1) \quad (\text{A.42})$$

in electron units. This formula, together with one for Compton scattering, was experimentally verified by Jauncey and others⁽⁴²⁾ for regions in which no TDS maxima occur.

The TDS maxima which do occur are due primarily to the first order scattering, since the first order scattering at any $\vec{S}$ is determined by a specific $\vec{q}$. The maxima in the second order scattering are much less, since at any $\vec{S}$ the second order scattering is due to contributions from many pairs of $\vec{q}$'s. The higher order scattering terms involve contributions from even many more combinations of wave vectors, with the result that the tendency of any single combination to cause a peaking is washed out. Thus, if one can determine that portion of (A.42) which corresponds to third and higher order scattering, then that expression should hold not only in regions of no diffuse maxima, but everywhere. Eldridge⁽¹⁸⁾ has shown that contributions of the various orders of scattering can be obtained by expanding the second exponential in (A.42).

$$I_{\text{1st}}(\vec{S}) = N f^2 e^{-2M} (2M + 2M^2 + \frac{4}{3}M^3 + \dots) \quad (\text{A.43})$$

The power of M indicates the order to which a particular term refers. Thus, for all orders above second one has

$$I_{\text{higher}}(\vec{S}) = N f^2 e^{-2M} (e^{2M} - 1 - 2M - 2M^2) \quad (\text{A.44})$$

Equations (A.34), (A.41), and (A.44) refer to the scattering per unit volume of reciprocal space in electron units. The obtaining of expressions for the measured

intensities requires multiplication by the polarization factor (Appendix C) and the absorption factor (Appendix D), followed by integration over the reciprocal volume element defined by the allowed incoming and outgoing rays. The effect of this integration is discussed in Appendix L. The measured intensities are expected to be of the form

$$I_1(\vec{S}) = \frac{B f^2 e^{-2M}}{2 \left(\frac{\mu}{\rho}\right) m^2} \left(\frac{1+k \cos^2 2\theta}{1+k} \right) \sum_j \frac{(\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \bar{E}_{\vec{q}_j}}{\omega_{\vec{q}_j}^2} \quad \vec{S} + \vec{q}_j = \vec{\tau} \quad (\text{A.45})$$

$$I_2(\vec{S}) = \frac{B V_c f^2 e^{-2M}}{32 \pi^3 \left(\frac{\mu}{\rho}\right) m^3} \left(\frac{1+k \cos^2 2\theta}{1+k} \right) \sum_{\vec{\tau}} \int \sum_{\substack{j, j' \\ \text{Inter.} \\ \text{Sections}}} \frac{(\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 (\vec{S} \cdot \vec{e}_{\vec{q}'_j})^2 \bar{E}_{\vec{q}_j} \bar{E}_{\vec{q}'_j}}{\omega_{\vec{q}_j}^2 \omega_{\vec{q}'_j}^2} d\Omega_{\vec{q}} \quad \vec{S} + \vec{q}_j + \vec{q}'_j = \vec{\tau} \quad (\text{A.46})$$

$$I_{\text{higher}}(\vec{S}) = \frac{B f^2 e^{-2M}}{2 \left(\frac{\mu}{\rho}\right) m} \left(\frac{1+k \cos^2 2\theta}{1+k} \right) (e^{2M} - 1 - 2M - 2M^2) \quad (\text{A.47})$$

where $\frac{\mu}{\rho}$ is the mass absorption coefficient

m is the atomic mass

B is the constant determined by the apparatus

k is the constant determined by the monochromator crystal.

Appendix B. Compton Scattering for a Monatomic Lattice

The Compton scattering must be accounted for if an accurate calculation of the expected diffuse scattering is to be made. There are two approaches which are available for this calculation.

I. Hartree-Fock Approach. If it is assumed that the incident radiation has a frequency considerably higher than any absorption frequency of the atom, and that the atomic wave function is a Slater determinant of product wave functions, where each member of the product is associated with a particular electron state, then the Compton scattering from a single atom, in electron units, can be shown to be

$$i_c(\vec{s}) = \left(\frac{\nu'}{\nu}\right)^2 \left[Z - \sum_k |f_{kk}|^2 - \sum_{\substack{k \\ k+l}} \sum_l |f_{kl}|^2 + Z d \right] \quad (\text{B.1})$$

where ν' is the frequency of scattered radiation

ν is the frequency of incident radiation

$\frac{\nu'}{\nu}$ is $1 / \left[1 + \frac{2h\lambda}{m_e c} \left(\frac{\sin \theta}{\lambda} \right)^2 \right]$

Z is the atomic number

f_{kk} is $\int \psi_k^* \psi_k e^{i\vec{s} \cdot \vec{r}} d^3r$

f_{kl} is $\int \psi_k^* \psi_l e^{i\vec{s} \cdot \vec{r}} d^3r$

ψ is an individual electron wave function

$\sum_{k,l}$ is taken over all pairs of different electrons

with the same spin

$d = \alpha^2 (1 + \cos 2\theta)^2 / \{ (1 + \cos^2 2\theta) [1 + \alpha(1 + \cos 2\theta)] \}$, $\alpha = h\nu / m_e c^2$

δ is a relativistic correction and is negligible at the x-ray wavelength which is used.

The problem in using (B.1) to calculate $\lambda_c(\vec{s})$ is that one must first know the electron wave functions. Recently Cromer and Mann⁽⁴³⁾ have calculated the Compton scattering for all spherically symmetric free atoms by using Hartree-Fock wave functions determined by Mann.⁽⁴⁴⁾ These calculations do not include the Compton scattering for Pb, although Cromer and Mann indicate that such calculations are forthcoming for aspherical atoms.* The Compton scattering for carbon and oxygen, which is necessary for the calculation of the amorphous scattering, also is not given by Cromer and Mann, but other calculations are readily available.⁽¹⁰⁾

There are two points to make concerning calculations which use (B.1). First, the total intensity of the Compton radiation is taken to be the sum of the intensities scattered by the individual atoms, and such intensities are calculated for free atoms. One would think that for a solid, where the outer electrons are affected by the presence of the other atoms, the total Compton scattering would be different from that obtained by summing the intensities calculated for free atoms. However, measurements

*A private communication from Cromer indicated that these calculations had not yet been made at the time of this writing.

of the Compton scattering^(45,46,47,48,49) have shown good agreement with such calculations. Secondly, it has been assumed in deriving (B.1) that the incident radiation has a frequency considerably higher than the frequency associated with any absorption edge of the atom. When copper radiation is used this is true for oxygen, carbon and hydrogen, which are involved in the amorphous scattering, but it is not true for lead. This apparently is something which has not been corrected for in any Compton calculations to date, but the effect of its neglect will undoubtedly be small for lead, since the Compton scattering turns out to be a very small fraction of the total diffuse scattering from lead.

II. Thomas-Fermi Approach. If calculations involving (B.1) are not available, it is necessary to use an approach in which the Thomas-Fermi atomic model⁽⁵⁰⁾ is used as a basis. In this model the atomic electrons are assumed to comprise a degenerate gas obeying Fermi-Dirac statistics and the Pauli principle, the ground state energy of the atom being the zero-point energy of the gas. Aside from a change of scale, the derived charge density has the same form for all atoms, and can be thought of as an average charge density in which maxima and minima due to different electron groups are smoothed out. In the heavier atoms such as lead the effect of an individual electron group on the charge density will not be so large as with the light

atoms, and it is expected that the average charge density will be a better approximation for the heavier atoms. Using the Thomas-Fermi atomic model, Heisenberg⁽²¹⁾ calculated the Compton scattering from a free atom. In electron units the Compton intensity was found to be

$$I_c(\vec{s}) = Z \left(\frac{v}{v'} \right)^2 S(\vec{s}) \quad (\text{B.2})$$

where
$$S = 1 - \int_0^{\xi_0} \xi^2 d\xi \left\{ \left[\frac{\phi(\xi)}{\xi} \right]^{1/2} - \eta \right\}^2 \left\{ \left[\frac{\phi(\xi)}{\xi} \right]^{1/2} + \frac{1}{2} \eta \right\}$$

$$\xi = rz^{1/3}/a$$

r is the distance measured from the center of the atom

Z is the atomic number

$a = 0.47/Z^{1/3} \text{ \AA} =$ distance characteristic of the atom

$\phi(\xi)$ is the potential at radius r in units of Ze/a

$$\eta = (0.176)(4\pi/\lambda) \sin\theta / Z^{2/3}$$

$$\xi_0 \text{ is determined by } \left[\frac{\phi(\xi_0)}{\xi_0} \right]^{1/2} = \eta$$

Pohler and Hanson⁽⁵¹⁾ most recently have tabulated S as a function of η .

For either (B.1) or (B.2) the scattering from identical atoms is given by

$$I_c(\vec{s}) = N I_c(\vec{s}) \equiv N \left(\frac{v}{v'} \right)^2 J_c(\vec{s}) \quad (\text{B.3})$$

When the polarization factor and the absorption factor are taken into account, and (B.3) is integrated over the

reciprocal volume element, one has

$$I_c(\vec{s}) = \frac{B \left(\frac{1+k \cos^2 2\theta}{1+k} \right)}{\left(\frac{\mu}{\rho} + \frac{\mu'}{\rho} \right) m} I_c(\vec{s}) \quad (B.4)$$

where m is atomic mass

$\frac{\mu}{\rho}$ is the mass absorption coefficient for incoming radiation

$\frac{\mu'}{\rho}$ is the mass absorption coefficient for scattered radiation.

Appendix C. Polarization Factor

In Appendices A and B the expressions for TDS and Compton scattering are given in electron units. This means that a particular scattered intensity is expressed in terms of the classical scattering from a single free electron placed in the position of the sample. It is possible to do this only if the sample is assumed to be ideally mosaic. Let I_e be the power per unit solid angle scattered classically by a free electron when I_0 is the power per unit area in the incident beam.

$$I_e = I_0 r_e^2 \left(\frac{1 + k \cos^2 2\theta}{1 + k} \right) \quad (C.1)$$

where r_e is the classical electron radius

2θ is the scattering angle

k is the ratio of that portion of the incident intensity associated with a polarization parallel to the diffraction plane to that portion of the incident intensity associated with a polarization $\perp$ to the diffraction plane.

The relevant geometry of the experiment is shown in Figure C-1.

Figure C-1. Polarization of Incident Radiation.

If it is assumed that the beam from the source, which strikes the monochromator, is unpolarized, then k depends on the nature of the monochromator crystal. Let $2\theta_m$ be the angle which the beam diffracted by the monochromator makes with the beam from the source. Then

$$k = k_m = \cos^2 2\theta_m \quad (52) \text{ if the monochromator crystal is ideally mosaic}$$

$$k = k_p = |\cos 2\theta_m| \quad (53) \text{ if the monochromator crystal is ideally perfect.}$$

For the lithium fluoride monochromator crystal used in the present work $2\theta = 45^\circ$ so that $k_m = 0.500$ and $k_p = 0.707$.

Workers who have determined dispersion curves from x-ray TDS have used $k = k_m$, but in 1963 Miyahe et al.⁽⁵⁴⁾ showed that the particular lithium fluoride monochromator crystal which they were using had a value for k between k_m and k_p . They considered the crystal to behave as if it were part ideally mosaic and part ideally perfect. More recently Jennings⁽⁵⁵⁾ measured the polarization ratio for his lithium fluoride monochromator by measuring integrated intensities for the (333) reflection from a perfect Ge crystal. He obtained $k = 0.722$, a value which not only is different from k_m , but which even does not fall between k_m and k_p . He explains this in terms of a large secondary extinction effect for a crystal having a small mosaic spread. Thus, it is obvious that k depends on the particular monochromator crystal used, and it is necessary that it be deter-

mined experimentally for each. In the present work k is obtained from the amorphous scattering.

Appendix D. Absorption Corrections

I. Absorption Factor for a Flat Surface. In electron units the expressions for TDS and Compton scattering are of the form

$$I(\vec{s}) = N i(\vec{s}) = \frac{V}{V_c} i(\vec{s}) \equiv V i''(\vec{s}) \quad (D.1)$$

where V is the crystal volume involved in the scattering

V_c is the volume of the primitive cell

N is the number of atoms involved in the scattering

$i(\vec{s})$ is the scattering in electron units per atom

When the scattering by a single electron is included,

(D.1) becomes

$$I(\vec{s}) = I_e r_e^2 \left(\frac{1+k \cos^2 2\theta}{1+k} \right) V i'(\vec{s}) \equiv I_e V i''(\vec{s}) \quad (D.2)$$

To account for absorption in the incident and scattered beams it is necessary to take V to be a crystal volume element at some point below the surface of the crystal, and then to modify (D.2) to include absorption along the incident and scattered paths. The total scattering is found by integrating over the irradiated crystal volume. This has the effect of adding the scattered intensity from different volume elements, which is the same as saying that the crystal is ideally mosaic.

In determining the absorption factor it is assumed that the crystal normal and the crystal symmetry direction do not coincide. It is also assumed that the diffraction vector is separated from the symmetry direction by the angle $\Delta\omega$, as would be the case when transverse modes are investigated. Figure D-1 shows the geometry of the problem. In (b) and (c) the diagrams showing the relationships among the angles are drawn with the crystal normal having a length of unity.

$$dV = \frac{ba}{\sin(\theta + \alpha + \Delta\omega)} dz = \frac{S dz}{\sin(\theta + \alpha + \Delta\omega)} \quad (D.3)$$

where S is the beam cross-section.

$$\begin{aligned} dI &= i''(\vec{s}) I_0 e^{-\mu z / \sin(\theta + \alpha + \Delta\omega)} e^{-\mu z / \sin(\theta - \alpha - \Delta\omega)} \frac{S dz}{\sin(\theta + \alpha + \Delta\omega)} \\ &= \frac{i''(\vec{s}) I_0 S e^{-\mu \left[\frac{1}{\sin(\theta + \alpha + \Delta\omega)} + \frac{1}{\sin(\theta - \alpha - \Delta\omega)} \right] z}}{\sin(\theta + \alpha + \Delta\omega)} dz \end{aligned} \quad (D.4)$$

$$\begin{aligned} I &= \int_0^T dI = \frac{i''(\vec{s}) I_0 S}{\sin(\theta + \alpha + \Delta\omega)} \int_0^T e^{-\mu \left[\frac{1}{\sin(\theta + \alpha + \Delta\omega)} + \frac{1}{\sin(\theta - \alpha - \Delta\omega)} \right] z} dz \\ &= \frac{i''(\vec{s}) I_0 S}{\mu \left[1 + \frac{\sin(\theta + \alpha + \Delta\omega)}{\sin(\theta - \alpha - \Delta\omega)} \right]} \left\{ 1 - e^{-\mu T \left[\frac{1}{\sin(\theta + \alpha + \Delta\omega)} + \frac{1}{\sin(\theta - \alpha - \Delta\omega)} \right]} \right\} \end{aligned} \quad (D.5)$$

where μ is the linear absorption coefficient and T is the crystal thickness. For $T \rightarrow \infty$ or $\mu T \gg 1$,

$$I = \frac{I_0 S}{\mu \left[1 + \frac{\sin(\theta + \alpha + \Delta\omega)}{\sin(\theta - \alpha - \Delta\omega)} \right]} i''(\vec{s}) \quad (D.6)$$

Change (D.6) to a form involving Θ , $\Delta\omega$, $\Delta\phi$, and β .

$$\begin{aligned} \frac{\sin(\Theta + \Delta\omega)}{\sin(\Theta - \Delta\omega)} &= \frac{\sin(\Theta + \Delta\omega) \cos \alpha + \cos(\Theta + \Delta\omega) \sin \alpha}{\sin(\Theta - \Delta\omega) \cos \alpha - \cos(\Theta - \Delta\omega) \sin \alpha} \\ &= \frac{\sin(\Theta + \Delta\omega) + \cos(\Theta + \Delta\omega) \tan \alpha}{\sin(\Theta - \Delta\omega) - \cos(\Theta - \Delta\omega) \tan \alpha} \end{aligned} \quad (D.7)$$

From Figure D-1. (c) it is seen that

$$\tan \alpha = \tan \beta \cos \Delta\phi \quad (D.8)$$

Therefore

$$I = \frac{I_0 S i''(\vec{s})}{\mu \left[1 + \frac{\sin(\Theta + \Delta\omega) + \cos(\Theta + \Delta\omega) \tan \beta \cos \Delta\phi}{\sin(\Theta - \Delta\omega) - \cos(\Theta - \Delta\omega) \tan \beta \cos \Delta\phi} \right]} \quad (D.9)$$

(D.9) should hold for traversals in off-symmetry directions.

However, for symmetry directions, for which $\Delta\omega = 0^\circ$, the sample can be aligned such that $\Delta\phi = 90^\circ$. Then

$$I = \frac{I_0 S i''(\vec{s})}{\mu \left[1 + \frac{\sin(\Theta + \Delta\omega)}{\sin(\Theta - \Delta\omega)} \right]} = \frac{I_0 S i''(\vec{s})}{2\mu} \quad \text{for } \Delta\omega = 0^\circ. \quad (D.10)$$

or

$$I = \frac{I_0 S}{2\mu V_c} r_0^2 \left(\frac{1 + k \cos^2 2\Theta}{1 + k} \right) i(\vec{s}) \quad (D.11)$$

But $\frac{\mu}{\rho}$, the mass absorption coefficient, is the quantity which is usually dealt with instead of μ , the linear absorption coefficient. ρ is the density of the sample.

Since V_c is the volume per atom, $\mu V_c = \left(\frac{\mu}{\rho}\right) \rho V_c = \frac{\mu}{\rho} m$,

where m is the atomic mass.

$$I(\vec{S}) = \frac{I_0 S}{2(\frac{\mu}{\rho})_m} r_0^2 \left(\frac{1+k \cos^2 2\theta}{1+k} \right) i(\vec{S}) \quad (D.12)$$

$I(\vec{S})$ is the scattered energy per unit volume of reciprocal space at the diffraction vector $\vec{S}$.

II. X-Ray Penetration Depth. From equations (D.5) and (D.6) with $\alpha = \Delta\omega = 0$, one has

$$\frac{I_x}{I_\infty} = G_x = 1 - e^{-\frac{2\mu x}{\sin\theta}} \quad (D.13)$$

where I_x is the intensity scattered from a surface layer of depth x

I_∞ is the intensity scattered from all depths.

(D.13) can be rewritten in the form

$$x = \frac{K_x \sin\theta}{2\mu}, \text{ where } K_x = \ln\left(\frac{1}{1-G_x}\right) \quad (D.14)$$

Figure D-2 shows the penetration depth x for lead plotted against 2θ for various values of G_x . Figure D-3 shows x for Pb, Al, Ni, and Cu plotted against 2θ for $G_x = 0.95$. The curves were calculated using $\mu_{Al} = 263 \text{ cm}^{-1}$, $\mu_{Ni} = 878 \text{ cm}^{-1}$, $\mu_{Cu} = 938 \text{ cm}^{-1}$, and $\mu_{Pb} = 2552 \text{ cm}^{-1}$. These numbers probably are not very precise, but they certainly are good enough to allow the different penetration depths to be compared.

μ is determined from the appropriate mass absorption coefficient and density. For example, in the case of lead, $\frac{\mu}{\rho} \approx 232 \text{ cm}^2/\text{g}$ for $\text{CuK}\alpha$ and $\rho = 11 \text{ g/cm}^3$. This gives $\mu_{Pb} = 2552 \text{ cm}^{-1}$.

Figure D-2. Effective Penetration Depths for Lead

Figure D-3. 95% Penetration Depth for Pb, Cu, Ni and Al

III. Effect of Surface Roughness on Absorption Factor.

Since the general problem becomes very complicated, one specific case will be treated in order to get some idea of this effect. Consider there to be incident upon the sample a beam of width "a" perpendicular to the diffraction plane and of width "b" in the diffraction plane. Let the sample surface consist of rows of 90° peaks having slant height h. Assume the rows to be perpendicular to the diffraction plane, and the scattering angle 2θ to be 90° , so that the incident and scattered beams are perpendicular to the sides of the peaks. Let $b = mh$, where m is an integer. Figure D-4 shows the geometry of the problem.

In the n^{th} region at the position (x,z) the absorption length for the incoming beam is z, while the absorption length for the outgoing beam is $nh - x$. Using only that part of the incident beam which strikes the first face, one finds that the intensity scattered from a volume element in region n is

$$dI = i''(\vec{s}) I_0 dV e^{-u(z+nh-x)} = I_0 a i''(\vec{s}) e^{-u(z+nh-x)} dz dx \quad (D.15)$$

$$\Delta I = a I_0 i''(\vec{s}) \left[\int_0^h dz \int_0^h dx e^{-u(z+h-x)} + \int_h^{2h} dz \int_0^h dx e^{-u(z+2h-x)} + \int_{2h}^{3h} dz \int_0^h dx e^{-u(z+3h-x)} + \dots \right]$$

$$= a I_0 i''(\vec{s}) \sum_{n=1}^{\infty} \int_{(n-1)h}^{nh} dz \int_0^h dx e^{-u(z+nh-x)} \quad (D.16)$$

Figure D-4. X-Ray Beam Scattered by 90° Peaks Through $2\theta=90^\circ$

where ΔI is the intensity for a beam of width h just covering one peak.

