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AN ABSTRACT OF THE THESIS OF B. Frederick Brace, Jr. for the Master of Science in Physics presented August 30, 1972.

Title: Measurements of the Mössbauer Fraction in Chromium.

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Precision measurements of the Mössbauer fraction of Fe^{57} in chromium were made using the black absorber technique over a range of temperatures from 78K to 792K. Because of uncertainty in corrections at high temperatures, only the data collected from 78K to 600K was used in analyzing the results.

The f values were analyzed in terms of a Debye approximation. This analysis of the data yielded a theoretical fit which was based on two adjustable parameters (a Debye temperature of 438K and an anharmonicity parameter of $2 \times 10^{-4} \text{K}^{-1}$).

The f measurements were also analyzed using a theory proposed by Mannheim in 1968. Two different phonon density of states functions

(Feldman, Muhlestein) were applied to Mannheim's theory, and the resulting theoretical fits to experimental values showed a decrease in the force constant as a result of introducing an impurity into the chromium. Feldman's phonon spectrum yielded a force constant ratio of $1.30^{+.07}$ and an anharmonicity parameter of $\epsilon = 2.5(^{+.5}) \times 10^{-4} \text{K}^{-1}$, and Muhlestein's spectrum gave a ratio of $1.25^{+.06}$ and an anharmonicity parameter $\epsilon = 2.0(^{+.5}) \times 10^{-4} \text{K}^{-1}$.

TO THE OFFICE OF GRADUATE STUDIES:

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August 30, 1972

MEASUREMENTS OF THE MÖSSBAUER FRACTION
IN CHROMIUM

by

B. FREDERICK BRACE, JR.

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
in
PHYSICS

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1972

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INTRODUCTION

The Mössbauer effect is the name given to the physical process in which a radioactive nucleus bound in a lattice emits a gamma ray without the creation of a lattice phonon. This thesis describes how the Mössbauer effect is used to make measurements of the mean square displacement of the emitting nucleus from its equilibrium position. Results are presented of such measurements made on a chromium sample containing radioactive Co^{57} , and a comparison is made between theoretical and experimental values for the mean square displacement of the cobalt impurity atom.

Chromium was chosen mainly because previous systematic precision Mössbauer measurements had been done on face centered cubic metals (Nussbaum et. al. (1, 2)), and it was desirable to begin similar studies on metals in the bcc system. Chromium is frequently used as a source for Mössbauer experiments, and yet a systematic study of the kind presented in this thesis has not been done. Also, two phonon density of states curves have been published recently for chromium (3, 4). These density of states functions allow the chromium measurements to be analyzed in terms of a theory proposed by Mannheim (5). According to this theory it is possible to calculate the mean square displacement of the impurity atom (Co^{57}) using the phonon density of states for the host

material (Cr). The chromium measurements have also been analyzed using the Debye theory.

This thesis contains three appendices. Appendix A describes measurements made of the internal magnetic field in chromium. Various experimenters have observed (6) that chromium undergoes two magnetic phase transitions. Measurements of the internal magnetic field in chromium were necessary to determine whether it would have any influence on the mean square displacement of the cobalt atoms.

Appendix B presents results of calculations of the moments of the frequency spectrum. These calculations are based on the phonon density of states function.

Appendix C lists the computer programs used in making the calculations of the mean square displacement of the Co^{57} atom using the Mannheim theory.

F MEASUREMENTS

I. EXPLANATION OF THE MÖSSBAUER FRACTION

Using the Mössbauer effect, it is possible to determine the mean square displacement of atoms whose nuclei are emitting gamma rays. Provided that the lifetime of the particular nuclear transition is long compared with the period of vibration of the atom,* Lipkin (?) has shown that:

$$f = \exp [-k^2 \langle x^2 \rangle] \quad (1)$$

Here $\langle x^2 \rangle$ represents the mean square displacement in the direction of emission of an atom which has emitted a gamma ray, k is the wave number of the gamma ray, and f , called the Mössbauer fraction, is the probability that an atom emitting a gamma ray will do so without creating a lattice phonon. In dealing with a large number of emitting nuclei, f can also be interpreted as being the fraction of those nuclei which, upon emission of a gamma ray, do not excite a normal mode of lattice vibration. This latter interpretation is more helpful in understanding the discussion on experimental f measurements which follows.