Let

$$\int_n \equiv \int_{(n-1)h}^{nh} dz \int_0^h dx e^{-u(z+nh-x)} = e^{-nhu} \int_{(n-1)h}^{nh} e^{-uz} dz \int_0^h e^{ux} dx \quad (D.17)$$

$$= -\frac{e^{-nhu}}{u^2} [e^{-nhu} - e^{-(n-1)hu}] [e^{uh} - 1]$$

$$= \frac{1}{u^2} (1 - e^{uh}) [e^{-2nhu} - e^{-(2n-1)uh}]$$

$$\sum_{n=1}^{\infty} \int_n = \frac{1}{u^2} (1 - e^{uh}) \sum_{n=1}^{\infty} [e^{-2nhu} - e^{-(2n-1)uh}] = \frac{1 - e^{uh}}{u^2} \sum_{n=0}^{\infty} (-1)^n e^{-nuh} \quad (D.18)$$

$$= \frac{1 - e^{uh}}{u^2} \left(-\frac{1}{1 + e^{uh}} \right) = \frac{1}{u^2} \left(\frac{e^{uh} - 1}{e^{uh} + 1} \right) \quad (D.19)$$

since the sum is a geometric series.

$$\Delta I = \frac{\alpha I_0 i''(\vec{s})}{u^2} \left(\frac{e^{uh} - 1}{e^{uh} + 1} \right) \quad (D.20)$$

Since the incident beam covers m peaks,

$$\begin{aligned} I &= \frac{\alpha I_0 i''(\vec{s}) mh}{u^2 h} \left(\frac{e^{uh} - 1}{e^{uh} + 1} \right) = \frac{I_0 S i''(\vec{s})}{2u} \left[\frac{2(e^{uh} - 1)}{uh(e^{uh} + 1)} \right] \\ &= \frac{2(e^{uh} - 1)}{uh(e^{uh} + 1)} I_{\text{flat}} \end{aligned} \quad (D.21)$$

where S is the incident beam cross-section and I_{flat} the intensity scattered from a flat surface.

$$\text{Therefore } I/I_{\text{flat}} = \frac{2(e^{uh} - 1)}{uh(e^{uh} + 1)} \quad (D.22)$$

I/I_{flat} is plotted against μh in Figure D-5. It is seen that in this particular case $I < I_{\text{flat}}$ for all values of μh .

$$I/I_{\text{flat}} = \frac{2}{\mu h} \left(\frac{e^{\mu h} - 1}{e^{\mu h} + 1} \right) \approx \frac{1}{1 + \frac{\mu h}{2}} \quad \begin{matrix} \mu h \ll 1 \\ \mu h \rightarrow 0 \end{matrix} \quad (\text{D.23})$$

$$I/I_{\text{flat}} \approx \frac{2}{\mu h} \quad \begin{matrix} \mu h \gg 1 \\ \mu h \rightarrow \infty \end{matrix} \quad (\text{D.24})$$

IV. Absorption Factor for Compton Scattering. The wavelength of the Compton radiation is larger than that of the incident radiation and is a function of the scattering angle 2θ . Since the absorption coefficient is a function of wavelength, it is necessary to account for the effect of this wavelength change on the absorption factor.

$(\Delta\lambda_{\text{Compton}})_{\text{max}} = 0.04852 \text{ \AA}$ and occurs at $2\theta = 180^\circ$. To include this effect the approach of Part I of this appendix is used, but with the linear absorption coefficient for the outgoing path taken to be μ' , where μ' is a function of 2θ . Then, instead of (D.6), one has

$$I = \frac{I_0 S}{\mu + \mu' \frac{\sin(\theta + \alpha + \Delta\omega)}{\sin(\theta - \alpha - \Delta\omega)}} i''(\vec{s}) \quad (\text{D.25})$$

If the sample is oriented such that α and $\Delta\omega$ are zero,

$$I = \frac{I_0 S}{\mu + \mu'} i''(\vec{s}) \quad (\text{D.26})$$

Figure D-5. I/I_{flat} Versus μh

The problem is to determine μ' for lead, and also for C, H, and O, which are components of the amorphous scatterers. A satisfactory expression for the mass absorption coefficient seems to be⁽³⁵⁾

$$\frac{\mu'}{\rho} = C\lambda^3 - D\lambda^4 + \sigma_{K-N} N^2/A \quad (D.27)$$

where C and D are functions of Z and change abruptly at an absorption edge

σ_{K-N} is the Klein-Nishina expression for the free electron scattering cross-section

N is Avogadro's number

Z is the atomic number

A is the atomic weight in atomic units (oxygen scale).

For wavelengths close to CuK_α radiation $N\sigma_{K-N}$ takes the form

$$N\sigma_{K-N} = (0.010)\lambda + .376 \quad (D.28)$$

Thus,
$$\frac{\mu'}{\rho} = C\lambda^3 - D\lambda^4 + [(0.010)\lambda + .376]^2/A \quad (D.29)$$

The values of C and D in the same wavelength region are given in the Table D-1 for H, C, O, and Pb.

Element($\frac{Z}{A}$)	C	D
H (.9921)	0.0127	0.466×10^{-5}
C (.4995)	1.22	0.0142
O (.5000)	3.18	0.0654
Pb(.3957)	91.4	20.0

Table D-1. C and D values for mass absorption coefficient expression. The wavelength is assumed to be near CuK_α .

The wavelength in $\text{\AA}$ for Compton scattering at a scattering angle 2θ is given by the usual expression⁽⁵⁶⁾

$$\lambda = \lambda_{\text{CuK}_\alpha} + (0.02426) (1 - \cos 2\theta) \quad (\text{D.30})$$

Appendix E. Atomic Scattering Factors and Dispersion Corrections

Atomic scattering factors computed from various atomic models now are available for all neutral atoms and many ions. In any calculation involving a scattering factor one has the problem of deciding which of the available scattering factors to use. Cromer⁽³⁰⁾ has compared scattering factors from four different atomic models, and comes to the conclusion that for the lighter elements up to Rb^+ the scattering factors given in the International Tables for X-Ray Crystallography⁽⁵⁷⁾ are probably the best. Most of these have been calculated from Hartree-Fock wave functions. Relativistic effects are not included, but for these lighter elements they have no appreciable effect. For elements heavier than Rb^+ Cromer finds that relativistic effects become important, and he suggests that scattering factors calculated from Dirac-Slater wave functions⁽³¹⁾ be used. These wave functions include relativistic and exchange effects, since they have been calculated by a self-consistent field approach using the Dirac equations with Slater's⁽⁵⁸⁾ approximate exchange correction. In the article which gives the Dirac-Slater scattering factors, Cromer and Waber⁽³¹⁾ list not only scattering factors, but also the coefficients

a_i , b_i , and c which fit the function

$$f_o\left(\frac{\sin \theta}{\lambda}\right) = \sum_{i=1}^4 a_i e^{-b_i (\sin \theta / \lambda)^2} + c$$

(E.1)

The coefficients are compiled for all of the Dirac-Slater scattering factors, and this function is very convenient to use in calculations requiring a computer.

Since lead is heavier than Rb^+ , the Dirac-Slater scattering factors are used. The appropriate coefficients are the following:

$$\begin{array}{lll} a_1 = 34.6835 & b_1 = 0.7510 & c = 13.8110 \\ a_2 = 15.6672 & b_2 = 3.8461 & \\ a_3 = 13.2207 & b_3 = 11.2247 & \\ a_4 = 4.5820 & b_4 = 49.8236 & \end{array}$$

The H, C, and O scattering factors, which are used in calculating amorphous scattering, are taken from the International Tables for X-Ray Crystallography.⁽⁵⁷⁾

The scattering factor calculations are made under the assumption that the energy of the incident radiation is much larger than that associated with the K absorption edge. This holds for H, C, and O, but it does not hold for lead when CuK_α radiation is used. In fact, CuK_α radiation falls not only below the K edge, but also the LI, LII, and LIII, edges. Using the Dirac-Slater wave functions, Cromer⁽³²⁾ has calculated dispersion corrections to the scattering factors for elements 10 through 98 for five different x-ray wavelengths, including CuK_α . If f_0 is the scattering factor given by (E.1), and $\Delta f'$ and $\Delta f''$ are the real and imaginary components of the anomalous dispersion, the total scattering factor, f ,

is given by

$$f = f_0 + \Delta f' + i \Delta f'' \quad (\text{E.2})$$

$\Delta f'$ and $\Delta f''$ are functions of $\sin \theta / \lambda$, but the variation is so small that it is usually neglected, as is the case here. For lead and CuK_α radiation Cromer finds that

$$\Delta f' = -4.64, \quad \Delta f'' = 1.83 \quad (\text{E.3})$$

Appendix F. Debye-Waller Factor

The Debye-Waller factor is of the form e^{-2M} , and it is shown in Appendix A that

$$2M = 16\pi^2 (\sin\theta/\lambda)^2 \bar{u}^2(\vec{s}) \quad (F.1)$$

$\bar{u}^2(\vec{s})$ is the mean square displacement of an atom in the direction of $\vec{s}$, the diffraction vector. Under the assumption that $\bar{u}^2(\vec{s})$ is independent of direction (F.1) is usually written in the form

$$2M = 2B(T) \left(\frac{\sin\theta}{\lambda} \right)^2 \quad (F.2)$$

If one uses the Debye approximation, in which the frequency of vibration is assumed to be a linear function of wave vector,

$$B(T) = \frac{6h^2T}{mk\Theta^2} \left[\phi(x) + \frac{x}{4} \right] \quad (F.3)$$

where Θ is the x-ray Debye temperature

$$x = \Theta/T$$

and $\phi(x) + x/4$ is the function shown in Figure F-1.

The vibrational spectrum of a crystal is not a Debye spectrum, and this deviation is accounted for by allowing Θ to have a temperature dependence. Thus, it is important for the researcher to know the Θ value for the particular temperature at which he is working. For the present work this is Θ_R , the room temperature value. Alexopoulos et al.⁽³⁴⁾ have measured $\Theta(T)$ for

lead in the range 100-500°K by measuring integrated intensities of several reflections as a function of temperature. This work seems to be the most complete to date, and it gives good agreement with previous work by Chipman.⁽⁵⁹⁾ The result is

$$\Theta_R = 85^\circ \pm 6^\circ \text{K} \quad (\text{F.4})$$

Let $\Theta_{R+} = 91^\circ \text{K}$, $\Theta_R = 85^\circ \text{K}$, $\Theta_{R-} = 79^\circ \text{K}$. With $T_R = 295^\circ \text{K}$ and using Figure F-1 to determine $\phi(\omega) + \frac{\kappa}{4}$ for each temperature, one finds

$$\begin{aligned} B_{R+} &= 1.98 \text{ \AA}^2 \\ B_R &= 2.27 \text{ \AA}^2 \\ B_{R-} &= 2.63 \text{ \AA}^2 \end{aligned} \quad (\text{F.5})$$

Thus

$$\begin{aligned} e^{-2M_{R+}} &= e^{-3.96(\sin\theta/\lambda)^2} \\ e^{-2M_R} &= e^{-4.54(\sin\theta/\lambda)^2} \\ e^{-2M_{R-}} &= e^{-5.26(\sin\theta/\lambda)^2} \end{aligned} \quad (\text{F.6})$$

This is an appreciable spread, but only e^{-2M_R} is used in the calculations. The use of e^{-2M_R} is given further backing by the recent work of Grimvall and Grimvall.⁽⁶⁰⁾ Using the lead frequency spectrum determined by Stedman et al.⁽³⁶⁾ they have calculated the room temperature Debye temperature to be 84°K.

Figure F-1. $\phi(x) + \frac{x}{4}$ Versus x

Appendix G. Amorphous Scattering and Absolute Intensity Measurements

In order to determine the absolute intensity of radiation scattered from the lead sample, it is necessary to measure high angle scattering from an amorphous material. Scattering from amorphous materials typically consists of a few broad low angle peaks followed by an intensity which changes very slowly with increasing angle. The scattering from lucite, as shown in Figure G-1, displays this form, and it was chosen as the primary amorphous standard.

Lucite is an amorphous material which is made up of large molecules, so the coherent and Compton scattering from molecules instead of single atoms must be considered. The large low angle peaks in amorphous scattering are due in part to intermolecular interference, but at high angles this becomes negligible, and not only do the molecules scatter independently, but the atoms within a molecule scatter independently.⁽⁶¹⁾ At high angles the unmodified scattering in electron units per molecule is

$$I_M(\vec{s}) = \sum_p n_p f_p^2 \quad (G.1)$$

where n_p is the number of atoms of the p^{th} kind in the molecule, and the sum is over the different kinds of atoms in the molecule.

In a similar manner the total Compton scattering from a molecule is the sum of the scattering by each of the atoms in the molecule.

$$I_{CM} = \sum_p n_p I_{cp} = \left(\frac{v'}{v}\right)^2 \sum_p n_p I_{cp} \quad (G.2)$$

where I_{cp} is the Compton scattering in electron units for the p^{th} kind of atom.

When absorption is accounted for and the scattering by a single free electron is included, one has from (D.11) and (D.26)

$$I(\vec{s}) = \frac{I_0 S}{2\mu V_c} r_0^2 \left(\frac{1+k \cos^2 2\theta}{1+k} \right) \sum_p n_p f_p^2 \quad (G.3)$$

$$I_c(\vec{s}) = \frac{I_0 S}{(\mu + \mu') V_c} r_0^2 \left(\frac{1+k \cos^2 2\theta}{1+k} \right) \left(\frac{v'}{v}\right)^2 \sum_p n_p I_{cp} \quad (G.4)$$

where V_c is the molecular volume and μ and μ' are the linear absorption coefficients for the unmodified and modified radiation, respectively. To express (G.3) and (G.4) in terms of the mass absorption coefficients note that

$$\mu V_c = \left(\frac{\mu}{\rho}\right) \rho V_c = \frac{\mu}{\rho} m_{\text{mol.}} \quad (G.5)$$

where $m_{\text{mol.}}$ is the molecular mass. Thus

$$I_{\text{tot}} = I + I_c = I_0 S r_0^2 \left(\frac{1+k \cos^2 2\theta}{1+k} \right) \left[\frac{\sum_p n_p f_p^2}{2\left(\frac{\mu}{\rho}\right) m_{\text{mol.}}} + \frac{\left(\frac{v'}{v}\right)^2 \sum_p n_p I_{cp}}{\left(\frac{\mu}{\rho} + \frac{\mu'}{\rho}\right) m_{\text{mol.}}} \right]$$

(G.6)

When (G.6) is integrated over the reciprocal volume element, as is shown in Appendix L the result is

$$I_{\text{meas}} = B \left(\frac{1 + k \cos^2 2\theta}{1 + k} \right) \left[\frac{\sum_p n_p f_p^2}{2 \left(\frac{\mu}{\rho} \right) m_{\text{mol.}}} + \frac{\left(\frac{v'}{v} \right)^2 \sum_p n_p d_{cp}}{\left(\frac{\mu}{\rho} + \frac{\mu'}{\rho} \right) m_{\text{mol.}}} \right] \quad (\text{G.7})$$

If $P = \frac{1 + k \cos^2 2\theta}{1 + k}$, the quantity which depends on the amorphous sample used is

$$\frac{I_{\text{meas}}}{BP} = \frac{\sum_p n_p f_p^2}{2 \left(\frac{\mu}{\rho} \right) m_{\text{mol.}}} + \frac{\left(\frac{v'}{v} \right)^2 \sum_p n_p d_{cp}}{\left(\frac{\mu}{\rho} + \frac{\mu'}{\rho} \right) m_{\text{mol.}}} \quad (\text{G.8})$$

$\frac{\mu}{\rho}$ for the material must be determined in terms of the mass absorption coefficients of the atoms which make up the molecule. If a beam of incident intensity I_0 passes through a distance x in the material

$$\frac{I_x}{I_0} = e^{-\mu x} = e^{-(\mu_1 + \mu_2 + \dots)x} \quad (\text{G.9})$$

where μ_1 , μ_2 , --- are the contributions to the total linear absorption coefficient from the different atoms comprising the material.

$$\frac{I_x}{I_0} = e^{-\left(\frac{\mu_1}{\rho_1} \rho_1 + \frac{\mu_2}{\rho_2} \rho_2 + \dots \right) x} \equiv e^{-\left(\frac{\mu}{\rho} \right) \rho x} \quad (\text{G.10})$$

$$\frac{\mu}{\rho} = \frac{\rho_1}{\rho} \left(\frac{\mu}{\rho} \right)_1 + \frac{\rho_2}{\rho} \left(\frac{\mu}{\rho} \right)_2 + \dots \quad (\text{G.11})$$

or

$$\frac{\mu}{\rho} = w_1 \left(\frac{\mu}{\rho} \right)_1 + w_2 \left(\frac{\mu}{\rho} \right)_2 + \dots \quad (\text{G.12})$$

where W_p is the fractional composition by weight of the p th kind of atom. In a material composed of one kind of molecule

$$W_p = \frac{\text{total mass of the } p^{\text{th}} \text{ kind of element in the molecule}}{\text{mass of molecule}}$$

$$= \frac{n_p m_p}{m_{\text{mol.}}} \quad (\text{G.13})$$

$$\text{Therefore } \left(\frac{u}{p}\right) m_{\text{mol.}} = \sum_p W_p \left(\frac{u}{p}\right)_p m_{\text{mol.}} = \sum_p n_p m_p \left(\frac{u}{p}\right)_p$$

$$\frac{I_{\text{meas}}}{BP} = \frac{\sum_p n_p f_p^2}{2 \sum_p n_p m_p \left(\frac{u}{p}\right)_p} + \frac{\left(\frac{v'}{v}\right)^2 \sum_p n_p u_{cp}}{\sum_p n_p m_p \left[\left(\frac{u}{p}\right)_p + \left(\frac{u'}{p}\right)_p\right]} \quad (\text{G.14})$$

Lucite is polymerized methyl methacrylate. It consists of long chain molecules, where each link in the chain is of the form

The chains can have different lengths, so that lucite really is composed of a mixture of molecules. However, since the case in which the atoms scatter independently is being treated, lucite can be considered to be composed of identical molecules given by (G.15). The relevant formula for one molecule is then $\text{C}_5\text{H}_8\text{O}_2$. For lucite (G.14) becomes

$$\frac{I_{\text{meas}}}{BP} = \frac{1}{2} \frac{5f_C^2 + 8f_H^2 + 2f_O^2}{5m_C(\frac{\mu}{\rho})_C + 8m_H(\frac{\mu}{\rho})_H + 2m_O(\frac{\mu}{\rho})_O} + \left(\frac{v'}{v}\right)^2 \frac{5d_{CC} + 8d_{CH} + 2d_{CO}}{5m_C[(\frac{\mu}{\rho})_C + (\frac{\mu'}{\rho})_C] + 8m_H[(\frac{\mu}{\rho})_H + (\frac{\mu'}{\rho})_H] + 2m_O[(\frac{\mu}{\rho})_O + (\frac{\mu'}{\rho})_O]} \quad (G.16)$$

$\frac{I_{\text{meas}}}{BP}$ can be calculated very easily as a function of 2θ by use of a computer if the 2θ dependence of the scattering factors, the Compton terms, and the mass absorption coefficients are known.

The scattering factors for H, C, and O were taken from the International Tables for X-Ray Crystallography, (57) squared, and plotted against $\sin\theta/\lambda$. The resulting curves were approximated by straight lines in the region $\sin\theta/\lambda = 0.5$ to $\sin\theta/\lambda = 0.6$, which includes the angular interval traversed for the amorphous scattering. With this approach

$$\begin{aligned} f_H^2 &= 0.02 - 0.03 \frac{\sin\theta}{\lambda} \\ f_C^2 &= 5.24 - 4.80 \frac{\sin\theta}{\lambda} \\ f_O^2 &= 13.90 - 16.87 \frac{\sin\theta}{\lambda} \end{aligned} \quad (G.17)$$

No dispersion corrections were applied since the energies of the K absorption edges are well below the photon energy of the CuK_α radiation.

The Compton scattering terms for C and O were also taken from the International Tables for X-Ray Crystallography, (10) and were approximated by a straight line between $\frac{\sin\theta}{\lambda} = 0.5$ and $\frac{\sin\theta}{\lambda} = 0.6$. The result is

$$\begin{aligned}
 \mu_{cc} &= 3.23 + 2.40 \frac{\sin \theta}{\lambda} \\
 \mu_{co} &= 4.12 + 3.44 \frac{\sin \theta}{\lambda} \\
 \mu_{cH} &= 1 - f_H^2 = 0.98 + 0.03 \frac{\sin \theta}{\lambda}
 \end{aligned}
 \tag{G.18}$$

As discussed in Appendix D.IV

$$\begin{aligned}
 \frac{\mu'}{\rho} &= c \lambda^3 - D \lambda^4 + [(0.010) \lambda + .376]^2 / A \\
 \lambda(\text{\AA}) &= \lambda_{CuK\alpha} + 0.02426 (1 - \cos 2\theta)
 \end{aligned}
 \tag{G.19}$$

where the coefficients depend on the element used. For the unmodified radiation (35)

$$\left(\frac{\mu}{\rho}\right)_c = 4.60, \quad \left(\frac{\mu}{\rho}\right)_H = 0.435, \quad \left(\frac{\mu}{\rho}\right)_o = 11.5 \text{ cm}^2/\text{g}
 \tag{G.20}$$

In order to determine BP as a function of scattering angle the calculated values of I_{meas}/BP are compared with measured values of the count rate, I_{meas} . Then

$$BP(2\theta) = \frac{I_{\text{meas}}}{I_{\text{meas}}/BP}
 \tag{G.21}$$

Now

$$BP = B \left(\frac{1+k \cos^2 2\theta}{1+k} \right) = \frac{B}{1+k} + \frac{Bk}{1+k} \cos^2 2\theta
 \tag{G.22}$$

The plot of BP versus $\cos^2 2\theta$ should show data approximating a straight line. A least squares fit to the data then gives $\frac{B}{1+k}$ and $\frac{Bk}{1+k}$, from which the values of B and k can be determined.

The results of the calculation of I_{meas}/BP for lucite over the region of interest are shown in Table G-1. Figure G-2 shows the values of BP versus $\cos^2 2\theta$ which correspond

to lucite data taken with the diffractometer slit system fixed as it was for most of the lead data. The straight line is a least squares fit to the BP data, and its slope and intercept give $B = (2.84 \pm .02) \times 10^{-21} \text{ cm}^2/\text{sec}$, and $k = 0.85 \pm .01$. Some of the earliest lead data was obtained with a slightly larger horizontal divergence exit slit, and the appropriate B and k values were $B = (3.99 \pm .02) \times 10^{-21} \text{ cm}^2/\text{sec}$ and $k = 0.86 \pm .01$.

2θ	$\cos^2 2\theta$	$\frac{I_{\text{meas}}}{BP} (\text{cm}^{-2})$	2θ	$\cos^2 2\theta$	$\frac{I_{\text{meas}}}{BP} (\text{cm}^{-2})$
119.46	.24188	28.707×10^{21}	128.07	.38023	28.167×10^{21}
119.73	.24593	28.687	128.34	.38481	28.151
120.01	.25015	28.673	128.62	.38957	28.136
120.29	.25440	28.654	128.90	.39434	28.116
120.57	.25867	28.634	129.18	.39912	28.101
120.84	.26280	28.616	129.46	.40391	28.082
121.12	.26712	28.598	129.73	.40854	28.069
121.40	.27145	28.580	130.01	.41335	28.052
121.68	.27581	28.561	130.29	.41817	28.037
121.96	.28019	28.545	130.57	.42299	28.022
122.23	.28443	28.527	130.85	.42782	28.006
122.51	.28885	28.507	131.12	.43249	27.992
122.79	.29329	28.490	131.40	.43733	27.974
123.07	.29775	28.471	131.68	.44219	27.961
123.34	.30207	28.453	131.96	.44704	27.947
123.62	.30657	28.437	132.23	.45173	27.928
123.90	.31108	28.422	132.51	.45660	27.914
124.18	.31561	28.403	132.79	.46147	27.899
124.46	.32017	28.384	133.07	.46634	27.883
124.73	.32457	28.369	133.35	.47122	27.868
125.01	.32915	28.353	133.62	.47592	27.853
125.29	.33376	28.335	133.90	.48081	27.840
125.57	.33837	28.318	134.18	.48569	27.824
125.84	.34284	28.300	134.46	.49058	27.811
126.12	.34749	28.284	134.73	.49529	27.799
126.40	.35215	28.265	135.01	.50018	27.781
126.68	.35682	28.250	135.29	.50506	27.768
126.96	.36151	28.236	135.57	.50995	27.752
127.23	.36605	28.309	135.85	.51483	27.738
127.51	.37076	28.198	136.12	.51954	27.724×10^{21}
127.79	.37549	28.181×10^{21}			

Table G-1. $\frac{I_{\text{meas}}}{BP}$ for Lucite.

Figure G-2. BP Values Obtained from Lucite Scattering

Appendix H. Second Order TDS in Terms of Interatomic Force Constants

In Appendix A it is shown that the second order TDS, $I_2(\vec{S})$, is given by

$$I_2(\vec{S}) = (\text{const.}) f^2 e^{-2M} \left(\frac{1+k \cos^2 2\theta}{1+k} \right) \sum_{\vec{\tau}} \sum_{\substack{jj' \\ \text{inter-} \\ \text{section}}} \frac{(\vec{S} \cdot \vec{e}_{\vec{q}j})^2 (\vec{S} \cdot \vec{e}_{\vec{q}'j'})^2 \bar{E}_{\vec{q}j} \bar{E}_{\vec{q}'j'}}{\omega_{\vec{q}j}^2 \omega_{\vec{q}'j'}^2} dV_{\vec{q}} \quad (\text{H.1})$$

subject to the condition that $\vec{S} - \vec{q} - \vec{q}' = \vec{\tau}$. For a given reciprocal lattice vector $\vec{\tau}$ the integral is over the intersection region of a first Brillouin zone centered on $\vec{S}$ and one centered on $\vec{\tau}$. It is desired to express (H.1) in terms of interatomic force constants instead of frequencies and polarization vectors. The treatment used is that briefly outlined by Froman.⁽¹⁵⁾

Using the harmonic approximation, Ziman⁽⁶²⁾ shows that for a lattice with one atom per unit cell

$$\sum_{\beta=1}^3 (D_{\alpha\beta}(\vec{q}) - \delta_{\alpha\beta} \omega_{\vec{q}}^2) e_{\vec{q}\beta} = 0 \quad \text{for } \alpha = 1, 2, 3. \quad (\text{H.2})$$

where $e_{\vec{q}\beta}$ is the β^{th} component of the polarization vector associated with the wave vector $\vec{q}$, and

$$D_{\alpha\beta}(\vec{q}) = \frac{1}{m} \sum_{\vec{h}} \left(\frac{\partial^2 V}{\partial n_{\vec{r}\alpha} \partial n_{\vec{r}+\vec{h}\beta}} \right)_{\text{equil.}} \cos(\vec{q} \cdot \vec{h}) \quad (\text{H.3})$$

m is the atomic mass, $n_{\vec{r}\alpha}$ is the α component of the displacement from its equilibrium position of the atom whose equilibrium position is defined by $\vec{l}$, $\vec{h} = \vec{l} - \vec{l}'$, and V is the lattice potential energy. $\partial^2 V / \partial n_{\vec{r}\alpha} \partial n_{\vec{r}+\vec{h}\beta}$ is identified as

the interatomic force constant which represents the force on the atom at $\vec{l}$ in the direction α when the atom at $\vec{l}'$ is displaced a unit distance in the direction β .

Now $|D_{\alpha\beta}(\vec{q}) - \delta_{\alpha\beta} \omega_{\vec{q}j}^2| = 0$ determines the three eigenvalues $\omega_{\vec{q}j}^2$, $j = 1, 2, 3$. (H.2) is then used to determine the eigenvectors $\vec{e}_{\vec{q}j}$, for which the orthogonality relation is $\vec{e}_{\vec{q}j} \cdot \vec{e}_{\vec{q}j'} = \delta_{jj'}$. Then (H.2) is of the form

$$\sum_{\beta=1}^3 (D_{\alpha\beta}(\vec{q}) - \delta_{\alpha\beta} \omega_{\vec{q}j}^2) e_{\vec{q}j\beta} = 0, \quad \alpha = 1, 2, 3; j = 1, 2, 3 \quad (\text{H.4})$$

If in (H.1) it is assumed that τ is high enough so that $\bar{E}_{\vec{q}j} = kT$ for each vibrational mode, and $\vec{S}$ is replaced by $|\vec{S}| \hat{S}$,

$$\sum_{\vec{q}} \rightarrow |\vec{S}|^4 (kT)^2 \sum_{\vec{q}} \int_{\text{Inter-section}} \sum_{jj'} \frac{(\hat{S} \cdot \vec{e}_{\vec{q}j})^2 (\hat{S} \cdot \vec{e}_{\vec{q}j'})^2}{\omega_{\vec{q}j}^2 \omega_{\vec{q}j'}^2} dv_{\vec{q}} \quad (\text{H.5})$$

$\vec{S} - \vec{q} - \vec{q}' = \vec{\tau}$

The integral of interest, which will be designated by $\int$, is

$$\int = \sum_{\vec{q}} \int_{\text{Inter-section}} \sum_{jj'} \frac{(\hat{S} \cdot \vec{e}_{\vec{q}j})^2 (\hat{S} \cdot \vec{e}_{\vec{q}j'})^2}{\omega_{\vec{q}j}^2 \omega_{\vec{q}j'}^2} dv_{\vec{q}} \quad (\text{H.6})$$

$\vec{S} - \vec{q} - \vec{q}' = \vec{\tau}$

To find (H.6) in terms of force constants, it is necessary to solve for $\sum_j \frac{(\hat{S} \cdot \vec{e}_{\vec{q}j})^2}{\omega_{\vec{q}j}^2}$ in terms of the constants.

$$\sum_j \frac{(\hat{S} \cdot \vec{e}_{\vec{q}j})^2}{\omega_{\vec{q}j}^2} = \sum_j \frac{\sum_{\alpha} (\hat{S}_{\alpha} e_{\vec{q}j\alpha}) \sum_{\beta} (\hat{S}_{\beta} e_{\vec{q}j\beta})}{\omega_{\vec{q}j}^2} = \sum_{\alpha} \sum_{\beta} \hat{S}_{\alpha} \hat{S}_{\beta} \sum_j \frac{e_{\vec{q}j\alpha} e_{\vec{q}j\beta}}{\omega_{\vec{q}j}^2} \quad (\text{H.7})$$

$$\text{From (H.4)} \quad \sum_{\beta=1}^3 \frac{D_{\alpha\beta}(\vec{q}) e_{\vec{q}j\beta}}{\omega_{\vec{q}j}^2} = e_{\vec{q}j\alpha}, \quad \alpha = 1, 2, 3; j = 1, 2, 3 \quad (\text{H.8})$$

Multiply (H.8) by $e_{\vec{q}j\alpha}$ and sum over j .

$$\sum_{\beta=1}^3 D_{\gamma\beta}(\vec{q}) \sum_{j=1}^3 \frac{e_{\vec{q}j\alpha} e_{\vec{q}j\beta}}{\omega_{\vec{q}j}^2} = \sum_{j=1}^3 e_{\vec{q}j\alpha} e_{\vec{q}j\gamma} \quad \gamma=1,2,3 \quad (\text{H.9})$$

(H.9) provides three sets of equations, with each set containing three equations in three unknowns. The unknowns are just the quantities $\sum_j \frac{e_{\vec{q}j\alpha} e_{\vec{q}j\beta}}{\omega_{\vec{q}j}^2}$ which are to be found.

As stated above, an orthogonality condition is

$$\sum_{\alpha=1}^3 e_{\vec{q}j\alpha} e_{\vec{q}j'\alpha} = \delta_{jj'} \quad (\text{H.10})$$

One can show a second orthogonality condition to be

$$\sum_{j=1}^3 e_{\vec{q}j\alpha} e_{\vec{q}j\gamma} = \delta_{\alpha\gamma} \quad (\text{H.11})$$

Thus (H.9) becomes

$$\sum_{\beta=1}^3 D_{\gamma\beta}(\vec{q}) \sum_{j=1}^3 \frac{e_{\vec{q}j\alpha} e_{\vec{q}j\beta}}{\omega_{\vec{q}j}^2} = \delta_{\alpha\gamma} \quad (\text{H.12})$$

By Kramer's rule one has

$$\sum_{j=1}^3 \frac{e_{\vec{q}j\alpha} e_{\vec{q}j\beta}}{\omega_{\vec{q}j}^2} = \frac{\Delta_{\alpha\beta}(\vec{q})}{\Delta(\vec{q})} \quad (\text{H.13})$$

where

$$\Delta(\vec{q}) = \det(D_{\gamma\beta})$$

$$\Delta_{\alpha\beta}(\vec{q}) = \det(D_{\gamma\beta}) \text{ with the } \beta \text{ column replaced by } \begin{pmatrix} \delta_{\alpha 1} \\ \delta_{\alpha 2} \\ \delta_{\alpha 3} \end{pmatrix}.$$

Thus $\Delta_{\alpha\beta}(\vec{q}) =$ cofactor associated with the element $D_{\alpha\beta}$
 $= (-1)^{\alpha+\beta}$ (minor of $D_{\alpha\beta}$).

From (H.6), (H.7), and (H.13)

$$\int = \sum_{\vec{q}} \int_{\text{inter-section}} \left[\sum_{\alpha} \sum_{\beta} \hat{S}_{\alpha} \hat{S}_{\beta} \frac{\Delta_{\alpha\beta}(\vec{q})}{\Delta(\vec{q})} \right] \left[\sum_{\alpha'} \sum_{\beta'} \hat{S}_{\alpha'} \hat{S}_{\beta'} \frac{\Delta_{\alpha'\beta'}(\vec{q}')}{\Delta(\vec{q}')} \right] dV_{\vec{q}}$$

$$\int = \sum_{\vec{\tau}} \int_{\text{inter-section}} \left[\frac{(\hat{s}) (\Delta_{\alpha\beta}(\vec{q})) (\hat{s})}{\Delta(\vec{q})} \right] \left[\frac{(\hat{s}) (\Delta_{\alpha\beta}(\vec{q}')) (\hat{s})}{\Delta(\vec{q}')} \right] d\vec{v}_{\vec{q}} \quad (\text{H.14})$$

$$\vec{s} - \vec{q} - \vec{q}' = \vec{\tau}$$

The intersection regions in (H.14) add to give the first Brillouin zone. It is desirable to replace $\sum_{\vec{\tau}} \int_{\text{intersection}}$ by an integral over the first zone.

$$\frac{\Delta_{\alpha\beta}(\vec{q}')}{\Delta(\vec{q}')} = \frac{\Delta_{\alpha\beta}(\vec{s} - \vec{q} - \vec{\tau})}{\Delta(\vec{s} - \vec{q} - \vec{\tau})} = \frac{\Delta_{\alpha\beta}(\vec{s} - \vec{q})}{\Delta(\vec{s} - \vec{q})}$$

since the elements of these determinants, which are of the form given in (H.3), are periodic in reciprocal space. Thus, for each different $\vec{\tau}$ in the sum over $\vec{\tau}$ in (H.14) $\Delta_{\alpha\beta}(\vec{s} - \vec{q} - \vec{\tau}) / \Delta(\vec{s} - \vec{q} - \vec{\tau})$ is replaced by $\Delta_{\alpha\beta}(\vec{s} - \vec{q}) / \Delta(\vec{s} - \vec{q})$, and the $\sum_{\vec{\tau}} \int_{\text{intersection}}$ becomes an integral over the first Brillouin zone. From (H.1), (H.5), and (H.6)

$$I_2(\vec{s}) = (\text{const.}) f^2 e^{-2M} \left(\frac{1 + k \cos^2 2\theta}{1 + k} \right) |\vec{s}|^4 (kT)^2$$

$$\times \int_{\text{1st Zone}} \left[\frac{(\hat{s}) (\Delta_{\alpha\beta}(\vec{q})) (\hat{s})}{\Delta(\vec{q})} \right] \left[\frac{(\hat{s}) (\Delta_{\alpha\beta}(\vec{s} - \vec{q})) (\hat{s})}{\Delta(\vec{s} - \vec{q})} \right] d\vec{v}_{\vec{q}} \quad (\text{H.15})$$

where $\Delta(\vec{q}) = \det(D_{\alpha\beta}(\vec{q})) = D_{11} D_{22} D_{33} + 2 D_{12} D_{13} D_{23} - (D_{11} D_{23}^2 + D_{22} D_{13}^2 + D_{33} D_{12}^2)$

$$\Delta_{11}(\vec{q}) = D_{22} D_{33} - D_{23}^2$$

$$\Delta_{22}(\vec{q}) = D_{11} D_{33} - D_{13}^2$$

$$\Delta_{33}(\vec{q}) = D_{11} D_{22} - D_{12}^2$$

$$\Delta_{12}(\vec{q}) = \Delta_{21}(\vec{q}) = -D_{12} D_{33} + D_{13} D_{23}$$

$$\Delta_{13}(\vec{q}) = \Delta_{31}(\vec{q}) = D_{12} D_{23} - D_{13} D_{22}$$

$$\Delta_{23}(\vec{q}) = \Delta_{32}(\vec{q}) = -D_{11} D_{23} + D_{12} D_{13}$$

$$D_{\alpha\beta}(\vec{q}) = \frac{1}{m} \sum_{\vec{h}} \left(\frac{\partial^2 V}{\partial n_{\vec{h}\alpha} \partial n_{\vec{h}\beta}} \right)_{\text{equil.}} \cos(\vec{q} \cdot \vec{h})$$

and the integral is over the first zone, which is defined by the planes $q_1 = \pm \frac{2\pi}{a}$, $q_2 = \pm \frac{2\pi}{a}$, $q_3 = \pm \frac{2\pi}{a}$, and $|q_1| + |q_2| + |q_3| = \frac{3\pi}{a}$.

$I_2(\vec{S})$ depends on $\hat{S}$, the unit vector in the direction of the diffraction vector, and on $D_{\alpha\beta}(\vec{q})$. From (H.3)

$$D_{\alpha\beta}(\vec{q}) = \frac{1}{m} \sum_{\vec{h}} \Phi_{\alpha\beta}(\vec{h}) \cos(\vec{q} \cdot \vec{h}) \quad (\text{H.16})$$

where the $\Phi_{\alpha\beta}$ now represent the force constants. In (H.16) the $\sum_{\vec{h}}$ contains the term $\vec{h}=0$. To eliminate this term consider the force in the α direction on the atom at the origin due to a displacement of the atom at $\vec{h}$.

$$F_{\alpha} = - \sum_{\beta} \Phi_{\alpha\beta}(\vec{h}) u_{\beta}(\vec{h}) \quad (\text{H.17})$$

For displacements of all atoms

$$F_{\alpha} = - \sum_{\beta} \sum_{\vec{h}} \Phi_{\alpha\beta}(\vec{h}) u_{\beta}(\vec{h}) \quad (\text{H.18})$$

In a translation of the lattice as a whole u_{β} is independent of $\vec{h}$. It is just the β component of the lattice translation, and $F_{\alpha} = 0$ since the entire lattice is displaced.

$$0 = \sum_{\beta} u_{\beta} \sum_{\vec{h}} \Phi_{\alpha\beta}(\vec{h}) \Rightarrow \sum_{\vec{h}} \Phi_{\alpha\beta}(\vec{h}) = 0$$

since u_{β} is arbitrary.

$$\text{Therefore } \Phi_{\alpha\beta}(0) = - \sum_{\vec{h} \neq 0} \Phi_{\alpha\beta}(\vec{h}) \quad (\text{H.19})$$

and
$$D_{\alpha\beta}(\vec{q}) = \frac{1}{m} \sum_{\vec{h} \neq 0} \Phi_{\alpha\beta}(\vec{h}) [\cos(\vec{q} \cdot \vec{h}) - 1] \quad (\text{H.20})$$

Thus, $D_{\alpha\beta}(\vec{q})$ can be determined by summing over all atomic positions outside the atom at the origin. Note that the $D_{\alpha\beta}$ are the components of a symmetric matrix since $\Phi_{\alpha\beta} = \Phi_{\beta\alpha}$. The $\sum_{\vec{h}}$ is usually carried out over shells of atoms around the origin, with each atom in a given shell located at a point demanded by the symmetry of the lattice. For a cubic material consider the atom at the lattice point $\vec{h}$ with coordinates $h_1 \frac{a}{2}, h_2 \frac{a}{2}, h_3 \frac{a}{2}$, where h_1, h_2 , and h_3 are three integers for which $h_1 \geq h_2 \geq h_3 \geq 0$. $(\Phi_{\alpha\beta}(\vec{h}))$ is its force constant matrix, and the matrices of the other atoms in the same shell consist of rearrangements of the same force constants. Thus, with a given shell of atoms one can associate at most six independent force constants. Squires⁽⁶³⁾ gives expressions for $D_{\alpha\beta}(\vec{q})$ in terms of sums over shells of atoms around the origin for fcc and bcc materials. In his notation

$$D_{ii} = \frac{\theta}{m} \sum_S \frac{n^S}{48} \sum_j \alpha_j^S \left[2 - C_{j,i}^S (C_{j+1,i+1}^S C_{j+2,i+2}^S + C_{j+2,i+1}^S C_{j+1,i+2}^S) \right] \quad (\text{H.21})$$

$$D_{i,i+1} = \frac{\theta}{m} \sum_S \frac{n^S}{48} \sum_j \beta_j^S C_{j,i+2}^S \left[S_{j+1,i}^S S_{j+2,i+1}^S + S_{j+2,i}^S S_{j+1,i+1}^S \right] \quad (\text{H.22})$$

where $C_{j,i}^S = \cos \frac{a}{2} h_j^S q_i$

$$S_{j,i}^S = \sin \frac{a}{2} h_j^S q_i$$

n^S is the number of atoms in the shell S

h_j^S refers to the coordinates of the atom in the shell S for which $h_1^S \geq h_2^S \geq h_3^S \geq 0$, where the force constants of this atom are

designated by

$$\phi_{11}(\vec{h}^S) = \alpha_1^S, \phi_{22}(\vec{h}^S) = \alpha_2^S, \phi_{33}(\vec{h}^S) = \alpha_3^S, \phi_{23}(\vec{h}^S) = \beta_1^S, \phi_{13}(\vec{h}^S) = \beta_2^S, \phi_{12}(\vec{h}^S) = \beta_3^S$$

Subscripts of the form $i+1$ and $i+2$, whose values are greater than 3, are to be interpreted as $i-2$ and $i-1$ respectively.

The force constant notation used in the literature can be confusing. The notation $\phi_{\alpha\beta}(\vec{h})$, with which I began, is used by Born and Huang⁽⁶⁴⁾ while Squires⁽⁶³⁾ uses a more restrictive notation of α_j^S and β_j^S to indicate the at most six independent force constants belonging to the shell S. There seems to be in general use a notation in which each independent force constant for a given shell is represented by a different Greek letter, with the shell index being given by a subscript. This is indicated in Table H-1 for eight sets of nearest neighbors.

Atom Representa-
tive of Shell S.

$$h_1^s \geq h_2^s \geq h_3^s \geq 0$$

$\frac{1}{2}a(h_1^s, h_2^s, h_3^s)$	S	$\phi_1(\vec{h}^s)$ α_1^s	$\phi_{22}(\vec{h}^s)$ α_2^s	$\phi_{33}(\vec{h}^s)$ α_3^s	$\phi_{23}(\vec{h}^s)$ β_1^s	$\phi_{13}(\vec{h}^s)$ β_2^s	$\phi_{12}(\vec{h}^s)$ β_3^s	n^s
$\frac{1}{2}a(1,1,0)$	1	α_1	α_1	β_1	0	0	γ	12
$\frac{1}{2}a(2,0,0)$	2	α_2	β_2	β_2	0	0	0	6
$\frac{1}{2}a(2,1,1)$	3	α_3	β_3	β_3	γ_3	δ_3	δ_3	24
$\frac{1}{2}a(2,2,0)$	4	α_4	α_4	β_4	0	0	γ_4	12
$\frac{1}{2}a(3,1,0)$	5	α_5	β_5	γ_5	0	0	δ_5	24
$\frac{1}{2}a(2,2,2)$	6	α_6	α_6	α_6	β_6	β_6	β_6	8
$\frac{1}{2}a(3,2,1)$	7	α_7	β_7	γ_7	δ_7	ϵ_7	ξ_7	48
$\frac{1}{2}a(4,0,0)$	8	α_8	β_8	β_8	0	0	0	6

Table H-1. Force constants for the eight nearest neighbor shells in an fcc lattice.