*The half-life_{1/2} of the 14.4 keV transition in Fe⁵⁷ has been found (8) to be around 10^{-7} sec. This is much longer than the period of vibration of an atom which is normally on the order of 10^{-13} sec.

The Co^{57} which diffused into the chromium sample decays according to the scheme shown in Stevers (8). The 14.4 keV gamma ray is the one used for Mössbauer measurements. In making Mössbauer measurements using Co^{57} one is, therefore, interested in measuring the fraction of 14.4 keV gamma rays which are emitted without creation of a lattice phonon and thus without loss of energy. Such gamma rays will henceforth be called "resonant" 14.4 keV gamma rays.

The technique used in making the f measurements of Cr was the "black absorber" technique developed by Housley and described by Dash (9). This technique depends upon the use of an absorber which is almost entirely opaque to the resonant 14.4 keV gamma rays and almost entirely transparent to the non-resonant 14.4 keV gamma rays. The latter consist of gamma rays emitted with resulting creation of one or more lattice phonons. Such an absorber is prepared by combining lithium and ammonium fluoroferrates containing enriched Fe^{57} . This mixture produces an absorber which has an absorption spectrum approximately twenty times as wide as the natural line width of the 14.4 keV gamma ray. (Natural line width is around 10^{-8} eV.) At the same time the width of the absorption spectrum is much less than the range of energies of the non-resonant gamma rays, which can be as large as .1 eV.

The fraction of 14.4 keV gamma rays which are resonant (the Mössbauer fraction) is given by:

$$f = \frac{\text{total number of 14.4 keV } \gamma \text{ rays} - \text{non-resonant 14.4 keV } \gamma \text{ rays}}{\text{total number of 14.4 keV } \gamma \text{ rays}} \quad (2)$$

or

$$f = \frac{(I_{\infty} - I_B) - (I_0 - I_B)}{I_{\infty} - I_B} \quad (3)$$

where I_{∞} represents the intensity of all the 14.4 keV gamma rays emitted by the source, I_0 the intensity of non-resonant 14.4 keV gamma rays, and I_B the intensity of gamma rays other than 14.4 keV gamma rays which fall within the energy band of the gamma ray detector and its associated counting equipment.

Therefore

$$f = \frac{I_{\infty} - I_0}{I_{\infty} - I_B} \quad (4)$$

In the actual determination of the Mössbauer fraction, three experimental quantities are measured: viz. I_{∞}' , I_0 and I_B' . Both I_{∞}' and I_B' must be corrected to yield the true values I_{∞} and I_B .

Therefore

$$f = \frac{\alpha I_{\infty}' - I_0}{\alpha' I_{\infty}' - \beta I_B'} \quad (5)$$

where α , α' and β are correction factors. The f values calculated from equation (5) are called "raw f " values. These raw f values must then be corrected for various effects described later to produce experimental f values.

The final expression for the Mössbauer fraction is:

$$f = \frac{\alpha I_{\infty}' - I_0}{\alpha I_{\infty}' - \beta I_B'} \times \frac{1}{C_B} \times \frac{1}{C_g} \quad (6)$$

with C_B representing correction for blackness of the absorber and C_g correction for geometry of the system.

The measurement of I_{∞}' , I_0 , and I_B' is made as follows. To facilitate the explanation, consider the source to be mounted on a loudspeaker and the absorber to be stationary. When the loudspeaker is driven at high frequencies, the energy of the emitted gamma rays is Doppler shifted, so that for the vast majority of the time, the resonant gamma rays' energy is either too large or too small to be absorbed by the Fe^{57} in the black absorber. In this case the detector, which is located beyond the absorber, measures the intensity of practically all of the 14.4 keV gamma rays emitted by the source (I_{∞}') plus the background radiation (I_B'). When the speakers are stopped, practically all resonant 14.4 keV gamma rays will be absorbed by the absorber, assuming that the emission spectrum is centered with respect to the absorption spectrum of the black absorber. In this case the detector measures the intensity of the non-resonant 14.4 keV gamma rays (I_0) plus background radiation (I_B'). In order to determine the background radiation, a copper foil is inserted between the absorber and the detector. This foil is almost completely opaque to the 14.4 keV gamma rays and almost completely transparent to the 122 keV gamma rays. The latter arise from the decay of Fe^{57} (see Muir (8)) and constitute the main source of background radiation.