Gilat⁽¹⁷⁾ has determined the force constants for lead out to eight neighbors by making a least squares fit of the phonon dispersion curves obtained by Brockhouse et al.⁽¹¹⁾ at 100°K by means of slow neutron scattering. The fit is unable to reproduce the Kohn anomalies present in the lead curves, and it has a mean deviation of 4% from the observed frequencies. Table H-2 gives these force constants.

S	Force Const. (dyne/cm)	S	Force Const. (dyne/cm)
1	$\alpha_1 = 3970$ $\beta_1 = -1110$ $\gamma_1 = 4990$	5	$\alpha_5 = -362$ $\beta_5 = -450$ $\gamma_5 = -482$ $\delta_5 = 63$
2	$\alpha_2 = 1540$ $\beta_2 = 387$	6	$\alpha_6 = 2$ $\beta_6 = 4$
3	$\alpha_3 = -126$ $\beta_3 = 13$ $\gamma_3 = 5$ $\delta_3 = -77$	7	$\alpha_7 = -11$ $\beta_7 = 108$ $\gamma_7 = 33$ $\delta_7 = 75$ $\epsilon_7 = -62$ $\xi_7 = 17$
4	$\alpha_4 = 736$ $\beta_4 = 127$ $\gamma_4 = 616$	8	$\alpha_8 = 620$ $\beta_8 = 467$

Table H-2. Lead force constants determined by Gilat. (37)

The force constants of Table H-1, together with equations (H.21) and (H.22) summed over eight nearest neighbors, yield the following expressions for the $D_{\alpha\beta}(\vec{q})$:

$$\begin{aligned}
 \frac{m}{8} D_{\alpha\beta} = & \frac{\alpha_1}{2} \left\{ 2 - C\left(\frac{aq_1}{2}\right) \left[C\left(\frac{aq_2}{2}\right) + C\left(\frac{aq_3}{2}\right) \right] \right\} + \frac{\beta_1}{2} \left[1 - C\left(\frac{aq_2}{2}\right) C\left(\frac{aq_3}{2}\right) \right] \\
 & + \frac{\alpha_2}{2} S^2\left(\frac{aq_1}{2}\right) + \frac{\beta_2}{2} \left[S^2\left(\frac{aq_2}{2}\right) + S^2\left(\frac{aq_3}{2}\right) \right] + \alpha_3 \left[1 - C(aq_1) C\left(\frac{aq_2}{2}\right) C\left(\frac{aq_3}{2}\right) \right] \\
 & + \beta_3 \left\{ 2 - C\left(\frac{aq_1}{2}\right) \left[C(aq_2) C\left(\frac{aq_3}{2}\right) + C\left(\frac{aq_2}{2}\right) C(aq_3) \right] \right\} + \frac{\alpha_4}{2} \left\{ 2 - C(aq_1) \left[C(aq_2) + C(aq_3) \right] \right\} \\
 & + \frac{\beta_4}{2} \left[1 - C(aq_2) C(aq_3) \right] + \frac{\alpha_5}{2} \left\{ 2 - C\left(\frac{3aq_1}{2}\right) \left[C\left(\frac{aq_2}{2}\right) + C\left(\frac{aq_3}{2}\right) \right] \right\} \\
 & + \frac{\beta_5}{2} \left\{ 2 - C\left(\frac{aq_1}{2}\right) \left[C\left(\frac{3aq_2}{2}\right) + C\left(\frac{3aq_3}{2}\right) \right] \right\} + \frac{\gamma_5}{2} \left[2 - C\left(\frac{3aq_2}{2}\right) C\left(\frac{aq_3}{2}\right) - C\left(\frac{aq_2}{2}\right) C\left(\frac{3aq_3}{2}\right) \right] \\
 & + \alpha_6 \left[1 - C(aq_1) C(aq_2) C(aq_3) \right] + \alpha_7 \left\{ 2 - C\left(\frac{3aq_1}{2}\right) \left[C(aq_2) C\left(\frac{aq_3}{2}\right) + C\left(\frac{aq_2}{2}\right) C(aq_3) \right] \right\} \\
 & + \beta_7 \left\{ 2 - C(aq_1) \left[C\left(\frac{aq_2}{2}\right) C\left(\frac{3aq_3}{2}\right) + C\left(\frac{3aq_2}{2}\right) C\left(\frac{aq_3}{2}\right) \right] \right\} \\
 & + \gamma_7 \left\{ 2 - C\left(\frac{aq_1}{2}\right) \left[C\left(\frac{3aq_2}{2}\right) C(aq_3) + C(aq_2) C\left(\frac{3aq_3}{2}\right) \right] \right\} + \frac{\alpha_8}{2} S^2(aq_1) \\
 & + \frac{\beta_8}{2} \left[S^2(aq_2) + S^2(aq_3) \right]
 \end{aligned}
 \tag{H.23}$$

$$\frac{m}{8} D_{22} = \frac{m}{8} D_{11} (q_1 \rightarrow q_2, q_2 \rightarrow q_3, q_3 \rightarrow q_1) \quad (\text{H.24})$$

$$\frac{m}{8} D_{33} = \frac{m}{8} D_{11} (q_1 \rightarrow q_3, q_2 \rightarrow q_1, q_3 \rightarrow q_2) \quad (\text{H.25})$$

$$\begin{aligned} \frac{m}{8} D_{12} = & \frac{\delta_1}{2} S\left(\frac{aq_1}{2}\right) S\left(\frac{aq_2}{2}\right) + \delta_3 C(aq_3) S\left(\frac{aq_1}{2}\right) S\left(\frac{aq_2}{2}\right) + \delta_3 C\left(\frac{aq_3}{2}\right) \left[S(aq_1) S\left(\frac{aq_2}{2}\right) + S\left(\frac{aq_1}{2}\right) S(aq_2) \right] \\ & + \frac{\delta_4}{2} S(aq_1) S(aq_2) + \frac{\delta_5}{2} \left[S\left(\frac{3aq_1}{2}\right) S\left(\frac{aq_2}{2}\right) + S\left(\frac{aq_1}{2}\right) S\left(\frac{3aq_2}{2}\right) \right] + \delta_6 C(aq_3) S(aq_1) S(aq_2) \\ & + \delta_7 C\left(\frac{3aq_3}{2}\right) \left[S(aq_1) S\left(\frac{aq_2}{2}\right) + S\left(\frac{aq_1}{2}\right) S(aq_2) \right] + \delta_7 C(aq_3) \left[S\left(\frac{aq_1}{2}\right) S\left(\frac{3aq_2}{2}\right) + S\left(\frac{3aq_1}{2}\right) S\left(\frac{aq_2}{2}\right) \right] \\ & + \delta_7 C\left(\frac{aq_3}{2}\right) \left[S\left(\frac{3aq_1}{2}\right) S(aq_2) + S(aq_1) S\left(\frac{3aq_2}{2}\right) \right] \end{aligned} \quad (\text{H.26})$$

$$\frac{m}{8} D_{23} = \frac{m}{8} D_{12} (q_1 \rightarrow q_2, q_2 \rightarrow q_3, q_3 \rightarrow q_1) \quad (\text{H.27})$$

$$\frac{m}{8} D_{13} = \frac{m}{8} D_{12} (q_1 \rightarrow q_3, q_2 \rightarrow q_1, q_3 \rightarrow q_2) \quad (\text{H.28})$$

where $C = \cos$ and $S = \sin$.

Equations (H.23) through (H.28) and equation (H.15) give all the expressions necessary for the calculation of $I_2(\vec{s})$ in any direction.

Appendix I. Lead Dispersion Curves at Room Temperature

Since the present work is done at room temperature, a calculation of the expected TDS requires that room temperature lead dispersion curves be used wherever possible. Brockhouse et al.⁽⁶⁵⁾ and Stedman et al.⁽¹²⁾ have investigated the temperature variation of lead dispersion curves. Their results are in good agreement, and since Brockhouse gives more information concerning the room temperature data, it was decided to use his results.

The room temperature data falls below, but is very similar to the 100°K data for which the most measurements were taken. In a later paper Brockhouse et al.⁽¹¹⁾ give the 100°K lead dispersion curves to such a sufficiently greater precision that several Kohn anomalies are observed. No room temperature work is reported in this later work, and although the room temperature data given by Stedman is of greater precision than that given by Brockhouse in the first article, there is not much of it. In order to use room temperature data displaying Kohn anomalies, it was decided to use Brockhouse's more precise data adjusted to room temperature. This is possible because of the type of information given with Brockhouse's less precise data. Each of the dispersion curves along a symmetry direction can be fitted by expressions of the form⁽⁶⁶⁾

$$m\omega^2 = \sum_{n=1}^N \Phi_n [1 - \cos(n\pi q/q_n)] \quad (I.1)$$

where Φ_n is an interplaner force constant

a_n is one-half the distance to the nearest

reciprocal lattice point in the direction of $\vec{q}$

N is the highest number Fourier component allowed

$\Phi_n = 0$ for $n > N$

In his earlier report Brockhouse gives Φ_n values to as large N as is necessary to get a good fit to the [100] and [111] dispersion curves at both 100°K and room temperature. This is also done in the later work, but at 100°K only. The Φ_n 's in the later work are slightly different because the dispersion curves are more precise. These reproduce the general shape of the dispersion curves quite well, but they cannot display small variations such as Kohn anomalies. The general effect of temperature changes on the dispersion curves can be determined by considering the changes in Φ_n with temperature. From (I.1)

$$\Delta v(\vec{q}) = \frac{1}{8\pi^2 m \omega(\vec{q})} \sum_{n=1}^N \Delta \Phi_n \left[1 - \cos\left(\frac{n\pi a_n}{a_m}\right) \right] \quad (\text{I.2})$$

If $\Delta v(\vec{q})$ is calculated for $T = 100^\circ\text{K} \rightarrow T = 296^\circ\text{K}$, and then is applied to the more precise data in Brockhouse's second publication, the room temperature frequencies are determined. This assumes that a Kohn anomaly as a whole shifts in the same way as the entire dispersion curve does as the temperature is increased to room temperature. This appears to be a good assumption when one looks at the room temperature data which Stedman presents. The $\Delta \Phi_n$

for Brockhouse's more precise 100°K data had to be determined from the corresponding $\Delta\phi_n$ associated with his earlier data. This was done by assuming that the fractional change in corresponding ϕ_n would be the same in both cases. Table I-1 gives Brockhouse's 100°K data, and the 100°K data corrected to room temperature by the above procedure. Figure I-1 shows the corresponding dispersion curves, with the error bars indicating typical errors quoted by Brockhouse.

$\frac{\omega}{2\pi}$	[100] T		[100] L		$\frac{\omega}{2\pi}$	[111] T		[111] L	
	100°K	296°K	100°K	296°K		100°K	296°K	100°K	296°K
0.20	0.47	0.43	0.87	0.83	0.143			0.82	0.79
0.30	0.73	0.67	1.27	1.25	0.19	0.35	0.29		
0.40	0.90	0.82	1.61	1.58	0.25			1.24	1.20
0.45	0.96	0.87	1.71	1.66	0.26	0.44	0.39		
0.50	1.04	0.95	1.83	1.76	0.332			1.51	1.48
0.55			1.91	1.83	0.35	0.55	0.50		
0.60	1.115	1.019	2.00	1.92	0.40	0.61	0.55		
0.65			2.07	2.01	0.433			1.76	1.74
0.70	1.10	1.02	2.14	2.10	0.45	0.66	0.58		
0.75			2.16	2.14	0.50	0.73	0.65		
0.80	1.03	0.99	2.15	2.15	0.519			1.91	1.90
0.85			2.14	2.15	0.55	0.77	0.69		
0.90	0.95	0.96	2.05	2.06	0.563			1.97	1.97
0.95			1.94	1.95	0.60	0.79	0.72		
1.00	0.89	0.93	1.86	1.87	0.606			2.00	2.00
					0.649			2.05	2.05
					0.65	0.805	0.746		
					0.693			2.085	2.085
					0.70	0.835	0.780		
					0.736			2.09	2.09
					0.75	0.86	0.80		
					0.779			2.08	2.07
					0.80	0.88	0.81		
					0.823			2.16	2.15
					0.867	0.89	0.82	2.185	2.175

Table I-1. Frequencies (10^{12} /sec) of lattice vibrations in lead at 100°K and 296°K.

Figure 1-1. Lead Dispersion Curves
 + 100°K
 o Corrected to Room Temperature

Appendix J. Calculation of the Diffuse Scattering from Lead for Reciprocal Lattice Directions of Interest

I. Introduction. In this section the manner in which the diffuse scattering is calculated for all directions of interest is displayed by considering the calculation for the region between the (400) and (420) reciprocal lattice points. The calculated values of I/BP are then plotted for all reciprocal lattice directions considered in the experiment, with the various phonon contributions plotted separately. B is the constant determined by the experimental apparatus, and P is the polarization factor.

Consider a zero layer plane in the reciprocal space of lead and determine how the diffraction vector $\vec{S}$ varies as one proceeds from the (400) to the (420) reciprocal lattice point. If the reciprocal lattice is represented by a dimensionless number space, the diffraction vector has a length given by $\frac{2a \sin \theta}{\lambda}$, where a is the lattice constant for lead. This is shown in Figure J-1.

Figure J-1. Zero Layer Plane for Lead Reciprocal Space

As seen from Figure J-1, for a traversal from (400) to (420),

$$\frac{2a \sin \theta}{\lambda} = (16 + n^2)^{1/2} \quad (\text{J.1})$$

$$\text{But } \vec{S} = |\vec{S}| \hat{S} = 4\pi \frac{\sin \theta}{\lambda} \hat{S} = \frac{2\pi}{a} (16 + n^2)^{1/2} \hat{S} \quad (\text{J.2})$$

where $\hat{S}$ is a unit vector in the direction of $\vec{S}$.

In terms of the unit vectors $\hat{i}$, $\hat{j}$, $\hat{k}$ along the 1, 2, and 3 axes (the 3 axis is perpendicular to the plane of the diagram)

$$\hat{S} = \hat{i} \cos \omega + \hat{j} \sin \omega = \frac{1}{\sqrt{16 + n^2}} (4\hat{i} + n\hat{j}) \quad (\text{J.3})$$

$$\vec{S} = \frac{2\pi}{a} (4\hat{i} + n\hat{j}) \quad (\text{J.4})$$

II. First Order TDS. From Appendix A

$$\frac{I_1(\vec{S})}{BP} = \frac{f^2 e^{-2M}}{2(\frac{M}{P}) m^2} \sum_j \frac{(\vec{S} \cdot \vec{e}_{\vec{q}_j})^2 \bar{E}_{\vec{q}_j}}{\omega_{\vec{q}_j}^2} \quad \vec{S} + \vec{q}_j = \vec{T} \quad (\text{J.5})$$

$$\text{where } \bar{E}_{\vec{q}_j} = \left(\frac{1}{e^{\hbar \omega_{\vec{q}_j}/kT} - 1} + \frac{1}{2} \right) \hbar \omega_{\vec{q}_j}$$

In this calculation of $I_{1/BP}$ and all other orders of scattering an absorption factor depending on ω , the angular deviation from the crystal normal, is neglected. The correction for this absorption is applied instead to the experimental data. When (J.4) is substituted into (J.5) and $\omega_{\vec{q}_j} = 2\pi \nu_{\vec{q}_j}$ is used, one gets

$$\frac{I_1(\vec{S})}{BP} = \left[\frac{h}{2(\frac{\mu}{\rho}) m^2 a^2} \right] f^2 e^{-2M} \sum_j \frac{[(4\hat{i} + n\hat{j}) \cdot \vec{e}_{qj}]^2}{v_{qj}} \left(\frac{1}{e^{\frac{h v_{qj}}{kT} - 1}} + \frac{1}{2} \right) \quad (J.6)$$

$\vec{S} + \vec{q} = \vec{\tau}$

Since the traversal from (400) to (420) is along a [100] symmetry direction, the polarization vectors $\vec{e}_{qj}$ lie along the axes 1, 2, and 3. That is,

$$\vec{e}_{q1} = \hat{i}, \quad \vec{e}_{q2} = \hat{j}, \quad \vec{e}_{q3} = \hat{k} \quad (J.7)$$

where $\vec{e}_{q1}$ and $\vec{e}_{q3}$ refer to the transverse(T) mode, and

$\vec{e}_{q2}$ refers to the longitudinal(L) mode. Substituting (J.7) into (J.6), one obtains

$$\frac{I_1(\vec{S})}{BP} = \left[\frac{h}{2(\frac{\mu}{\rho}) m^2 a^2} \right] f^2 e^{-2M} \left\{ \frac{16}{v_{qT}} \left[\frac{1}{e^{\frac{h v_{qT}}{kT} - 1}} + \frac{1}{2} \right] + \frac{n^2}{v_{qL}} \left[\frac{1}{e^{\frac{h v_{qL}}{kT} - 1}} + \frac{1}{2} \right] \right\} \quad (J.8)$$

From Appendix F, $e^{-2M} = e^{-4.54(\frac{\sin \theta}{\lambda})^2} = e^{-4.54(\frac{16+n^2}{4a^2})}$, and with $m = 34.3925 \times 10^{-23} \text{ g}$, $\frac{\mu}{\rho} = 232 \text{ cm}^2/\text{g}$, $a = 4.9502 \text{ \AA}$,⁽⁶⁷⁾ and $T = 295^\circ \text{K}$, (J.8) becomes

$$\frac{I_1(\vec{S})}{BP} = (0.4926 \times 10^{29}) f^2 e^{-0.0463(16+n^2)} (d_T + d_L) \quad (J.9)$$

where

$$d_T = \frac{16}{v_{qT}} \left[\frac{1}{e^{(1.627 \times 10^{-13}) v_{qT} - 1}} + \frac{1}{2} \right]$$

$$d_L = \frac{n^2}{v_{qL}} \left[\frac{1}{e^{(1.627 \times 10^{-13}) v_{qL} - 1}} + \frac{1}{2} \right]$$

(J.9) is set up very easily for computer calculation. As discussed in Appendix E, $f = f_0 + \Delta f' + i \Delta f''$, where f_0 is given by the expansion (E.1). The appropriate values of v_{qL} and v_{qT} are those given in Table I-1, and n is given

the values 0.20 to 1.80 in steps of 0.10 (except for $\eta = 0.45$ and $\eta = 1.55$).

III. Second Order TDS. From equations (A.46) and (H.15)

$$\frac{I_2(\vec{s})}{8P} = \frac{\pi v_c f^2 e^{-2M}}{8^{(u/p)} m} \left(\frac{\sin \theta}{\lambda} \right)^4 (kT)^2 \int_{1st \text{ Zone}} \rho(\vec{q}) \rho(\vec{s}-\vec{q}) dV_{\vec{q}} \quad (J.10)$$

where $\rho(\vec{q}) \equiv \frac{8}{m} \frac{(\hat{s}) (\Delta_{AB}(\vec{q})) (\hat{s})}{\Delta(\vec{q})}$. $\rho(\vec{q})$ is defined in

this manner in order to eliminate a factor $\frac{m}{8}$ which occurs in the product $(\hat{s}) (\Delta_{AB}(\vec{q})) (\hat{s}) / \Delta(\vec{q})$, as can be seen from equations (H.15) and (H.23) through (H.28). Multiplying by $\frac{8}{m}$ is equivalent to representing $\rho(\vec{q})$ by $(\hat{s}) (\Delta_{AB}(\vec{q})) (\hat{s}) / \Delta(\vec{q})$ with the D_{ij} which compose the Δ 's replaced by $\mathcal{D}_{ij} = \frac{m}{8} D_{ij}$. Thus, equations (H.23) through (H.28) can be applied without carrying along an $\frac{m}{8}$ factor.