II. F CORRECTION FACTORS

α Correction Factor

The correction factor α is applied to I_{∞} to account for the fraction of time during each cycle when the loudspeakers are at or very close to zero velocity. During this time the resonant 14.4 keV gamma rays are absorbed, and the intensity of all 14.4 keV gamma rays as measured by the detector will be less than it actually is.

In order to understand how α is determined, it is necessary to know something about the loudspeaker system used in our Mössbauer experiments. It consists of two loudspeakers placed back to back. Their diaphragms are connected to each other by a metal tube through their centers. This tube causes the two speakers to vibrate together. One speaker is driven by an oscillator. The coil on the second speaker, which is vibrating with the first, produces an output voltage proportional to the velocity at which the speakers are vibrating. A constant, called the speaker constant, is characteristic of the system and gives the relationship between the velocity of the speakers and the output voltage. The speaker constant for the system used in making Mössbauer measurements on chromium was 95.1 mm/sec/volt.

In finding α , a source was mounted on the speakers, and the black absorber placed between the source and the detector. A signal was fed into the speakers from an oscillator, and the output voltage fed into an oscilloscope. The voltage read off the oscilloscope was converted to speaker velocity using the speaker constant. For each frequency a measurement of the 14.4 keV gamma ray intensity was made using the detector. A graph of count rate versus $1/\text{Amplitude in } (\text{mm/sec})^{-1}$ is shown in

figure 1. The graph extrapolated to 0 (corresponding to infinite amplitude) gives the expected count rate if none of the resonant gamma rays were absorbed by the black absorber. The count rate at infinite amplitude divided by the count rate corresponding to the amplitude of the speakers during measurement of the Mössbauer fraction gives the correction factor (α). In the analysis of the chromium data α was 1.006.

β Correction Factor

The correction factor β applied to the measured background intensity is necessary because the copper foil which is placed between the absorber and the detector is neither completely opaque to 14.4 keV gamma rays nor completely transparent to the 122 keV gamma rays. In general, the intensity of gamma rays transmitted by a material is given by:

$$I(d) = I(o)\exp(-\mu_m \xi) \quad (7)$$

where $I(o)$ is the incident intensity, μ_m is the mass absorption coefficient, and ξ is the absorber thickness in gm/cm^2 .

The copper foil used in the chromium f measurements consisted of four nearly identical thicknesses of foil. One of these thicknesses was measured and found to have an area of 131 cm^2 and a mass of 2.175 gm. The ξ for one thickness was, therefore, $16.6 \times 10^{-3} \text{ gm}/\text{cm}^2$ and for the four thicknesses 66.4×10^{-3} . The values of the mass absorption coefficient for 14.4 keV and 122 keV gamma rays in copper were found (12) to be $.83 \text{ cm}^2/\text{gm}$ and $.29 \text{ cm}^2/\text{gm}$ respectively. Calculations using equation (7) showed that .3 percent of the incident 14.4 keV gamma rays and 98.1 percent of the 122 keV gamma rays are transmitted by the copper foil.

Figure 1. Graph of count rate versus 1/amplitude from which the correction factor (1.006) was determined. This value corresponds to the value 1/amplitude at which the speakers operate.

Therefore

$$I_B' = .981 (\epsilon I_{122}) + .003 I_{\infty}(14.4) \quad (7a)$$

where ϵ is the efficiency ratio ($\epsilon_{122}/\epsilon_{14.4}$) which describes the ability of the detector to "detect" these gamma ray energies. ϵI_{122} is the actual background I_B :

$$\begin{aligned} \epsilon I_{122} = I_B &= (1/.981)I_B' - (.003/.981) I_{\infty} \\ &= 1.019I_B' - .003I_{\infty} \end{aligned} \quad (7b)$$

the denominator of equation (3) becomes:

$$\begin{aligned} I_{\infty} - I_B &= \alpha I_{\infty}' + .003 I_{\infty} - 1.019I_B' \\ &= \alpha I_{\infty}' - 1.019I_B' + .003(1.006I_{\infty}') \\ &= 1.009I_{\infty}' - 1.019I_{\infty}' \end{aligned} \quad (7c)$$

From this equation the constants α' and β are seen to be 1.009 and 1.019 respectively.

C_g Geometry Correction Factor

C_g , called the geometry correction, corrects for reradiation by the absorber into the detector. There are two main sources of these re-radiated gamma rays: 1) re-emission of 14.4 keV gamma rays by absorbing nuclei in the absorber and 2) incoherent Compton scattering of resonant gamma rays in the absorber.

The correction C_g is found from the equation given by Housley (11),

$$C_g = \frac{1 - \frac{\Omega_{SA}\Omega_{AD}}{(1+\alpha)4\pi\Omega_{SD}}}{1 + 1.5 (\exp[\sigma_c x_c] - 1) \frac{\Omega_{SA}\Omega_{AD}}{4\pi\Omega_{SD}}} \quad (8)$$

where $\sigma_c x_c$ is the Compton thickness of the absorber, α the internal conversion coefficient, and Ω_{SA} , Ω_{AD} , Ω_{SD} are solid angles which are defined in figure 2.

Figure 2. Scale diagram of experimental setup. The measurements shown were used in calculating the solid angles for the geometry correction factor, C_g .

This equation can be simplified by letting

$$B = \frac{\Omega_{SA} \Omega_{AD}}{4\pi \Omega_{SD}} \quad (9)$$

so that

$$C_g = \frac{1 - \frac{1}{1+\alpha} B}{1 + 1.5(\exp[\sigma_c \alpha] - 1) B} \quad (10)$$

The Compton thickness of the absorber was found in the following manner. A source was mounted on the loudspeaker system. The loudspeakers were driven and count rates measured with and without the black absorber in place. The count rate with the absorber in place was less due to various interactions between the gamma rays and the electrons in the absorber, the most important of these interactions being photoelectric effect and Compton scattering. The equation representing transmitted intensity of gamma rays through the absorber is given by

$$I(d) = I(0) \exp -(\mu/\rho)_t d \quad (11)$$

where $(\mu/\rho)_t$ is the total cross section minus the cross section for coherent scattering, $I(0)$ is the incident intensity, and d is the thickness of the absorber in gm/cm^2 .

After correcting $I(d)$ for the time during which the loud speakers are at 0 velocity, the ratio $I(d)/I(0)$ was found to be .425. Using equation (11) the "total thickness" of the black absorber $((\mu/\rho)_t d)$ was found:

$$(\mu/\rho)_t d = -\ln .425 = .85 \quad (12)$$

In order to "separate out" the Compton thickness from the total thickness, it was assumed that the chemical formula for the black

absorber is $\text{LiF} \cdot \text{NH}_4\text{F} \cdot \text{FeF}_2$ and that

$$\frac{(\mu/\rho)_t d}{(\mu/\rho)_c d} = \frac{(\mu/\rho)_t}{(\mu/\rho)_c} \quad (13)$$

where $(\mu/\rho)_c d$ is the Compton thickness and $(\mu/\rho)_c$ is the cross section for incoherent Compton scattering from bound electrons.

The ratio $(\mu/\rho)_t/(\mu/\rho)_c$ was calculated using the chemical formula for the black absorber and tables of photon cross sections (12). These cross sections are shown in table I.

Using the value calculated for the ratio, an estimate of the Compton thickness was made:

$$\begin{aligned} (\mu/\rho)_c d &= .85 \times \frac{2.393}{66.075} \\ &= .0308 \end{aligned} \quad (14)$$

This value for the Compton thickness was then substituted into equation (10) with the result:

$$C_g = \frac{1 - \frac{1}{1+\alpha} B}{1 + .045B} \quad (15)$$

For Fe^{57} the internal conversion coefficient, α , is 8.2. Substituting this value into equation (15) and using the binomial expansion:

$$C_g = (1 - .093B)(1 - .045B) \quad (16)$$

$$\text{or} \quad C_g = 1 - .138B \quad (17)$$

The various solid angles contained in B were found using the measurements in figure 2, and C_g was calculated to be .9992. (In the actual calculations in this thesis .9983 was used for C_g . This number was based on erroneous values for the cross sections. These errors were