The integral in (J.10) is over the first Brillouin zone, the boundaries of which are the planes $q_1 = \pm \frac{2\pi}{a}$, $q_2 = \pm \frac{2\pi}{a}$, $q_3 = \pm \frac{2\pi}{a}$, and $|q_1| + |q_2| + |q_3| = \frac{3\pi}{a}$. These are planes in a wave vector space, and in order to facilitate computer calculation of (J.10), it is best to change to an integral over a dimensionless number space. Let x_1 , x_2 , and x_3 be the coordinates in this space. Then

$$\vec{q} = \frac{2\pi}{a} (x_1 \hat{i} + x_2 \hat{j} + x_3 \hat{k}) = \frac{2\pi}{a} \vec{x} \quad (J.11)$$

$$dV_{\vec{q}} = dq_1 dq_2 dq_3 = \frac{8\pi^3}{a^3} dx_1 dx_2 dx_3 \quad (J.12)$$

The first zone boundaries become $x_1 = \pm 1$, $x_2 = \pm 1$, $x_3 = \pm 1$, and $|x_1| + |x_2| + |x_3| = 3/2$. Since $V_c = a^3/4$,

$$\frac{I_2(\vec{S})}{BP} = \frac{\pi^4 (kT)^2}{4m(\frac{\mu}{p})} f^2 e^{-2M} \left(\frac{\sin \theta}{\lambda}\right)^4 \int_{1st\ Zone} \rho\left(\frac{2\pi}{a}\vec{x}\right) \rho\left(\vec{S} - \frac{2\pi}{a}\vec{x}\right) dx_1 dx_2 dx_3 \quad (J.13)$$

To calculate (J.13) it is necessary to change the integral to a sum.

$$\int \rho\left(\frac{2\pi}{a}\vec{x}\right) \rho\left(\vec{S} - \frac{2\pi}{a}\vec{x}\right) dx_1 dx_2 dx_3 \rightarrow \sum_k \rho\left(\frac{2\pi}{a}\vec{x}_k\right) \rho\left(\vec{S} - \frac{2\pi}{a}\vec{x}_k\right) w_k \quad (J.14)$$

where the sum is over all points $\vec{x}_k$ on the surface of and within the first zone. w_k is the volume to be associated with the point $\vec{x}_k$. The allowed $\vec{x}_k$ and w_k are determined by the size of the mesh over which the sum is taken. The mesh chosen is one in which the allowed points are separated by 0.1 units along the $\hat{i}$, $\hat{j}$, and $\hat{k}$ directions. For points inside the zone $w_k = w = 10^{-3}$, but points on the zone surface will each be associated with only a portion of the cube having cube edge of 0.1 units. In general

$$w_k = a_k w = 10^{-3} a_k \quad (J.15)$$

where $a_k \leq 1$. (J.14) is a sum over the entire first zone, but it can be replaced by a sum over the first octant only, since for any term in (J.14) referring to a point in the first octant there are terms associated with corresponding points in the other octants. Consider the point (x_{k1}, x_{k2}, x_{k3}) in the first octant. The corresponding points in the other octants are $(x_{k1}, x_{k2}, -x_{k3})$,

$(-x_{k1}, x_{k2}, x_{k3}), (-x_{k1}, x_{k2}, -x_{k3}), (-x_{k1}, -x_{k2}, x_{k3}), (-x_{k1}, -x_{k2}, -x_{k3}),$
 $(x_{k1}, -x_{k2}, x_{k3}),$ and $(x_{k1}, -x_{k2}, -x_{k3})$. The procedure is to sum over the first octant only, with the terms in the other octants corresponding to a given point in the first octant being accounted for by a sign change process. Furthermore, the first octant sum contains points on and within the boundaries of the first octant. Some of these boundaries coincide with boundaries of the other octants, and in order that a single point not be summed over more than once it is necessary in the sign change process to use only those points in the other octants obtained by changing the sign of the non-zero components of a point in the first octant. Let $\sum_p$ indicate the sum over the first octant, and let m_p be the number of points corresponding to $\vec{x}_p$ in the first octant when all octants are taken into account. m_p is given as follows:

$$\begin{aligned}
 m_p &= 8 \text{ for } x_{p1} \neq 0, x_{p2} \neq 0, x_{p3} \neq 0 \\
 m_p &= 4 \text{ for one component } = 0 \\
 m_p &= 2 \text{ for two components } = 0 \\
 m_p &= 1 \text{ for the origin.}
 \end{aligned}$$

(J.14) then becomes

$$\int = (10^3) \sum_p a_p \sum_{i=1}^{m_p} \rho\left(\frac{2\pi}{\alpha} \vec{x}_{pi}\right) \rho\left(\vec{S} - \frac{2\pi}{\alpha} \vec{x}_{pi}\right) \quad (\text{J.16})$$

where $\vec{x}_{pi}$ is the coordinate of the p^{th} point in the first octant, and $i=2 \rightarrow m_p$ gives the corresponding points

in the appropriate other octants. From (J.13) and (J.16), with the constant evaluated for room temperature, one has

$$\frac{I_2(\vec{s})}{BP} = (5.06099 \times 10^{22}) f^2 e^{-2M} \left(\frac{\sin \theta}{\lambda} \right)^4 \sum_p a_p \sum_{i=1}^{m_p} \rho\left(\frac{2\pi}{a} \vec{x}_{pi}\right) \rho\left(\vec{s} - \frac{2\pi}{a} \vec{x}_{pi}\right) \quad (J.17)$$

Table J-1 gives the first octant values of (x_1, x_2, x_3) along with the associated values of m_p and a_p .

(J.17) is applicable to any reciprocal space direction, but the form of $\rho\left(\frac{2\pi}{a} \vec{x}_{pi}\right)$ depends on the direction chosen. For the (400) to (420) reciprocal space traversal

$$\rho(\vec{q}) = \frac{(\hat{s} \cdot (\Delta_{\alpha\beta}(\vec{q}))(\hat{s}))}{\Delta(\vec{q})}, \quad \hat{s} = \frac{1}{\sqrt{16+\pi^2}} (4\hat{i} + \pi\hat{j}) \quad (J.18)$$

where the values of the Δ 's are given with equation (H.15). For this unit vector

$$(\hat{s} \cdot (\Delta_{\alpha\beta}(\vec{q}))(\hat{s})) = \frac{16\Delta_{11} + 8\pi\Delta_{12} + \pi^2\Delta_{22}}{16 + \pi^2} \quad (J.19)$$

$$\text{Therefore } \rho(\vec{q}) = \frac{1}{16 + \pi^2} \frac{16(\Delta_{22}\Delta_{33} - \Delta_{23}^2) + 8\pi(\Delta_{13}\Delta_{23} - \Delta_{12}\Delta_{33}) + \pi^2(\Delta_{11}\Delta_{33} - \Delta_{13}^2)}{\Delta_{11}\Delta_{22}\Delta_{33} + 2\Delta_{12}\Delta_{13}\Delta_{23} - \Delta_{11}\Delta_{23}^2 - \Delta_{22}\Delta_{13}^2 - \Delta_{33}\Delta_{12}^2} \quad (J.20)$$

Equations (H.23) through (H.28) show that the Δ_{ij} are sums of products of sines and cosines, the arguments of which are of the form $nq_j/2$, where $n = 1, 2, 3$, $j = 1, 2, 3$. Since $q_j = \frac{2\pi}{a} x_j$, the arguments become $n\pi x_j$. Remembering this form and the dependence of $\rho(\vec{q})$ on n , one can write $\rho(\vec{x}_{pi}, n)$ in place of $\rho(\vec{q})$ or $\rho\left(\frac{2\pi}{a} \vec{x}_{pi}\right)$. When $\rho(\vec{s} - \vec{q})$ is considered, the arguments of the sine and cosine terms

Table J-1. First octant vectors and associated a_p and m_p values.

x_1	x_2	x_3	m_p	a_p	x_1	x_2	x_3	m_p	a_p	x_1	x_2	x_3	m_p	a_p
0	0	0	1	1	.2	.4	0	4	1	.7	.8	0	4	7/24
.1	0	0	2	1	.3	.4	0	4	1	.0	.9	0	4	1
.2	0	0	2	1	.4	.4	0	4	1	.1	.9	0	4	1
.3	0	0	2	1	.5	.4	0	4	1	.2	.9	0	4	1
.4	0	0	2	1	.6	.4	0	4	1	.3	.9	0	4	1
.5	0	0	2	1	.7	.4	0	4	1	.4	.9	0	4	1
.6	0	0	2	1	.8	.4	0	4	1	.5	.9	0	4	23/24
.7	0	0	2	1	.9	.4	0	4	1	.6	.9	0	4	7/24
.8	0	0	2	1	1	.4	0	4	1/2	0	1	0	2	1/2
.9	0	0	2	1	0	.5	0	2	1	.1	1	0	4	1/2
1	0	0	2	1/2	.1	.5	0	4	1	.2	1	0	4	1/2
0	.1	0	2	1	.2	.5	0	4	1	.3	1	0	4	1/2
.1	.1	0	4	1	.3	.5	0	4	1	.4	1	0	4	1/2
.2	.1	0	4	1	.4	.5	0	4	1	.5	1	0	4	1/4
.3	.1	0	4	1	.5	.5	0	4	1	0	0	.1	2	1
.4	.1	0	4	1	.6	.5	0	4	1	.1	0	.1	4	1
.5	.1	0	4	1	.7	.5	0	4	1	.2	0	.1	4	1
.6	.1	0	4	1	.8	.5	0	4	1	.3	0	.1	4	1
.7	.1	0	4	1	.9	.5	0	4	23/24	.4	0	.1	4	1
.8	.1	0	4	1	1	.5	0	4	1/4	.5	0	.1	4	1
.9	.1	0	4	1	0	.6	0	2	1	.6	0	.1	4	1
1	.1	0	4	1/2	.1	.6	0	4	1	.7	0	.1	4	1
0	.2	0	2	1	.2	.6	0	4	1	.8	0	.1	4	1
.1	.2	0	4	1	.3	.6	0	4	1	.9	0	.1	4	1
.2	.2	0	4	1	.4	.6	0	4	1	1	0	.1	4	1/2
.3	.2	0	4	1	.5	.6	0	4	1	0	.1	.1	4	1
.4	.2	0	4	1	.6	.6	0	4	1	.1	.1	.1	8	1
.5	.2	0	4	1	.7	.6	0	4	1	.2	.1	.1	8	1
.6	.2	0	4	1	.8	.6	0	4	23/24	.3	.1	.1	8	1
.7	.2	0	4	1	.9	.6	0	4	7/24	.4	.1	.1	8	1
.8	.2	0	4	1	0	.7	0	2	1	.5	.1	.1	8	1
.9	.2	0	4	1	.1	.7	0	4	1	.6	.1	.1	8	1
1	.2	0	4	1/2	.2	.7	0	4	1	.7	.1	.1	8	1
0	.3	0	2	1	.3	.7	0	4	1	.8	.1	.1	8	1
.1	.3	0	4	1	.4	.7	0	4	1	.9	.1	.1	8	1
.2	.3	0	4	1	.5	.7	0	4	1	1	.1	.1	8	1/2
.3	.3	0	4	1	.6	.7	0	4	1	0	.2	.1	4	1
.4	.3	0	4	1	.7	.7	0	4	23/24	.1	.2	.1	8	1
.5	.3	0	4	1	.8	.7	0	4	7/24	.2	.2	.1	8	1
.6	.3	0	4	1	.0	.8	0	2	1	.3	.2	.1	8	1
.7	.3	0	4	1	.1	.8	0	4	1	.4	.2	.1	8	1
.8	.3	0	4	1	.2	.8	0	4	1	.5	.2	.1	8	1
.9	.3	0	4	1	.3	.8	0	4	1	.6	.2	.1	8	1
1	.3	0	4	1/2	.4	.8	0	4	1	.7	.2	.1	8	1
0	.4	0	2	1	.5	.8	0	4	1	.8	.2	.1	8	1
.1	.4	0	4	1	.6	.8	0	4	23/24	.9	.2	.1	8	1

[illegible]

First octant vectors and associated a_p and m_p values. (continued)

[illegible]

Table J-1. First octant vectors and associated a_p and m_p

values. (continued)

x_1	x_2	x_3	m_p	a_p	x_1	x_2	x_3	m_p	a_p	x_1	x_2	x_3	m_p	a_p
8	2	4	8	1/2	0	0	5	2	1	1	5	8	1	1
9	2	4	8	1/2	1	0	5	4	1	1	5	8	1	1
0	3	4	8	1	2	0	5	4	1	2	5	8	1	1
1	3	4	8	1	3	0	5	4	1	3	5	8	1	1
2	3	4	8	1	4	0	5	4	1	4	5	8	1	1
3	3	4	8	1	5	0	5	4	1	5	5	8	1	1
4	3	4	8	1	6	0	5	4	1	6	5	8	1	1
5	3	4	8	1	7	0	5	4	1	7	5	8	1	1
6	3	4	8	1	8	0	5	4	1	8	5	8	1	1
7	3	4	8	1	9	0	5	4	1	9	5	8	1	1
8	3	4	8	1/2	0	1	5	4	1/4	1	6	8	1	1
0	4	4	8	1	1	1	5	4	1	2	6	8	1	1
1	4	4	8	1	2	1	5	4	1	3	6	8	1	1
2	4	4	8	1	3	1	5	4	1	4	6	8	1	1
3	4	4	8	1	4	1	5	4	1	5	6	8	1	1
4	4	4	8	1	5	1	5	4	1	6	6	8	1	1
5	4	4	8	1	6	1	5	4	1	7	6	8	1	1
6	4	4	8	1	7	1	5	4	1	8	6	8	1	1
7	4	4	8	1	8	1	5	4	1	9	6	8	1	1
8	4	4	8	1/2	9	1	5	4	1/2	0	7	8	1	1
0	5	4	8	1	0	2	5	4	1	1	7	8	1	1
1	5	4	8	1	1	2	5	4	1	2	7	8	1	1
2	5	4	8	1	2	2	5	4	1	3	7	8	1	1
3	5	4	8	1	3	2	5	4	1	4	7	8	1	1
4	5	4	8	1	4	2	5	4	1	5	7	8	1	1
5	5	4	8	1	5	2	5	4	1	6	7	8	1	1
6	5	4	8	1	6	2	5	4	1	7	7	8	1	1
7	5	4	8	1	7	2	5	4	1	8	7	8	1	1
8	5	4	8	1	8	2	5	4	1	9	7	8	1	1
9	5	4	8	1	9	2	5	4	1	0	7	8	1	1
0	6	4	8	1/2	0	3	5	4	1/2	1	8	8	1	1
1	6	4	8	1	1	3	5	4	1	2	8	8	1	1
2	6	4	8	1	2	3	5	4	1	3	8	8	1	1
3	6	4	8	1	3	3	5	4	1	4	8	8	1	1
4	6	4	8	1	4	3	5	4	1	5	8	8	1	1
5	6	4	8	1	5	3	5	4	1	6	8	8	1	1
6	6	4	8	1	6	3	5	4	1	7	8	8	1	1
7	6	4	8	1	7	3	5	4	1	8	8	8	1	1
8	6	4	8	1/2	8	3	5	4	1/2	9	8	8	1	1
9	6	4	8	1	9	3	5	4	1	0	8	8	1	1
0	7	4	8	1	0	4	5	4	1	1	9	8	1	1
1	7	4	8	1	1	4	5	4	1	2	9	8	1	1
2	7	4	8	1	2	4	5	4	1	3	9	8	1	1
3	7	4	8	1	3	4	5	4	1	4	9	8	1	1
4	7	4	8	1	4	4	5	4	1	5	9	8	1	1
5	7	4	8	1	5	4	5	4	1	6	9	8	1	1
6	7	4	8	1	6	4	5	4	1	7	9	8	1	1
7	7	4	8	1	7	4	5	4	1	8	9	8	1	1
8	7	4	8	1	8	4	5	4	1	9	9	8	1	1
9	7	4	8	1	9	4	5	4	1	0	9	8	1	1
0	8	4	8	1/2	0	5	5	4	1/2	1	0	8	1	1
1	8	4	8	1	1	5	5	4	1	2	0	8	1	1
2	8	4	8	1	2	5	5	4	1	3	0	8	1	1
3	8	4	8	1	3	5	5	4	1	4	0	8	1	1
4	8	4	8	1	4	5	5	4	1	5	0	8	1	1
5	8	4	8	1	5	5	5	4	1	6	0	8	1	1
6	8	4	8	1	6	5	5	4	1	7	0	8	1	1
7	8	4	8	1	7	5	5	4	1	8	0	8	1	1
8	8	4	8	1	8	5	5	4	1	9	0	8	1	1
9	8	4	8	1	9	5	5	4	1	0	0	8	1	1
0	9	4	8	1/2	0	6	5	4	1/2	1	0	0	1	2
1	9	4	8	1	1	6	5	4	1	2	0	0	1	2
2	9	4	8	1	2	6	5	4	1	3	0	0	1	2
3	9	4	8	1	3	6	5	4	1	4	0	0	1	2
4	9	4	8	1	4	6	5	4	1	5	0	0	1	2
5	9	4	8	1	5	6	5	4	1	6	0	0	1	2
6	9	4	8	1	6	6	5	4	1	7	0	0	1	2
7	9	4	8	1	7	6	5	4	1	8	0	0	1	2
8	9	4	8	1	8	6	5	4	1	9	0	0	1	2
9	9	4	8	1	9	6	5	4	1	0	0	0	1	2
0	0	5	4	1	0	7	5	4	1	1	0	0	1	2
1	0	5	4	1	1	7	5	4	1	2	0	0	1	2
2	0	5	4	1	2	7	5	4	1	3	0	0	1	2
3	0	5	4	1	3	7	5	4	1	4	0	0	1	2
4	0	5	4	1	4	7	5	4	1	5	0	0	1	2
5	0	5	4	1	5	7	5	4	1	6	0	0	1	2
6	0	5	4	1	6	7	5	4	1	7	0	0	1	2
7	0	5	4	1	7	7	5	4	1	8	0	0	1	2
8	0	5	4	1	8	7	5	4	1	9	0	0	1	2
9	0	5	4	1	9	7	5	4	1	0	0	0	1	2
0	1	5	4	1/2	0	8	5	4	1/2	1	0	0	1	2
1	1	5	4	1	1	8	5	4	1	2	0	0	1	2
2	1	5	4	1	2	8	5	4	1	3	0	0	1	2
3	1	5	4	1	3	8	5	4	1	4	0	0	1	2
4	1	5	4	1	4	8	5	4	1	5	0	0	1	2
5	1	5	4	1	5	8	5	4	1	6	0	0	1	2
6	1	5	4	1	6	8	5	4	1	7	0	0	1	2
7	1	5	4	1	7	8	5	4	1	8	0	0	1	2
8	1	5	4	1	8	8	5	4	1	9	0	0	1	2
9	1	5	4	1	9	8	5	4	1	0	0	0	1	2
0	2	5	4	1	0	9	5	4	1	1	0	0	1	2
1	2	5	4	1	1	9	5	4	1	2	0	0	1	2
2	2	5	4	1	2	9	5	4	1	3	0	0	1	2
3	2	5	4	1	3	9	5	4	1	4	0	0	1	2
4	2	5	4	1	4	9	5	4	1	5	0	0	1	2
5	2	5	4	1	5	9	5	4	1	6	0	0	1	2
6	2	5	4	1	6	9	5	4	1	7	0	0	1	2
7	2	5	4	1	7	9	5	4	1	8	0	0	1	2
8	2	5	4	1	8	9	5	4	1	9	0	0	1	2
9	2	5	4	1	9	9	5	4	1	0	0	0	1	2
0	3	5	4	1	0	0	5	4	1	1	0	0	1	2
1	3	5	4	1	1	0	5	4	1	2	0	0	1	2
2	3	5	4	1	2	0	5	4	1	3	0	0	1	2
3	3	5	4	1	3	0	5	4	1	4	0	0	1	2
4	3	5	4	1	4	0	5	4	1	5	0	0	1	2
5	3	5	4	1	5	0	5	4	1	6	0	0	1	2
6	3	5	4	1	6	0	5	4	1	7	0	0	1	2
7	3	5	4	1	7	0	5	4	1	8	0	0	1	2
8	3	5	4	1	8	0	5	4	1	9	0	0	1	2
9	3	5	4	1	9	0	5	4	1	0	0	0	1	2
0	4	5	4	1	0	1	5	4	1	1	0	0	1	2
1	4	5	4	1	1	1	5	4	1	2	0	0	1	2
2	4	5	4	1	2	1	5	4	1	3	0	0	1	2
3	4	5	4	1	3	1	5	4	1	4	0	0	1	2
4	4	5	4	1	4	1	5	4	1	5	0	0	1	2
5	4	5	4	1	5	1	5	4	1	6	0	0	1	2
6	4	5	4	1	6	1	5	4	1	7	0	0	1	2
7	4	5	4	1	7	1	5	4	1	8	0	0	1	2
8	4	5	4	1	8	1	5	4	1	9	0	0	1	2
9	4	5	4	1	9	1	5	4	1	0	0	0	1	2
0	5	5	4	1	0	2	5	4	1	1	0	0	1	2
1	5	5	4	1	1	2	5	4	1	2	0	0	1	2
2	5	5	4	1	2	2	5	4	1	3	0	0	1	2
3	5	5	4	1	3	2	5	4	1	4	0	0	1	2
4	5	5	4	1	4	2	5	4	1	5	0	0	1	2
5	5	5	4	1	5	2	5	4	1	6	0	0	1	2
6	5	5	4	1	6	2	5	4	1	7				

Table J-1. First octant vectors and associated a_p and m_p values. (continued)

x_1	x_2	x_3	m_p	a_p	x_1	x_2	x_3	m_p	a_p	x_1	x_2	x_3	m_p	a_p
.7	.2	.6	8	1/2	.1	.2	.7	8	1	.5	.2	.8	8	1/2
0	.3	.6	4	1	.2	.2	.7	8	1	0	.3	.8	4	1
.1	.3	.6	8	1	.3	.2	.7	8	1	.1	.3	.8	8	1
.2	.3	.6	8	1	.4	.2	.7	8	1	.2	.3	.8	8	1
.3	.3	.6	8	1	.5	.2	.7	8	1	.3	.3	.8	8	1
.4	.3	.6	8	1	.6	.2	.7	8	1/2	.4	.3	.8	8	1/2
.5	.3	.6	8	1	0	.3	.7	4	1	0	.4	.8	4	1
.6	.3	.6	8	1/2	.1	.3	.7	8	1	.1	.4	.8	8	1
0	.4	.6	4	1	.2	.3	.7	8	1	.2	.4	.8	8	1
.1	.4	.6	8	1	.3	.3	.7	8	1	.3	.4	.8	8	1/2
.2	.4	.6	8	1	.4	.3	.7	8	1	0	.5	.8	4	1
.3	.4	.6	8	1	.5	.3	.7	8	1/2	.1	.5	.8	8	1
.4	.4	.6	8	1	0	.4	.7	4	1	.2	.5	.8	8	1/2
.5	.4	.6	8	1/2	.1	.4	.7	8	1	0	.6	.8	4	1
0	.5	.6	4	1	.2	.4	.7	8	1	.1	.6	.8	8	1/2
.1	.5	.6	8	1	.3	.4	.7	8	1	0	.7	.8	4	7/24
.2	.5	.6	8	1	.4	.4	.7	8	1/2	0	0	.9	2	1
.3	.5	.6	8	1	0	.5	.7	4	1	.1	0	.9	4	1
.4	.5	.6	8	1/2	.1	.5	.7	8	1	.2	0	.9	4	1
0	.6	.6	4	1	.2	.5	.7	8	1	.3	0	.9	4	1
.1	.6	.6	8	1	.3	.5	.7	8	1/2	.4	0	.9	4	1
.2	.6	.6	8	1	0	.6	.7	4	1	.5	0	.9	4	1
.3	.6	.6	8	1/2	.1	.6	.7	8	1	.6	0	.9	4	7/24
0	.7	.6	4	1	.2	.6	.7	8	1/2	0	.1	.9	4	1
.1	.7	.6	8	1	0	.7	.7	4	1	.1	.1	.9	8	1
.2	.7	.6	8	1/2	.1	.7	.7	8	1/2	.2	.1	.9	8	1
0	.8	.6	4	1	0	.8	.7	4	7/24	.3	.1	.9	8	1
.1	.8	.6	8	1/2	0	0	.8	2	1	.4	.1	.9	8	1
0	.9	.6	4	7/24	.1	0	.8	4	1	.5	.1	.9	8	1/2
0	0	.7	2	1	.2	0	.8	4	1	0	.2	.9	4	1
.1	0	.7	4	1	.3	0	.8	4	1	.1	.2	.9	8	1
.2	0	.7	4	1	.4	0	.8	4	1	.2	.2	.9	8	1
.3	0	.7	4	1	.5	0	.8	4	1	.3	.2	.9	8	1
.4	0	.7	4	1	.6	0	.8	4	1	.4	.2	.9	8	1/2
.5	0	.7	4	1	.7	0	.8	4	7/24	0	.3	.9	4	1
.6	0	.7	4	1	0	.1	.8	4	1	.1	.3	.9	8	1
.7	0	.7	4	1	.1	.1	.8	8	1	.2	.3	.9	8	1
.8	0	.7	4	7/24	.2	.1	.8	8	1	.3	.3	.9	8	1/2
0	.1	.7	4	1	.3	.1	.8	8	1	0	.4	.9	4	1
.1	.1	.7	8	1	.4	.1	.8	8	1	.1	.4	.9	8	1
.2	.1	.7	8	1	.5	.1	.8	8	1	.2	.4	.9	8	1/2
.3	.1	.7	8	1	.6	.1	.8	8	1/2	0	.5	.9	4	1
.4	.1	.7	8	1	0	.2	.8	4	1	.1	.5	.9	8	1/2
.5	.1	.7	8	1	.1	.2	.8	8	1	0	.6	.9	4	7/24
.6	.1	.7	8	1	.2	.2	.8	8	1	0	0	1	2	1/2
.7	.1	.7	8	1/2	.3	.2	.8	8	1	.1	0	1	4	1/2
0	.2	.7	4	1	.4	.2	.8	8	1	.2	0	1	4	1/2