TABLE I
CROSS SECTIONS USED IN EVALUATION OF C_g

ELEMENT	NUMBER OF ATOMS	$(\mu/e)_t^*$	$(\mu/e)_c^*$
Hydrogen	4	.175	.144
Lithium	1	8.92	.540
Nitrogen	1	1.02	.148
Fluorine	4	1.46	1.456
Iron	1	54.5	.105
TOTAL		66.075	2.393

* In the tables of photon cross sections (12), $(\mu/e)_t$ is called $(\mu/e)_{tot, t-coh}$, and $(\mu/e)_c$ is called $(\mu/e)_{inc, t}^{BD}$.

only discovered after the work had been completed. This discrepancy will have a negligible effect on the results.)

C_B Blackness Correction Factor

The final correction applied to the f values is the blackness correction, C_B . This correction is necessary because the black absorber is not a perfect absorber (ie. some of the resonant gamma rays can pass through it).

In order to make this correction, the chromium was mounted in the furnace described by Steen (13) and lineshape measurements using the black absorber were made at 353 K, 454 K, and 633 K. (One of these lineshapes is shown in figure 3.) The lineshape itself is actually the result of the convolution of the emission line of Co^{57} and the absorption line of the lithium and ammonium fluoroferrate mixture.

The shapes of these emission and absorption lines differ with the result that about 3% of the resonant radiation is not absorbed. About 2.5% of this amount is due to escape of resonant radiation through the wings of the emission line shape (the shaded section in figure 4 below)

Figure 4. Shaded region shows area where emission spectrum and absorption spectrum do not overlap.

This 2.5% was arrived at by assuming a Lorentzian shape for the emission line and a simplified shape for the absorption line and integrating

Figure 3. Lineshape taken using the Cr source and the black absorber with the Cr held at 80°C. C represents the center line of the lineshape.

over the wings on both sides.

The remaining part of the $\frac{3}{4}\%$ correction is due to resonant radiation which passes through the absorber without meeting an absorbing nucleus. The size of this correction was found by measuring the Mössbauer fraction with one absorber and two absorbers and noting the increase in apparent $\text{raw } f$ due to the decrease in transmitted resonant gamma rays.

The diagram above shows the emission line centered with respect to the absorption line. In making f measurements over a range of temperatures, the position of the emission line shifts. This change in energy is a result of second order Doppler shift. As the temperature of the chromium sample increases, the speed at which the Co atoms vibrate increases, and the energy of the emitted gamma rays is altered. A consequence of this shift in emission line is that the amount of resonant radiation escaping through the wings of the emission line changes.

In making f measurements one is concerned with the position of the emission line at zero velocity (loudspeakers at rest). For each of the three lineshapes taken using the chromium and the black absorber, the position of emission line at 0 velocity was found. The shift of the position of the emission line with respect to the center of the lineshape was then plotted as a function of temperature. This shift, called "isomer shift", is composed of two parts: 1) thermal shift which was described above, and 2) a shift caused by changing s electron density at the nucleus of the emitting atom, a result of expansion in the material. Assuming the relationship between this isomer shift and temperature is linear, the position of the emission line at 0 velocity could then be found for any temperature. (The graph of isomer shift vs. temperature is shown in figure 5.)

Figure 5. Graph of isomer shift versus temperature used in determining the blackness correction factor, C_B .

Since the lineshape is a convolution of the emission line of the 14.4 keV gamma rays and the absorption line of the black absorber, any point on the flat bottom of the lineshape represents essentially constant overlapping of the two lines. This constant overlap corresponds to the 3% correction for transmission of resonant gamma rays. For any point off the bottom of the lineshape, the overlap of the emission and absorption lines is decreased which necessitates a larger correction for transmission of resonant gamma rays. For determining the correction a vertical linear scale was placed beside the graph of the lineshape. The bottom of the scale corresponded to 97% absorption of resonant gamma rays and the top to 0% absorption. The zero velocity of the emission line for a particular temperature was marked on the graph, and the correction for transmission of resonant gamma rays was read from the vertical scale. This process is illustrated in figure 6.