Table J-1. First octant vectors and associated a_p and m_p values. (continued)

x_1	x_2	x_3	m_p	a_p
.3	0	1	4	$1/2$
.4	0	1	4	$13/24$
.5	0	1	4	$1/4$
0	.1	1	4	$1/2$
.1	.1	1	8	$1/2$
.2	.1	1	8	$1/2$
.3	.1	1	8	$25/48$
.4	.1	1	8	$17/48$
0	.2	1	4	$1/2$
.1	.2	1	8	$1/2$
.2	.2	1	8	$25/48$
.3	.2	1	8	$17/48$
0	.3	1	4	$1/2$
.1	.3	1	8	$25/48$
.2	.3	1	8	$17/48$
0	.4	1	4	$13/24$
.1	.4	1	8	$17/48$
0	.5	1	4	$1/4$

are of the form $\frac{n\alpha}{2}(s_i - q_i) = n\pi(\frac{\alpha}{2\pi} s_i - x_i)$. In Section I it is shown that $\vec{s} = \frac{2\pi}{\alpha}(4\hat{i} + n\hat{j})$. Thus, the sine and cosine arguments are of the form $n\pi(4 - x_1)$, $n\pi(n - x_2)$, and $-n\pi x_3$. Then $\rho(\vec{s} - \vec{q})$ can be represented by $\rho(4 - x_{p11}, n - x_{p12}, -x_{p13}, n)$.

$$\frac{I_2(\vec{s})}{BP} = (5.06099 \times 10^{22}) f^2 e^{-2M} \left(\frac{\sin\theta}{\lambda}\right)^4 \sum_P a_P \sum_{i=1}^{m_P} \rho(x_{p11}, x_{p12}, x_{p13}, n) \rho(4 - x_{p11}, n - x_{p12}, -x_{p13}, n)$$

(J.21)

(J.21) with (J.20) and (H.23) through (H.28) give the mathematical relationships necessary for the computer calculation of $\frac{I_2(\vec{s})}{BP}$. $\left(\frac{\sin\theta}{\lambda}\right)^2$ is $\frac{16+n^2}{4a^2} = \frac{16+n^2}{98.01792}$ and, as in Section II, $2M = 0.0463(16+n^2)$. The input data are eighteen values of n , designated by E , and the 711 values each of a_P , x_{p11} , x_{p12} , x_{p13} , respectively designated by A , X1 , X2 , and X3 . In steps of 0.10 the values of n range from 0.15 to 1.85, a set which differs from that used for the first order TDS. This is necessary because the first order n values place the scattering vector exactly at points on the net over which the second order sum is taken, and such a condition causes the sum to diverge. The second order TDS at the n values used with the first order then is obtained by interpolation. The output data are the $\sum_P$ portion of (J.21), designated by SUM 420, and $I_2(\vec{s})/BP$, designated by TDS in the computer program body. The program consists of two parts, the main program which calculates $I_2(\vec{s})/BP$, and a subprogram which is used each time one of the ρ 's is to be calculated. For $n = .45$ to

1.25 the main program and the subprogram, written in FORTRAN IV, are shown in Figures J-2 and J-3, respectively.

IV. Higher Order TDS and Compton Scattering. The expression for TDS of third order and higher is given by equation (A.47). When the appropriate values of $\frac{\mu}{\rho}$ and m are inserted, the equation used to calculate the higher order TDS is

$$\frac{I_{\text{higher}}}{BP} = (6.26631 \times 10^{18}) f^2 e^{-2M} \left[e^{2M - 1 - 2M - \frac{(2M)^2}{2}} \right] \quad (J.22)$$

The Compton scattering for lead is calculated by use of the Thomas-Fermi approach, as discussed in Appendix B.

Figures J-4, J-5, J-6, and J-7 display I_{total}/BP and its various components for the directions in reciprocal space of interest.

```

1  DIMENSION E(18),A(711),X1(711),X2(711),X3(711)
2  FORMAT (3F5.2)
3  FORMAT (9F8.5)
4  FORMAT (9F4.1)
5  FORMAT (48H          SUM 420 DIRECTION      SECOND ORDER TDS)
6  FORMAT (/1H ,12X,E13.6,9X,E12.5)
7  READ(5,2) (E(3*I-2),E(3*I-1),E(3*I),I=1,6)
8  OREAD(5,3) (A(9*I-8),A(9*I-7),A(9*I-6),A(9*I-5),A(9*I-4),A(9*I-3),A
1(9*I-2),A(9*I-1),A(9*I),I=1,79)
9  OREAD(5,4) (X1(3*I-2),X2(3*I-2),X3(3*I-2),X1(3*I-1),X2(3*I-1),X3(3*
1I-1),X1(3*I),X2(3*I),X3(3*I),I=1,237)
10 DO 34 I=1,18
11 DO 33 J=1,711
12 OPROD1 =P420(X1(J),X2(J),X3(J),E(I))*P420(4.-X1(J),E(I)-X2(J),-X3
1(J),E(I))
13 OPROD2 =P420(X1(J),X2(J),-X3(J),E(I))*P420(4.-X1(J),E(I)-X2(J),X3
1(J),E(I))
14 IF(X3(J).EQ.0.0) PROD2 =0.0
15 OPROD3 =P420(-X1(J),X2(J),X3(J),E(I))*P420(4.+X1(J),E(I)-X2(J),-X
13(J),E(I))
16 IF(X1(J).EQ.0.0) PROD3 =0.0
17 OPROD4 =P420(X1(J),-X2(J),X3(J),E(I))*P420(4.-X1(J),E(I)+X2(J),-X
13(J),E(I))
18 IF(X2(J).EQ.0.0) PROD4 =0.0
19 OPROD5 =P420(-X1(J),X2(J),-X3(J),E(I))*P420(4.+X1(J),E(I)-X2(J),X
13(J),E(I))
20 IF(X1(J).EQ.0.0.OR.X3(J).EQ.0.0) PROD5 =0.0
21 OPROD6 =P420(-X1(J),-X2(J),X3(J),E(I))*P420(4.+X1(J),E(I)+X2(J),-
1X3(J),E(I))
22 IF(X1(J).EQ.0.0.OR.X2(J).EQ.0.0) PROD6 =0.0
23 OPROD7 =P420(X1(J),-X2(J),-X3(J),E(I))*P420(4.-X1(J),E(I)+X2(J),X
13(J),E(I))
24 IF(X2(J).EQ.0.0.OR.X3(J).EQ.0.0) PROD7 =0.0
25 OPROD8 =P420(-X1(J),-X2(J),-X3(J),E(I))*P420(4.+X1(J),E(I)+X2(J),
1X3(J),E(I))
26 IF(X1(J).EQ.0.0.OR.X2(J).EQ.0.0.OR.X3(J).EQ.0.0) PROD8 =0.0
27 OAJSUM =A(J)*(PROD1 +PROD2 +PROD3 +PROD4 +PROD5 +PROD6
1 +PROD7 +PROD8 )
28 IF(J.GT.1) GO TO 32
29 SUM420=AJSUM
31 GO TO 33
32 SUM420=SUM420+AJSUM
33 CONTINUE
   TWOM=0.0463*(16.+E(I)*E(I))
   S2=(16.+E(I)*E(I))/98.01792
   OF2= (34.6835*EXP(-0.7510*S2) + 15.6672*EXP(-3.8461*S2) + 13.2207*E
1XP(-11.2247*S2) + 4.5820*EXP(-49.8236*S2) + 9.1710)**2 +61.31
   TDS=5.06099E+22*F2*EXP(-TWOM)*S2*S2*SUM420
   IF(I.GT.1) GO TO 34
   WRITE(6,5)
34 WRITE(6,6) SUM420,TDS
   STOP
   END

```

1	FUNCTION P42(14,4,C,D)	1
2	C1A=COS(3.14159*A)	2
3	C2PA=COS(3.2531*A)	3
4	C3PA=COS(9.4247*A)	4
5	S1A=SIN(3.14159*A)	5
6	S2PA=SIN(6.2531*A)	6
7	S3PA=SIN(9.4247*A)	7
8	C1B=COS(3.14159*B)	8
9	C2PB=COS(6.2531*B)	9
10	C3PB=COS(9.4247*B)	10
11	S1B=SIN(3.14159*B)	11
12	S2PB=SIN(6.2531*B)	12
13	S3PB=SIN(9.4247*B)	13
14	C1C=COS(3.14159*C)	14
15	C2PC=COS(6.2531*C)	15
16	C3PC=COS(9.4247*C)	16
17	S1C=SIN(3.14159*C)	17
18	S2PC=SIN(6.2531*C)	18
19	S3PC=SIN(9.4247*C)	19
20	CD11=1985.*(2.-C1A*(C1B+C1C)) - 555.*(1.-C1B*C1C) + 770.*S1A*S1A +	20
21	1193.5*(S1B*S1B+S1C*S1C) - 126.*(1.-C2PA*C1B*C1C) + 13.*(2.-C1A*(C2	21
22	2PB+C1C*(C2B+C2C)) + 368.*(2.-C2PA*(C2PB+C2PC)) + 63.5*(1.-C2PB*C2P	22
23	3C) - 181.*(2.-C3PA*(C1B+C1C)) - 225.*(2.-C1A*(C3PB+C3PC)) - 241.*(	23
24	42.-C3PB*C1C-C1B*C3PC) + 2.*(1.-C2PA*(C2PB+C2PC)) - 11.*(2.-C3PA*(C2P	24
25	5C*(C1B+C1C*(C2B+C2C)) + 108.*(2.-C2PA*(C1B+C3PB+C3PC+C3PB*C1C)) + 33.*(2.-C1	25
26	6A*(C3PB+C2PC+C2PB*(C1C)) + 310.*S2PA*S2PA + 233.5*(S2PB*S2PB+S2PC*	26
27	7S2PC)	27
28	CD22=1985.*(2.-C1B*(C1C+C1A)) - 555.*(1.-C1C*C1A) + 770.*S1B*S1B +	28
29	1193.5*(S1C*S1C+S1A*S1A) - 126.*(1.-C2PB*(C1C+C1A)) + 13.*(2.-C1B*(C2	29
30	2PC+C1A*(C2C+C2A)) + 368.*(2.-C2PB*(C2PC+C2PA)) + 63.5*(1.-C2PC*(C2P	30
31	3A) - 181.*(2.-C3PB*(C1C+C1A)) - 225.*(2.-C1B*(C3PC+C3PA)) - 241.*(	31
32	42.-C3PC*(C1A-C1C*(C3A)) + 2.*(1.-C2PB*(C2PC+C2PA)) - 11.*(2.-C3PB*(C2P	32
33	5C*(C1A+C1C*(C2A)) + 108.*(2.-C2PB*(C1C+C3PA+C3PC+C3PA*(C1C)) + 33.*(2.-C1	33
34	6B*(C3PC+C2PA+C2PC*(C1A)) + 310.*S2PB*S2PB + 233.5*(S2PC*S2PC+S2PA*	34
35	7S2PA)	35
36	CD33=1985.*(2.-C1C*(C1A+C1B)) - 555.*(1.-C1A*C1B) + 770.*S1C*S1C +	36
37	1193.5*(S1A*S1A+S1B*S1B) - 126.*(1.-C2PC*(C1A+C1B)) + 13.*(2.-C1C*(C2	37
38	2PA+C1B*(C2A+C2B)) + 368.*(2.-C2PC*(C2PA+C2PB)) + 63.5*(1.-C2PA*(C2P	38
39	3B) - 181.*(2.-C3PC*(C1A+C1B)) - 225.*(2.-C1C*(C3PA+C3PB)) - 241.*(	39
40	42.-C3PA*(C1B-C1A*(C3B)) + 2.*(1.-C2PC*(C2PA+C2PB)) - 11.*(2.-C3PC*(C2P	40
41	5C*(C1B+C1A*(C2B)) + 108.*(2.-C2PC*(C1A+C3PB+C3PA*(C1C)) + 33.*(2.-C1	41
42	6C*(C3PA+C2PB+C2PC*(C1B)) + 310.*S2PC*S2PC + 233.5*(S2PA*S2PA+S2PB*	42
43	7S2PB)	43
44	CD12=2495.*S1A*S1B + 5.*C2PC*(S1A*S1B) - 77.*C1C*(S2PA*S1B+S1A*S2PB) +	44
45	130.*S2PC*S2PB + 31.5*(S3PA*S1B+S1A*S3PB) + 4.*C2PC*(S2PA*S2PB) + 75.	45
46	2*(S1PC*(S2PA*S1B+S1A*S2PB)) - 62.*C2PC*(S1A*S3PB+S3PA*S1B) + 17.*C1C	46
47	3*(S3PA*S2PB+S2PB*S3PB)	47
48	CD23=2495.*S1B*S1C + 5.*C2PA*(S1B*S1C) - 77.*C1A*(S2PB*S1C+S1B*S2PC) +	48
49	130.*S2PB*S2PC + 31.5*(S3PB*S1C+S1B*S3PC) + 4.*C2PA*(S2PB*S2PC) + 75.	49
50	2*(S1PC*(S2PB*S1C+S1B*S2PC)) - 62.*C2PA*(S1B*S3PC+S3PB*S1C) + 17.*C1A	50
51	3*(S3PB*S2PC+S2PC*S3PC)	51
52	CD13=2495.*S1C*S1A + 5.*C2PB*(S1C*S1A) - 77.*C1B*(S2PC*S1A+S1C*S2PA) +	52
53	130.*S2PC*S2PA + 31.5*(S3PC*S1A+S1C*S3PA) + 4.*C2PB*(S2PC*S2PA) + 75.	53
54	2*(S1PC*(S2PC*S1A+S1C*S2PA)) - 62.*C2PB*(S1C*S3PA+S3PC*S1A) + 17.*C1B	54
55	3*(S3PC*S2PA+S2PA*S3PA)	55
56	CD14=10.*C11*(C12+C13)+3.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	56
57	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	57
58	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	58
59	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	59
60	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	60
61	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	61
62	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	62
63	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	63
64	10.*C11*(C12+C13)+10.*C11*(C13+C12)+10.*C11*(C12+C13)+10.*C11*(C13+C12)	64

Figure J-3. Computer Subprogram

```

1 FUNCTION P420(A,B,C,D)
2 CPA=COS(3.14159*A)
3 C2PA=COS(6.28318*A)
4 C3PA=COS(9.42478*A)
5 SPA=SIN(3.14159*A)
6 S2PA=SIN(6.28318*A)
7 S3PA=SIN(9.42478*A)
8 CPB=COS(3.14159*B)
9 C2PB=COS(6.28318*B)
10 C3PB=COS(9.42478*B)
11 SPB=SIN(3.14159*B)
12 S2PB=SIN(6.28318*B)
13 S3PB=SIN(9.42478*B)
14 CPC=COS(3.14159*C)
15 C2PC=COS(6.28318*C)
16 C3PC=COS(9.42478*C)
17 SPC=SIN(3.14159*C)
18 S2PC=SIN(6.28318*C)
19 S3PC=SIN(9.42478*C)
20 OD11=1985.*(2.-CPA*(CPB+CPC)) - 555.*(1.-CPB*CPC) + 770.*SPA*SPA +
1193.5*(SPB*SPB+SPC*SPC) - 126.*(1.-C2PA*CPB*CPC) + 13.*(2.-CPA*(C2
2PB*CPC+CPB*C2PC)) + 368.*(2.-C2PA*(C2PB+C2PC)) + 63.5*(1.-C2PB*C2P
3C) - 181.*(2.-C3PA*(CPB+CPC)) - 225.*(2.-CPA*(C3PB+C3PC)) - 241.*(
42.-C3PB*CPC-CPB*C3PC) + 2.*(1.-C2PA*C2PB*C2PC) - 11.*(2.-C3PA*(C2P
5B*CPC+CPB*C2PC)) + 108.*(2.-C2PA*(CPB*C3PC+C3PB*CPC)) + 33.*(2.-CP
6A*(C3PB*C2PC+C2PB*C3PC)) + 310.*S2PA*S2PA + 233.5*(S2PB*S2PB+S2PC*
7S2PC)
21 OD22=1985.*(2.-CPB*(CPC+CPA)) - 555.*(1.-CPC*CPA) + 770.*SPB*SPB +
1193.5*(SPC*SPC+SPA*SPA) - 126.*(1.-C2PB*CPC*CPA) + 13.*(2.-CPB*(C2
2PC*CPA+CPC*C2PA)) + 368.*(2.-C2PB*(C2PC+C2PA)) + 63.5*(1.-C2PC*C2P
3A) - 181.*(2.-C3PB*(CPC+CPA)) - 225.*(2.-CPB*(C3PC+C3PA)) - 241.*(
42.-C3PC*CPA-CPC*C3PA) + 2.*(1.-C2PB*C2PC*C2PA) - 11.*(2.-C3PB*(C2P
5C*CPA+CPC*C2PA)) + 108.*(2.-C2PB*(CPC*C3PA+C3PC*CPA)) + 33.*(2.-CP
6B*(C3PC*C2PA+C2PC*C3PA)) + 310.*S2PB*S2PB + 233.5*(S2PC*S2PC+S2PA*
7S2PA)
22 OD33=1985.*(2.-CPC*(CPA+CPB)) - 555.*(1.-CPA*CPB) + 770.*SPC*SPC +
1193.5*(SPA*SPA+SPB*SPB) - 126.*(1.-C2PC*CPA*CPB) + 13.*(2.-CPC*(C2
2PA*CPB+CPA*C2PB)) + 368.*(2.-C2PC*(C2PA+C2PB)) + 63.5*(1.-C2PA*C2P
3B) - 181.*(2.-C3PC*(CPA+CPB)) - 225.*(2.-CPC*(C3PA+C3PB)) - 241.*(
42.-C3PA*CPB-CPA*C3PB) + 2.*(1.-C2PC*C2PA*C2PB) - 11.*(2.-C3PC*(C2P
5A*CPB+CPA*C2PB)) + 108.*(2.-C2PC*(CPA*C3PB+C3PA*CPB)) + 33.*(2.-CP
6C*(C3PA*C2PB+C2PA*C3PB)) + 310.*S2PC*S2PC + 233.5*(S2PA*S2PA+S2PB*
7S2PB)
23 OD12=2495.*SPA*SPB + 5.*C2PC*SPA*SPB - 77.*CPC*(S2PA*SPB+SPA*S2PB) +
1308.*S2PA*S2PB + 31.5*(S3PA*SPB+SPA*S3PB) + 4.*C2PC*S2PA*S2PB + 75.
2*C3PC*(S2PA*SPB+SPA*S2PB) - 62.*C2PC*(SPA*S3PB+S3PA*SPB) + 17.*CPC
3*(S3PA*S2PB+S2PA*S3PB)
24 OD23=2495.*SPB*SPC + 5.*C2PA*SPB*SPC - 77.*CPA*(S2PB*SPC+SPB*S2PC) +
1308.*S2PB*S2PC + 31.5*(S3PB*SPC+SPB*S3PC) + 4.*C2PA*S2PB*S2PC + 75.
2*C3PA*(S2PB*SPC+SPB*S2PC) - 62.*C2PA*(SPB*S3PC+S3PB*SPC) + 17.*CPA
3*(S3PB*S2PC+S2PB*S3PC)
25 OD13=2495.*SPC*SPA + 5.*C2PB*SPC*SPA - 77.*CPB*(S2PC*SPA+SPC*S2PA) +
1308.*S2PC*S2PA + 31.5*(S3PC*SPA+SPC*S3PA) + 4.*C2PB*S2PC*S2PA + 75.
2*C3PB*(S2PC*SPA+SPC*S2PA) - 62.*C2PB*(SPC*S3PA+S3PC*SPA) + 17.*CPB
3*(S3PC*S2PA+S2PC*S3PA)
26 OANUM=16.*(D22*D33-D23*D23)+8.*D*(D13*D23-D12*D33)+D*D*(D11*D33-D13
1*D13)
27 ODEM=D11*D22*D33+2.*D12*D13*D23-D11*(D23**2)-D22*(D13**2)-D33*(D12*
1*2)
28 IF(DEM.EQ.0.0) GO TO 31
29 P420=(1./((16.+D*D)))*(ANUM/DEM)
30 RETURN
31 P420=0.0
32 RETURN
33 END

```

Figure J-4. Calculations Corresponding to $[111]$ Longitudinal Data

Figure J-5. Calculations Corresponding to [111] Transverse Data

$\frac{I}{BP} \times 10^{-21} (\text{cm}^{-2})$

Figure J-6. Calculations Corresponding to [100] Longitudinal Data

Figure J-7. Calculations Corresponding to
[100] Transverse Data

Appendix K. Pre-Monochromator

I. Monochromator Geometry and Description. The monochromator employed is designed according to descriptions detailed by Warren⁽²⁴⁾ and Chipman.⁽²⁵⁾ The (200) reflection from a doubly bent single crystal of lithium fluoride is utilized to achieve the desired focusing of the beam from the spot focus of the x-ray tube. The diffraction plane geometry is shown in Figure K-1. The monochromator crystal to sample distance, D , which is the same as the distance from the spot focus to the crystal, is taken to be the same as the sample to counter distance. This is not a necessary requirement, but it turns out to be a convenient choice due to the manner in which the diffractometer is constructed. In the diffraction plane the crystal is bent to a radius of $2R$, where R is the radius of the circle defined by the spot source, the monochromator crystal, and the sample. This crystal bend tends to bring the beam to a vertical line focus at the sample, but a perfect line focus is not theoretically possible unless the crystal is also ground to a radius R . This is not done. If the monochromator is then bent in the vertical plane to the surface generated by rotating its diffraction plane section about the axis PS , a vertical line focus at the sample is maintained, but, in addition, the beam now tends toward a horizontal line focus at the zero angle 2θ position on the diffractometer circle. Ideally this geometry eliminates

Figure K-1. Pre Monochromator Geometry for Picker Unit

incident vertical divergence, because rays emanating from a vertical line on the monochromator crystal, striking the sample at a position along the line focus particular to each ray, and proceeding to a point at the counter slit in the diffraction plane define the same diffraction vector.

The monochromator and diffraction system are shown in Figure K-2. The x-ray tube normally is aligned such that its long axis is nearly perpendicular to the incident beam direction, and the tube head is mounted at the monochromator crystal location. To get it into the position for use with the monochromator, the tube is mounted on a rotatable base whose rotation axis is so located that when the tube is rotated through the monochromator angle $2\alpha = 45^\circ$, the spot source to monochromator crystal distance is D, which in this case is 5.73 inches. This rotatable base is good only for CuK_α radiation and a lithium fluoride crystal, for some other radiation or crystal would require a different rotation angle while maintaining the monochromator crystal to spot source distance at D. The x-ray beam issues from the tube head at S, passes through a lead-lined aluminum shaft, A, which contains a 4-way adjustable slit, strikes the monochromator crystal at C inside the lead-lined aluminum box, D, and the diffracted beam then passes through the lead-lined aluminum shaft at E which contains another 4-way adjustable slit. This latter slit defines the incident beam divergence. The lead lining in the various pieces is necessary

Figure K-2. Top View of Diffraction System

to shield against the higher energy portions of the white radiation which accompanies the line spectrum. In addition, during operation the entire monochromator is covered on the outside with sheet lead.

Since the x-ray tube must be rotated in order to get it into the correct position for the monochromator, one of the major design considerations was that of making the axis of rotation as nearly perpendicular as possible to the diffraction plane. Upon rotation it is then hoped that any motion of the spot source out of the diffraction plane is held well below the tube head's maximum vertical adjustment range, which is 0.8 mm. Measurements indicate that the actual vertical change is about 10% of this value, a very satisfactory result. An additional design feature is that if it is desired to operate without the monochromator, the tube can easily be rotated back to its original position and still be mounted correctly on its rotatable base. In Figure K-3, if the monochromator crystal, its mount M, and the associated shielding are removed, the tube and its support can be rotated into the bracket at Z upon which the monochromator was mounted. Two screws which screw into the tube head support through the bracket allow the tube to be fastened securely in place without disturbing any of its alignment with respect to its rotatable base. This means that when the monochromator is used again the only tube adjustment is that of rotating it into its monochromator position.

Figure K-3. Monochromator Side View

Figure K-3 provides a clear view of the monochromator crystal mount. The crystal is mounted on a goniometer head, which in turn is mounted on a rotatable base. This rotation is controlled by the screw B acting on the lever L against the spring-backed pin P. Once the correct rotational position is found during monochromator alignment, the rotatable base is locked into position by two set screws.

II. Monochromator Alignment. Figure K-4 shows the arrangement for monochromator alignment. The Aperture S₁ between the source and the crystal is closed down to form a vertical opening of width 0.5 mm. Shaft E of Figure K-2 is replaced by a similar shaft which contains the very narrow vertical slit S₂ used in aligning the original diffractometer. The zero alignment gauge, which contains another very narrow slit S₃, is placed in the sample position. The source and S₁ define the direction of the narrow beam incident on the monochromator crystal, while S₂ and S₃ define the corresponding very narrow exit direction. The position at which these two beams intersect is the position at which the approximate center of the monochromator crystal should be located. If the angle between the two intersecting beams is correct, one should obtain a diffracted beam through S₂ and S₃. If no beam is obtained, the angle is not correct and can be changed slightly by moving the x-ray source along a line perpen-

Figure K-4. Arrangement for Monochromator Alignment

dicular to the incident direction.

In practice, the alignment is very easy to perform. The x-ray tube is first rotated through approximately 45° . This corresponds to the center position between the two lock screws at F in Figure K-2. The shaft A telescopes and also rotates on the rounded portion of the shield at D. This allows the shaft to fit snugly against the x-ray port for x-ray tube positions varying over a small range. The procedure is to align the monochromator crystal as well as possible for a given source position, and then slightly change the source position in the manner indicated above. The x-ray tube is run at its minimum values of 12 KV and 2 ma during this process. The crystal alignment and source position changes are continued until a maximum diffracted beam is acquired. Motions carried out in aligning the crystal are defined with respect to the XYZ axes shown in Figure K-4. Translations along the Y and Z axes, and rotation about the X axis are not critical. These positionings are carried out by eye. The Z and Y rotations, and the X translation are the motions to which correct alignment is most sensitive. The Z rotation is carried out by motion of the lever L in Figure K-3, while the other motions are allowed by the goniometer head.

III. Monochromator Crystal. The configuration for cutting the die used in bending the lithium fluoride crystal to the proper double curvature is shown in Figure K-5. This

figure is taken from Figure 3 in the article by Chipman.⁽²⁵⁾ The procedure has been used previously in this laboratory by J. Costello.⁽²³⁾ The brass cylinder B is mounted on a lathe, and then turned down to the desired shape by having the cutting tool follow the path defined by the guide G. The radius of curvature of G, which is $2R$, provides the proper curvature in the monochromator plane, while the tilt angle γ and the distance of the lathe's rotational axis from the cutting tool determine the radii of curvature about the line PS in Figure K-1. When point P at the center of the guide is reached, the cutting tool should be at point Q on the die, where the distance from Q to the axis of rotation is the radius r shown in Figure K-1. The appropriate dimensions are $2R = 14.975$ inches, $r = 2.896$ inches, and $\gamma = 7^\circ 51'$.

Several monochromator crystals were prepared from $1'' \times 1'' \times \frac{1}{4}''$ lithium fluoride blanks obtained from Harshaw Chemical Company. In order to get crystals thin enough for bending, the blanks have to be cleaved into sections of about 1 mm thickness. The cleaving is made much easier if the blanks are first hardened by x-ray produced imperfections. This is done by irradiating each blank for about $1\frac{1}{2}$ hours at 180 KV, 20 ma in a medical x-ray machine with the result that each blank acquires a uniform yellow coloring. The cleaving is done with a single edge stainless steel razor blade which has been cleaned in acetone. The razor blade is placed on the

adjusted accordingly. The required S value is 2.6 mm.

II. Resolution in Reciprocal Space. The angular divergences define the region of reciprocal space which is sampled at each diffractometer setting. This is the reciprocal volume element, and its dimensions in the diffraction plane parallel and perpendicular to the diffraction vector indicate the resolution in reciprocal space in these directions. Figure L-7 shows the horizontal divergences in the diffraction plane, and Figure L-8 shows the corresponding reciprocal volume element cross section. Each point in this cross section is labeled to indicate the pair of rays in Figure L-7 to which it corresponds. X-EGL-Y-AIJ outlines the cross section corresponding to the case of perfect focusing, but in which the angular divergences Θ_1 and Θ_2 for the non-perfect case are used. If there actually were perfect focusing, both slits would have to be widened to allow these divergences. The actual cross section, which is contained within this outline, is EGJ-EGL-MGL-AIJ-NIJ. It can be thought of as being swept out by DHJ-DHL-BHL-BHJ, the cross section for perfect focusing as determined by Θ_1' and Θ_2' , when $\vec{S}$ takes on directions allowed by the finite width of the focus. Since most of the radiation comes from the center line of the monochromator crystal, the cross section CGJ-CGL-CIL-CIJ, which corresponds to it, is used in defining the resolution in reciprocal space. Figures L-9a and L-9b

Figure L-5. Incident Vertical Divergence

that there is a main central, parallel beam as shown in Figure L-5. Under this model there is an incident vertical divergence given by the angle α , the half angle of which is shown. With the indicated dimensions $\alpha = 12'$.

E. Exit Vertical Divergence. If the incident vertical divergence is neglected, rays from any point on the vertical line focus to a point in the diffraction plane at the detector slit correspond to the same diffraction vector. Thus, the exit vertical divergence is given by the angle γ shown in Figure L-6.

Figure L-6. Exit Vertical Divergence

In this case γ is assigned the value of 1° and S is

is in reverse. There is then no rotational motion at the sample position. The result is $\Theta_2' = 28.5'$, a value which gives a detector slit width of 1.2 mm. Equation (L.1) with Θ_1 replaced by Θ_2 , and a slit-to-focus distance of 146 mm, yields a Θ_2 value of $52'$.

D. Incident Vertical Divergence. As indicated above there is supposed to be no incident vertical divergence. Any rays arriving at the detector at a point in the diffraction plane and originating from a vertical line on the monochromator should have the same diffraction vector. Ideally, the incident beam vertical aperture then simply helps to define how much of the monochromator crystal is used. The actual situation was investigated by taking photographs of the beam cross section at positions along the incident beam with no sample in place. Theoretically, this beam should come to a horizontal line focus at the detector position, but this was not found to be the actual case. The beam does initially converge toward a focus at the detector, but after about 6 cm from the sample position toward the detector the beam maintains about a 2 mm height. This is shown in Figure L-5. The slit width S is fixed at 3.5 mm. With perfect focusing the geometry as shown dictates a vertical height at the focus of 2.4 mm. The measured height is 2.5 mm, so the focusing properties up to the sample position are quite good. The non-focusing properties after 6 cm beyond the sample position indicate

Figure L-3. Angle Subtended at Monochromator by Focus Width

C. Exit Horizontal Divergence. This divergence is determined by the width of the focus and a slit placed in front of the detector. There is also a scatter slit at the vacuum chamber window, but this slit is wide enough that it has no effect on the exit horizontal divergence, and it is not considered in this discussion. The geometry, shown in Figure L-4, is the reverse of that in Figure L-2.

θ_2 is the exit horizontal divergence angle, and θ_2' is the corresponding divergence for a perfect line focus.

Figure L-4. Exit Horizontal Divergence.

θ_2' was determined experimentally by placing a fine slit at the sample position and driving the detector arm across the 2θ zero angle position. To do this the 2θ drive is operated in the forward position, while the ω drive

from the monochromator crystal does not emanate uniformly from all parts of the crystal, but primarily from three vertical lines as shown in Figure L-1. The incident horizontal divergence slit is placed such that radiation from lines 1 and 3 is eliminated. The incident horizontal divergence is then given by the angle Θ_i , shown in Figure L-2, and Θ'_i is the angular divergence in the case

Figure L-2. Incident Horizontal Divergence

of a perfect line focus. A consideration of the geometry shows that

$$\tan \frac{\Theta_i}{2} = \frac{x+s}{2y}, \quad \tan \frac{\Theta'_i}{2} = \frac{s}{2y} \quad (L.1)$$

As determined from photographs x is 1 mm and s is .75 mm, while y , which is fixed by the monochromator geometry, is 63.5 mm. These values give $\Theta_i = 1^\circ 35'$ and $\Theta'_i = 40'$.

As will be seen later, one other angle of interest is the angle β , subtended by the focus at the monochromator crystal center line, the line from which most of the incident beam radiation emanates. This is shown in Figure L-3, and it should be noted that the center line and the focus determine β , with the incident horizontal divergence slit having no effect. h is 146 mm so that β is $24'$.

Figure K-5. Assembly for Cutting Monochromator
Crystal Die

corner of the upright blank and given a sharp tap with a hammer. The blank usually splits nicely into two sections. This process is continued until blanks of about 1 mm thickness are attained. The coloration is removed by annealing the crystals at 540°C for six hours in vacuum. To bend the crystals a rectangular piece sufficiently large to accommodate 1" x 1" crystals is removed from the cylindrical brass die formed according to Figure K-5. The bending is accomplished in warm water saturated with lithium fluoride, and the bend is produced simply by uniform pressure applied with the thumbs to the crystal placed against the brass form. The bent crystal and die are then placed against a rubber pillow in a screw press and heated to about 175°C for twenty minutes, after which the apparatus is allowed to cool to room temperature and the crystal is removed. With this latter treatment the crystals are found to conform well to the die surface indefinitely. The crystals are mounted with silastic on lucite rods which fit into the goniometer head. How far this rod is inserted into the goniometer head determines the vertical position of the monochromator crystal.

The crystal used in the monochromator was chosen from among three which appeared to have the most uniform bends. The choice was determined by which of the three gave the best focusing properties. The crystal so chosen is 1.5 mm thick. Figure K-6(a) shows cross sections of the diffracted beam taken at the four-way slit of shaft

E in Figure K-2, and at four successive positions 3 cm apart along the diffracted beam. The third photograph is quite close to the sample position, and shows that there is an attempt at focusing to a vertical line at the sample. Beyond this there is also a tendency toward a horizontal line focus, one of the desired properties. These photographs were taken with the four-way slit wide open, and they clearly show the beam structure which is mentioned in Appendix L. This structure was present with the other two crystals and was unchanged when the old x-ray tube was replaced with a new one. Thus, it most likely occurs as a result of the crystal bending. Figure K-6(b) shows the beam cross section at the four-way slit and at the sample position when the slit is closed down to its operating condition. Note that only the strong center line of the beam structure is allowed through.

Figure K-6. Photographs of the X-Ray Beam Cross Section

(a) Slit at Monochromator Wide Open

(b) Slit Closed to Operating Condition

Appendix L. Instrument Resolution

I. Angular Divergences.

A. Introduction. As described in Appendix K, for a point x-ray source, the monochromator system employed is one which tends to bring the incident beam to a vertical line focus at the sample position, and a horizontal line focus at the zero angle detector position with no sample present. Ideally, this geometry eliminates incident beam vertical divergence, while in practice this divergence is greatly reduced with respect to that obtained with other geometries.

B. Incident Horizontal Divergence. The lithium fluoride monochromator crystal does not provide a vertical line focus at the sample, but a focus of 1 mm width, a fact which is due primarily to imperfect crystal bending and no grinding, and to a lesser extent to a finite x-ray source size and mosaic spread of the crystal. The beam reflected

Figure L-1. Diffraction Plane Section of Incident Beam

Figure L-7. Horizontal Divergences in the Diffraction Plane

$\vec{S}_0$ = Wave Vector of Incident Radiation, $|\vec{S}_0| = 2\pi/\lambda$
 $\vec{S}_s$ = Wave Vector of Scattered Radiation, $|\vec{S}_s| = 2\pi/\lambda$
 $\vec{S}$ = Diffraction Vector, $|\vec{S}| = 4\pi \sin \theta / \lambda$

Figure L-8. Diffraction Plane Section of the Reciprocal Volume Element

give the geometry necessary for the determination of appropriate dimensions in this cross section. Note from Figure L-9a that

$$\begin{aligned}\delta &= \frac{\pi}{2} - 2\theta \\ \beta &= \pi - \delta - 2\theta - \frac{1}{2}(\pi - 2\theta) = \frac{\pi}{2} - \theta - \delta = \theta\end{aligned}\quad (\text{L.2})$$

$$\begin{aligned}d_{||} \cos(\beta - \epsilon) &= \frac{2\pi}{\lambda} \theta'_2 \cos \epsilon \\ d_{||} &= \frac{2\pi}{\lambda} \theta'_2 \frac{\cos \epsilon}{\cos(\theta - \epsilon)} = \frac{2\pi}{\lambda} \theta'_2 \left[\frac{1}{\cos \theta + \sin \theta \tan \epsilon} \right]\end{aligned}\quad (\text{L.3})$$

To determine $\tan \epsilon$, observe that

$$\begin{aligned}\frac{2\pi}{\lambda} (\theta_2 - \theta'_2) \cos \epsilon &= \frac{2\pi}{\lambda} \beta_0 \cos\left(\frac{\pi}{2} - \delta - \epsilon\right) = \frac{2\pi}{\lambda} \beta_0 \cos(2\theta - \epsilon) \\ \frac{\theta_2 - \theta'_2}{\beta_0} &= \cos 2\theta + \sin 2\theta \tan \epsilon = 2 \cos \theta (\cos \theta + \sin \theta \tan \epsilon) - 1 \\ \frac{1}{\cos \theta + \sin \theta \tan \epsilon} &= 2 \cos \theta / \left(\frac{\theta_2 - \theta'_2}{\beta_0} + 1 \right)\end{aligned}\quad (\text{L.4})$$

$$\text{Therefore} \quad d_{||} = \frac{4\pi}{\lambda} \theta'_2 \cos \theta / \left(1 + \frac{\theta_2 - \theta'_2}{\beta_0} \right) \quad (\text{L.5})$$

For $d_{\perp}$

$$\begin{aligned}\frac{2\pi}{\lambda} \beta_0 \cos \delta &= d_{\perp} \cos \beta \\ d_{\perp} &= \frac{2\pi}{\lambda} \beta_0 \frac{\sin 2\theta}{\cos \theta} = \frac{4\pi}{\lambda} \beta_0 \sin \theta\end{aligned}\quad (\text{L.6})$$

$d_{||}$ and $d_{\perp}$ are taken to be a measure of the resolution in reciprocal space parallel and perpendicular to the diffraction vector, respectively. It should be noted in (L.5) that the factor $\frac{4\pi}{\lambda} \theta'_2 \cos \theta$ turns out to be the

resolution associated with DHJ-DHL-BHL-BHJ, the cross section for perfect focusing. In terms of a dimensionless reciprocal space, one has

$$\Delta S_{\parallel} = \frac{a}{2\pi} d_{\parallel} = \frac{2a}{\lambda} \theta_2' \cos \theta / \left(1 + \frac{\theta_2 - \theta_2'}{\theta_0}\right) \quad (\text{L.7})$$

$$\Delta S_{\perp} = \frac{a}{2\pi} d_{\perp} = \frac{2a}{\lambda} \theta_0 \sin \theta \quad (\text{L.8})$$

(L.7) gives the resolution for a constant diffraction vector, but in the experimental arrangement $\Delta S_{\parallel}$ is increased because of the 2θ sweep motion and the channel dwell time of the multichannel analyzer. Let θ_a and θ_b be the angles associated with the endpoints of a particular channel, and θ_0 the midpoint.

$$\theta_a \equiv \theta_0 - \frac{\phi}{2}, \quad \theta_b \equiv \theta_0 + \frac{\phi}{2} \Rightarrow 2\theta_0 - \phi < 2\theta < 2\theta_0 + \phi$$

In terms of the dimensionless reciprocal space the length of the diffraction vector at each of the endpoints is

$$\begin{aligned} S_a &= \frac{2a}{\lambda} \sin \theta_a = \frac{2a}{\lambda} \sin(\theta_0 - \frac{\phi}{2}) \\ S_b &= \frac{2a}{\lambda} \sin \theta_b = \frac{2a}{\lambda} \sin(\theta_0 + \frac{\phi}{2}) \end{aligned} \quad (\text{L.9})$$

The resolution, $\Delta S'_{\parallel}$, corresponding to a single channel of data is

$$\begin{aligned} \Delta S'_{\parallel} &= S_b - S_a + \frac{1}{2} \Delta S_{\parallel}(\theta_a) + \frac{1}{2} \Delta S_{\parallel}(\theta_b) \\ &= \frac{2a}{\lambda} \left[\sin(\theta_0 + \frac{\phi}{2}) - \sin(\theta_0 - \frac{\phi}{2}) \right] + \frac{a\theta_2'}{\lambda} \left(\frac{1}{1 + \frac{\theta_2 - \theta_2'}{\theta_0}} \right) \left[\cos(\theta_0 + \frac{\phi}{2}) + \cos(\theta_0 - \frac{\phi}{2}) \right] \\ &= \frac{4a}{\lambda} \cos \theta_0 \sin \frac{\phi}{2} + \frac{2a\theta_2'}{\lambda} \left(\frac{1}{1 + \frac{\theta_2 - \theta_2'}{\theta_0}} \right) \cos \theta_0 \cos \frac{\phi}{2} \end{aligned}$$

$$\begin{aligned}
 \text{or } \Delta S'_{11} &= \frac{2a}{\lambda} \theta'_2 \left(\frac{\cos \theta_0}{1 + \frac{\theta_2 - \theta'_2}{\beta_0}} \right) \left[\cos \frac{\phi}{2} + \frac{2}{\theta'_2} \left(1 + \frac{\theta_2 - \theta'_2}{\beta_0} \right) \sin \frac{\phi}{2} \right] \\
 &= \Delta S_{11}(\theta_0) \left[\cos \frac{\phi}{2} + \frac{2}{\theta'_2} \left(1 + \frac{\theta_2 - \theta'_2}{\beta_0} \right) \sin \frac{\phi}{2} \right] \quad (\text{L.10})
 \end{aligned}$$

If Ω is the 2θ scan rate and τ is the channel dwell time,

$$2\phi = \Omega\tau \Rightarrow \phi/2 = \Omega\tau/4$$

In this experiment $\Omega = \frac{1}{30}^\circ/\text{sec}$ and $\tau = \frac{25}{3}$ sec, so that

$\phi/2 = 5/12^\circ = .00122$ radians. Since $\phi/2$ is so small,

$\cos \phi/2 \approx 1$ and $\sin \phi/2 \approx \phi/2$. (L.10) then becomes

$$\Delta S'_{11} = \Delta S_{11}(\theta_0) \left[1 + \frac{\phi}{\theta'_2} \left(1 + \frac{\theta_2 - \theta'_2}{\beta_0} \right) \right] \quad (\text{L.11})$$

Table L-1 gives the resolution for three different $2\theta_0$ angles characteristic of the experiment. The values of θ_2 , θ'_2 , and β_0 used are those given in section I of this appendix.