Figure 6. Magnified graph of the lineshape of figure 3. The 0 velocity position corresponds to a point on the lineshape which in turn corresponds to a particular blackness correction on the left.

EXPERIMENTAL PROCEDURE

I. SOURCE PREPARATION

The chromium source was prepared from a single crystal chip of the metal. Prior to electroplating Co^{57} activity onto the surface of the chromium, the chromium chip was degreased with acetone, mounted, and etched with dilute HCl. The technique used in mounting the chromium was identical to that described by Steen (13) except that Taconite rather than polystyrene was used to coat the copper connecting lead and the edges and back of the chromium sample. The etch with dilute HCl produces a dull surface better suited for electrodeposition.

The electrolyte used is that described by Dezsi (14), viz. an aqueous solution of 2.5 gm/100 ml hydrazine hydrate and 2.5 gm/100 ml ammonium dicitrate. The pH of the electrolyte is then adjusted to 10 with the addition of concentrated ammonium hydroxide. During electroplating, ammonia must be added periodically to the electrolyte to maintain this pH. Activity was added to the electrolyte in the form of CoCl_2 in .1N HCl.

The setup for the electroplating operation is shown in figure 7. The chromium serves as the cathode and the platinum crucible as the anode. Current through the electrolytic cell is controlled by a current regulator. The magnetic field, in acting on the ions in solution, stirs

Figure 7. Electrolytic cell used in plating Co^{57} onto chromium.

the electrolyte and thus helps increase the efficiency of electrodeposition.

The source was prepared by maintaining a cell voltage of 2V and cell current of 5mA for the major part of the electroplating operation. When the chromium was taken out of the electrolyte to check its activity and then put back into the electrolyte, it was observed that some of the activity redissolved in the electrolyte. During the last five hours of the electroplating, the current was raised to 20mA with a cell voltage of 10V. This increase did not seem to produce any harmful results. The whole electrodeposition process lasted twenty-five hours and produced a source of .87mC before diffusion and cleaning.

The chromium source was then placed in a quartz tube and the tube filled with hydrogen. The quartz tube containing the sample was placed in a tube furnace and heated to $1050 \pm 2^\circ\text{C}$. At 500°C and 1000°C the tube was flushed with hydrogen. After four hours in the furnace, the tube was quickly drawn from the furnace and plunged into a bucket of cold water. The sample was then cleaned with pumice soap and rinsed with distilled water. Its activity after cleaning was .6mC.

After a quick etch with 6N HCl, the chromium source was mounted on the loudspeakers and a Mössbauer line shape measurement taken (see Steen (13)). The Mössbauer line shape of the source (see figure 8) was slightly broader than natural (.23mm/sec compared with .20mm/sec). The line shape showed no irregularity and, based on past experience with other sources, it was assumed that the vast majority of Co^{57} atoms had found their way into substitutional sites in the chromium lattice.

Figure 8. Lineshape taken using the chromium source and a natural iron absorber. The chromium source is a single line source. It represents the convolution of the single line chromium source and the two inner lines of the iron spectrum.

II. EXPERIMENTAL METHODS

A series of room temperature f measurements was made with the sample mounted on the loudspeaker system. At the same time the positions of the sample, absorber and detector were noted so that geometry corrections could be made.

The experimental technique used in making the chromium f measurements was essentially the same for both high and low temperature cases. For the high temperature measurements the sample was mounted in a small furnace and room temperature f measurements were made. These f measurements, when compared with the original room temperature f measurements, allowed corrections to be made for the different geometry of the furnace and for absorption and scattering in the beryllium windows of the furnace. The same procedure was followed in low temperature work to obtain the correction factor for the cryostat geometry. The temperature inside the furnace was increased and held at particular values by a Cryogenic Research TC 103 Temperature Controller which controlled the temperature to within ± 1 K. At each temperature two or three f measurements were taken. The second and third values gave a check on the consistency of the results. This procedure was continued to a temperature of 792K.

For the low temperature measurements, the chromium sample was mounted inside a cryostat and the loudspeakers on which the black absorber was mounted were suspended vertically below the cryostat. Following the method used in the high temperature work, f measurements were taken from 78K to room temperature.