$2\theta_0$	$\frac{2a}{\lambda} \theta'_2 \cos \theta_0$	$\Delta S_{11}(\theta_0)$	$\Delta S'_{11}(\theta_0)$	$\Delta S_1(\theta_0)$
46.00°	0.049	0.025	0.040	0.017
77.00°	0.042	0.021	0.033	0.028
107.90°	0.031	0.016	0.025	0.036

Table L-1. Resolution in Reciprocal Space

III. Angular Independence of the Scattering with Respect to the Reciprocal Volume Element. At the end of Appendix A it is mentioned that in order to get the expressions for

the measured intensities, it is necessary to multiply the formulas derived there by the polarization factor and the absorption factor, and then integrate over the reciprocal volume element. That this integration does not introduce any new 2θ dependence is what is to be proved. Since the reciprocal volume element is introduced through this integration, and since it changes its shape and size when 2θ changes, such a proof shows that the diffuse scattering is independent of the shape and size of the reciprocal volume element.

For the sake of argument assume that the monochromator is perfect and thus provides a vertical line focus at the sample. The effect in reciprocal space is shown in Figure L-10.

Figure L-10. Reciprocal Volume Element for Perfect Focusing.

Any of the diffuse scattering terms are of the form $D(\vec{s})$, where $\vec{s}$ is the diffraction vector, and D is the scattered intensity per unit volume of reciprocal space at $\vec{s}$. D can be expressed as the product of $I_0(\vec{s})$ and $O(\vec{s})$, where $I_0(\vec{s})$ is the incident intensity per unit angle as a function of η . $I_{\text{meas}}(\vec{s})$ as found in the literature is expressed in the form of a constant $\times O(\vec{s})$, so that all of the angular dependence of $I_{\text{meas}}(\vec{s})$ is assumed to be introduced in $O(\vec{s})$ before the integration occurs. This assumption is what the following discussion proves. If dV_s is a differential volume element of the reciprocal volume element, the differential of the diffuse scattering is

$$dI = I_0(\vec{s}) O(\vec{s}) dV_s \quad (\text{L.12})$$

Integrate (L.12) over the reciprocal volume element, using the (X,Y,Z) axes shown, where Z is out of the plane of the figure. The vertical angular divergence, γ , is to be associated with the Z direction. Each particular $\vec{s}$ (or η) is associated with a slab of approximate area $(\frac{2\pi}{\lambda} \theta_2)(\frac{2\pi}{\lambda} \gamma) = \frac{4\pi^2}{\lambda^2} \gamma \theta_2$ at a specific value of Y. Assume that for a given η $O(\vec{s})$ varies slowly over this area. Then

$$dI(Y) = I_0(Y) O(Y) \left(\frac{4\pi^2}{\lambda^2} \gamma \theta_2 \right) dY \quad (\text{L.13})$$

where $O(Y)$ is the value of $O(\vec{s})$ at the center of the area $\frac{4\pi^2}{\lambda^2} \gamma \theta_2$ for a particular Y, and $I_0(Y)$ is now the incident intensity per unit Y interval.

$$\begin{aligned}
 I_{\text{meas}} &= \frac{4\pi^2}{\lambda^2} r\theta_2 \int I_0(Y) \mathcal{O}(Y) dY \\
 &\approx \frac{4\pi^2}{\lambda^2} r\theta_2 \mathcal{O}(Y_0) \int I_0(Y) dY
 \end{aligned}
 \tag{L.14}$$

where it is assumed that $\mathcal{O}(Y)$ varies so slowly with Y that it can be taken outside the integral and given the value it acquires at the center of the reciprocal volume element. Removal of $\mathcal{O}$ from the integral implies the neglect of divergence corrections. If $\int I_0(Y) dY$ is independent of 2θ , the integration over the reciprocal volume element does not add any 2θ dependence to that already present in $\mathcal{O}$, and it removes any such dependence in $I_0(\xi_0)$.

$$\int_{-\frac{\theta_1}{2}}^{\frac{\theta_1}{2}} I_0(Y) dY = \int I_0(n) dn = \text{constant},
 \tag{L.15}$$

where the constant depends only on the divergence in the incident beam. $I_0(Y)$ is a function of 2θ , since a given dY corresponds to a different dn as 2θ changes, but its integral is not a function of 2θ .

$$\text{Therefore } I_{\text{meas}} = (\text{const.}) \mathcal{O}(Y_0)
 \tag{L.16}$$

and all of the 2θ dependence occurs in $\mathcal{O}$.

Appendix M. Affect of Temperature and Pressure Changes on Absolute Intensity.

When absolute intensities are measured it is necessary that all count rates be referred to the same atmospheric temperature and pressure, since part of the beam path is through the air. This allows for variations in air absorption to be accounted for. The MCA scan technique accomplishes this for a specific 2 θ scan interval, but each such interval will have its own average temperature and pressure, and it is because of this that there must be correction to a reference temperature and pressure.

In the scan procedure one scans over a specified region of reciprocal space in a time less than ten minutes, which is short compared to the times characteristic of temperature and pressure variations. Thus, in any one scan the count rates at various reciprocal space positions will be in the proper ratios with respect to one another. However, if the temperature and pressure vary, the count at a particular point during one pass will be different from that at the same point at another time. Let n_i be the count added to a channel during the i^{th} pass, and let there be N passes in all. The count rate to be associated with this channel is

$$CR = \frac{1}{N\tau} \sum_{i=1}^N n_i \quad (M.1)$$

where τ is the channel dwell time. In addition to purely statistical fluctuations the n_i differ from one another because of pressure and temperature variations. Let n_{oi} be the number of counts which would be added to a channel during the i^{th} pass at temperature T_0 and pressure P_0 . If $\frac{\Delta I_i}{I_0}$ is the corresponding relative change in the beam intensity

$$n_i = n_{oi} \left(1 + \frac{\Delta I_i}{I_0}\right) \quad (\text{M.2})$$

Then if

$$CR_{\text{corrected}} = \frac{1}{N\tau} \sum_{i=1}^N n_{oi} = \frac{CR}{1 + \frac{\Delta I}{I_0}} = \frac{\frac{1}{N\tau} \sum_{i=1}^N n_i}{1 + \frac{\Delta I}{I_0}}$$

$$\left(1 + \frac{\Delta I}{I_0}\right) \sum_{i=1}^N n_{oi} = \sum_{i=1}^N n_{oi} \left(1 + \frac{\Delta I_i}{I_0}\right) \quad (\text{M.3})$$

Let n_0 be the expected count to be added to the channel at $P=P_0$ and $T=T_0$. As far as statistical fluctuations are concerned

$$\left(1 + \frac{\Delta I}{I_0}\right) \sum_{i=1}^N n_{oi} = \left(1 + \frac{\Delta I}{I_0}\right) \sum_{i=1}^N n_0 = N n_0 \left(1 + \frac{\Delta I}{I_0}\right)$$

$$\sum_{i=1}^N n_{oi} \left(1 + \frac{\Delta I_i}{I_0}\right) = \sum_{i=1}^N n_0 \left(1 + \frac{\Delta I_i}{I_0}\right)$$

From (M.3) $1 + \frac{\Delta I}{I_0} = \frac{1}{N} \sum_{i=1}^N \left(1 + \frac{\Delta I_i}{I_0}\right) \quad (\text{M.4})$

$CR_{\text{corrected}}$ then is obtained from $CR_{\text{corr}} = CR / \left(1 + \frac{\Delta I}{I_0}\right)$.

$\frac{\Delta I}{I_0}$ is determined from continuous temperature and pressure charts. Thus, the sum $\frac{\Delta I}{I_0} = \frac{1}{N} \sum_{i=1}^N \frac{\Delta I_i}{I_0}$ must be

changed to an integral.

$$d\left(\frac{\Delta I}{I_0}\right) = \frac{1}{N} \frac{\Delta I(t)}{I_0} \frac{dt}{\Delta t}$$

where Δt is the time for one pass and $N\Delta t = t_t$ is the total time for all passes.

$$\text{Therefore } \frac{\Delta I}{I_0} = \frac{1}{t_t} \int_0^{t_t} \frac{\Delta I(t)}{I_0} dt \quad (\text{M.5})$$

(M.5) can be expressed in terms of relative pressure and temperature changes.

$$I = I_0 e^{-(\frac{\mu}{\rho})\rho x} \Rightarrow \frac{dI}{I} = -\left(\frac{\mu}{\rho}\right)x d\rho \quad (\text{M.6})$$

$\frac{\mu}{\rho}$, x , and ρ are the mass absorption coefficient, path length of the x-ray beam, and density, respectively, for air, the absorbing medium. Assume air to be a perfect gas. This has been shown to be a good assumption as far as the effects on x-ray absorption are concerned. (22)

$$PV = nRT \Rightarrow P = \frac{nRT}{V} = \frac{R}{M} \frac{nM}{V} T = a\rho T \quad (\text{M.7})$$

where R is the universal gas constant

n is the number of moles

M is the molecular weight

a is a constant $= \frac{P}{\rho T}$ at S.T.P.

$$\rho = \frac{P}{aT} \Rightarrow d\rho = \frac{dP}{aT} - \frac{P}{aT^2} dT = \frac{P}{aT} \left(\frac{dP}{P} - \frac{dT}{T} \right) \quad (\text{M.8})$$

Therefore
$$\frac{dI}{I} = -\left(\frac{\mu}{\rho}\right) \frac{xP}{\alpha T} \left(\frac{dP}{P} - \frac{dT}{T} \right) \quad (M.9)$$

With the vacuum chamber in place $x = 30.6$ cm.

$$\left(\frac{\mu}{\rho}\right)_{air} = W_{N_2} \left(\frac{\mu}{\rho}\right)_N + W_{O_2} \left(\frac{\mu}{\rho}\right)_O + W_{Ar} \left(\frac{\mu}{\rho}\right)_{Ar} \quad (M.10)$$

The w 's are the relative compositions by weight. Taking $W_{N_2} = .78$, $W_{O_2} = .21$, $W_{Ar} = .01$, $\left(\frac{\mu}{\rho}\right)_N = 7.52$, $\left(\frac{\mu}{\rho}\right)_O = 11.5$, and $\left(\frac{\mu}{\rho}\right)_{Ar} = 123$ cm²/g for CuK α radiation, one obtains $\left(\frac{\mu}{\rho}\right)_{air} = 9.51$ cm²/g. The values of x , $\frac{\mu}{\rho}$, and α , together with a conversion of pressure to inches of mercury and temperature to °F, give

$$\frac{dI}{I} = -\frac{3.43P}{5(T-32) + 273} \left(\frac{dP}{P} - \frac{dT}{T+459.4} \right) \quad (M.11)$$

The lab temperature was maintained at about 72°F, but on extremely hot days a maximum of 74°F would be reached in the late afternoon, with a minimum of 70°F being attained the next morning. Therefore, the reference temperature T_0 is taken to be 72°F, and the maximum possible deviation from T_0 is ± 2 F°. A survey of pressures for the year preceeding the data accumulation showed a mean of about 30.20 inches, a low pressure of 29.40 inches, and a high of 30.85 inches. P_0 is taken to be 30.20 inches, and the maximum possible deviation from P_0 is about ± 0.80 inches. With $P=P_0$ and $T=T_0$, (M.11) becomes

$$\frac{dI}{I_0} = -(0.351) \left(\frac{dP}{30.2} - \frac{dT}{531.4} \right) \quad (M.12)$$

$|(\frac{dI}{I_0})_T| = 0.12\%$ for a 0.1 inch pressure change and
 $|(\frac{dI}{I_0})_P| = 0.07\%$ for a 1 F° temperature change. Thus,

$$\frac{dI}{I_0} = (0.7 \times 10^{-3}) dT - (1.2 \times 10^{-3}) dP \quad (M.13)$$

when dT is in F° and dP is in tenths of inches. (M.13) gives the intensity change due to variation of air absorption along the path length. There was also found to be a temperature dependence of $\frac{dI}{I_0}$ which was observed for temperature changes too small to allow the effect of the absorption change to be noticed. The count rate was found to increase when the room temperature decreased and vice versa. This is attributed to temperature variations of the detector system efficiency, and can be accounted for by adding to (M.13) a term $-(1.9 \times 10^{-3}) dT$. Then

$$\frac{dI}{I_0} = -(1.2 \times 10^{-3}) (dT + dP) \quad (M.14)$$

Thus $|(\frac{dI}{I_0})_T| = |(\frac{dI}{I_0})_P| = 0.12\%$ for a 0.1 inch pressure change and a 1 F° temperature change, respectively. It has been stated that in the laboratory $T = T_0 \pm 2^\circ$ as a maximum temperature interval, and $P = P_0 \pm 0.80$ inches as a maximum pressure interval. If these limits were reached during a single run, then count rates at the same reciprocal space position at the times corresponding to these limits would be different.

$|(\frac{dI}{I_0})_P| = 0.48\%$ for a 4 F° temperature change.

$|(\frac{dI}{I_0})_T| = 1.92\%$ for a 1.60 inch pressure change.

These changes, especially that due to pressure, are not negligible, but since it is the average $\frac{\Delta I}{I_0}$ for an entire run which is of interest, the effect can turn out to be negligible. It depends on how pressure and temperature vary with time during the run. From (M.5) and (M.14) one has

$$\frac{\Delta I}{I_0} = - \frac{1.2 \times 10^{-3}}{t_t} \int_0^{t_t} [\Delta T(t) + \Delta P(t)] dt \quad (M.15)$$

where ΔT is measured in F° and ΔP in tenths of inches. (M.15) is calculated by use of Simpson's rule with a time interval between measurements of ΔT and ΔP of one hour. That is

$$\int_0^{t_t} f(t) dt = \frac{1}{3} [f_0 + f_n + 4(f_1 + f_3 + \dots + f_{n-1}) + 2(f_2 + f_4 + \dots + f_{n-2})] \Delta t,$$

where $\Delta t = \frac{t_t}{n} = 1$ hour, and n is an even integer.

Appendix N. Conversion of [111] Longitudinal Data to Frequencies

From Appendix A the first order scattering is

$$\frac{I(\vec{S})}{BP} = \frac{f^2 e^{-2M}}{2 \left(\frac{\mu}{\rho}\right) m^2} \sum_j \frac{(\vec{S} \cdot \vec{e}_{qj})^2 \bar{E}_{qj}}{\omega_{qj}^2} \quad \vec{S} + \vec{q} = \vec{\tau} \quad (N.1)$$

For $\vec{S}$ along [111], $\vec{S} \cdot \vec{e}_{qj} \neq 0$ only for j corresponding to the longitudinal mode, for which $\vec{S}$ and $\vec{e}_{qj}$ are parallel. Then

$$\frac{I(\vec{S})}{BP} = A \left(\frac{\sin \theta}{\lambda}\right)^2 f^2 e^{-2M} \left[\frac{1}{e^{h\nu_L/kT} - 1} + \frac{1}{2} \right] \frac{1}{h\nu_L/kT} \quad (N.2)$$

where $A = \frac{2h^2}{m^2 \left(\frac{\mu}{\rho}\right) kT} = 7.856 \times 10^{17}$, if $\frac{\sin \theta}{\lambda}$ is expressed in $\text{\AA}^{-1}$, and $T = 295^\circ\text{K}$.

To determine $\nu_L(\vec{q})$ one first determines $\left(\frac{I_{\text{total}}}{BP}\right)_{\text{meas}}$, and then subtracts $\left(\frac{I_2 + I_{\text{higher}}}{BP}\right)_{\text{calc.}}$ to get $\left(\frac{I_1}{BP}\right)_{\text{meas}}$, which is then set equal to (N.2)

$$\left(\frac{I_1}{BP}\right)_{\text{meas}} = A \left(\frac{\sin \theta}{\lambda}\right)^2 \left[\frac{1}{e^x - 1} + \frac{1}{2} \right] \frac{1}{x} \quad (N.3)$$

where $A \left(\frac{\sin \theta}{\lambda}\right)^2 = A f^2 e^{-2M} \left(\frac{\sin \theta}{\lambda}\right)^2$ and $x = \frac{h\nu_L}{kT}$. Thus, for each $\frac{\sin \theta}{\lambda}$ value of interest, x must satisfy the equation

$$C \left(\frac{\sin \theta}{\lambda}\right) x = \frac{1}{e^x - 1} + \frac{1}{2} \quad (N.4)$$

where $C \left(\frac{\sin \theta}{\lambda}\right) = \left(\frac{I_1}{BP}\right)_{\text{meas}} / A \left(\frac{\sin \theta}{\lambda}\right)^2$.

The frequency determination has been made for the

original [111] data, for which the exit horizontal divergence was slightly larger than that for later data. The appropriate values of B and k are 3.99×10^{-21} and 0.86 , respectively. (N.4) is solved for x graphically by determining the intersection of the curve $y = \frac{1}{e^x - 1} + \frac{1}{2}$ with the line $C(\frac{\sin \theta}{\lambda})x$ for each $\sin \theta / \lambda$ value. The resulting frequencies, along with the neutron results, plotted against the reduced, dimensionless wave vector are shown in Figure N-1. The dispersion curves fall below that of the neutron data, and they should all coincide, since they are supposed to represent the same dispersion curve. Each curve is associated with the reciprocal space traversal indicated, and it is seen that the shape of the two curves for the (111) to (222) traversal is quite similar to the shape of the corresponding two curves associated with the (222) to (333) traversal. The two curves for a traversal between reciprocal lattice points, however, are quite different, and this is due to the asymmetry in the measured count rate.

Figure N-1. Lead [111] L Dispersion Curves
Calculated from X-Ray Data

Appendix O. Switch Settings for a Typical TDS Run

The use of the 128 channel analyzer in conjunction with the diffractometer 2θ scans has been described in detail in the literature.⁽¹⁶⁾ The switches which control the operation of the analyzer are shown clearly in Appendix K, Figure K-2. S_1 is the start switch, the signal from which causes the analyzer to start in channel zero during operation in the multiscaling mode. S_2 is the stop switch, which must be closed after the completion of a cycle and before the initiation of the next cycle by the start switch, which otherwise causes the multiscaling to start in any channel at random. S_3 is the hold switch, whose signal causes the analyzer to suspend multiscaling while the 2θ high angle turn around occurs. The 2θ high and low angle turn around switches on the diffractometer control the diffractometer's cycling.

In operation, channels 1 through 62 collect data for increasing 2θ , while channels 63 through 124 collect data for decreasing 2θ . When the start switch is closed, channel zero is activated and the analyzer remains there for the prescribed dwell time, but no data is accumulated. This time delay has to be allowed for in order that channel 1 correspond to the desired angular interval. The hold switch is set so as to be closed just when channel 62 jumps to channel 63. After the high angle turn, which is accomplished while the hold is on, the multiscaling then

starts at the beginning of channel 63. Throughout several days of running, the switch settings are found to vary in such a way that the hold occurs at the end of channel 62 plus or minus 6% of one channel. Thus, channels 63 to 124 coincide well with channels 62 to 1, and a folding of the data can be carried out. Channels 125 to 127 are discarded. The chosen 2θ sweep speed of 2° per minute, and the chosen channel dwell time of 8.33 seconds dictate that the angular interval covered for 62 channels is 17.22° 2θ , while the 2θ interval per channel is 0.28° . When turn around time is included, each cycle requires about nineteen minutes to complete. Table 0-1 shows the desired and actual angular settings for a representative data run between the (200) and (300) reciprocal lattice points.

<u>Occurrence</u>	<u>Desired 2θ Position</u>	<u>Actual 2θ Position</u>
Low Angle Turn	37.86°	37.82°
Stop Off		38.42°
Start On	38.87°	38.87°
Start Off		39.80°
Hold On	56.37°	56.37°
High Angle Turn	56.57°	56.46°
Hold Off	56.37°	56.37°
Start On		39.53°
Start Off		38.65°
Channel Run Out	38.31°	38.31°
Stop On	38.01°	38.04°

Table 0-1. Angular Settings for a Typical Data Run

Appendix P. Ion Bombardment and Sputtering

The lead samples had to be ion bombarded and sputtered in order to produce surfaces which would not oxidize. The chamber used for this purpose was designed and built by Mr. John Beaver. The main part of the apparatus consists of a glass envelope containing two electrodes, the upper one carbon, and the lower an aluminum dish in which the sample is placed. The general setup is shown in Figure P-1. A coil surrounds the entire apparatus and is used to produce a magnetic field along the axis of the tube. The polarities shown apply to the case when the chamber is used for sputtering. An argon atmosphere is maintained at a pressure of about 20-30 microns. The sputtering operation is used when it is desired to cover the sample with a thin carbon layer in order to protect the surface from oxidation. With the 400 V applied as shown argon ions are accelerated toward the carbon electrode, where carbon atoms are knocked out and sprayed throughout the tube. A covering should slowly be built upon the sample. If both the polarities are reversed, the system is in the ion bombardment configuration. The sample then is bombarded with argon ions in the hope that any surface contamination will be removed.

In practice, after the sample is placed into its proper location, the system is pumped down to about .002 microns for a day or so. This causes the removal of a

Figure P-1. Ion Bombardment and Sputtering Chamber

kerosene surface layer which is applied to protect the crystal from oxidation during transfer from the acid polishing apparatus to the chamber. Argon gas is then allowed to flow through the chamber at such a rate that about a 20-30 micron pressure is maintained. The sample is first ion bombarded for about an hour, after which the polarities are reversed, and sputtering is carried on for about eight hours. During the bombardment process the discharge emits a bright violet light, while during sputtering at the same pressure the emitted light is much more subdued. Upon removal from the chamber the crystal is always found to have a shiny surface which can be maintained indefinitely if the sputtering time is about the eight hours mentioned above. If the sputtering time is only one hour or so, the surface will be oxidized after having been exposed overnight to the air.

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