The results of both sets of measurements are presented in table II.

For both sets of measurements the correction for the shift of the

emission line was made. However, above 600K the uncertainty involved in reading the correction off the graph was so large that these high temperature f values have been deleted from the analysis described in the next section.

TABLE II
EXPERIMENTAL F. VALUES

TEMPERATURE (K)	RAW f	CORRECTED* f	-Ln f	-Ln f (Debye theory)
78	.867	.910	.094	.095
103	.856	.899	.107	.107
120	.847	.890	.116	.116
138	.837	.880	.128	.126
174	.818	.861	.150	.149
208	.801	.843	.171	.172
251	.775	.816	.203	.202
294	.756	.793	.232	.234
334	.733	.769	.263	.265
376	.709	.744	.295	.297
413	.687	.722	.326	.326
453.5	.663	.698	.360	.360
494.5	.639	.673	.396	.394
543	.610	.645	.439	.434
593	.579	.617	.483	.477
644	.549	.595	.519	.522
693	.516	.573	.557	.566
742	.485	.557	.584	.600
792	.445	.535	.626	.656

*The error involved in these f values is given by the sum of the statistical accuracy of the individual measurements (better than .5%) and the systematic errors introduced by the correction factors (estimated at .5%).

ANALYSIS OF DATA

I. DEBYE APPROXIMATION

The corrected f values shown in table II have been analyzed using two methods. The method used in this section depends on the assumption that the chromium with its Co^{57} impurity behaves like a Debye solid. A Debye solid is described by a phonon density of states function:

$$\begin{aligned} \gamma(\omega) &= a\omega^2 & \text{for } \omega \leq \omega_{\max} \\ \gamma(\omega) &= 0 & \text{for } \omega > \omega_{\max} \end{aligned} \quad (18)$$

$\omega_{\max}$ is known as the characteristic cut-off frequency.

As mentioned previously, if the lifetime of the excited nuclear state is long compared with the period of vibration of the emitting atom, then the Mössbauer fraction can be expressed by

$$f = \exp[-k^2 \langle x^2 \rangle] \quad (19)$$

For analysis of experimental results it is more convenient to write the above equation in the form

$$f = \exp(-2W) \quad (20)$$

where $2W$ is the familiar Debye-Waller factor of x-ray scattering. Assuming that the solid under study is a Debye solid, f can be written as (see Muir (15))

$$f = \exp \left\{ -3 \frac{(\hbar k)^2}{mk' \Theta} \left[\frac{1}{4} + \left(\frac{T}{\Theta} \right)^2 \int_0^{\Theta/T} \frac{x}{e^x - 1} dx \right] \right\} \quad (21)$$

where k' is Boltzman's constant, Θ the characteristic Debye temperature, and $x = \hbar \omega / k' T$.

In order to simplify the expression on the right, consider a gamma ray emitted from a free nucleus. Conservation of momentum requires that the momentum of the gamma ray and that of the recoiling nucleus be equal and opposite.

Therefore

$$\begin{array}{c} \leftarrow \text{---} \bigcirc \text{---} \rightarrow \\ \hbar k = E/c \end{array} \quad (22)$$

$$\text{or} \quad \frac{\hbar^2 k^2}{2m} = \frac{E^2}{c^2} \times \frac{1}{2m} \quad (23)$$

$$E_r = \frac{\hbar^2 k^2}{2m} = \frac{E^2}{2mc^2} \quad (24)$$

where E_r is the recoil energy of the nucleus and E is the energy of the gamma ray. The recoil energy of a Co^{57} nucleus emitting a 14.4 keV gamma ray can be easily calculated and is equal to 1.957×10^{-3} eV.

Using equation (24) allows (21) to be written as:

$$f = \exp \left\{ -6 \frac{E_r}{k' \Theta} \left[\frac{1}{4} + \left(\frac{T}{\Theta} \right)^2 \int_0^{\Theta/T} \frac{x}{e^x - 1} dx \right] \right\} \quad (25)$$

Next factoring out $1/4$ and letting $z = \frac{\Theta}{T}$:

$$f = \exp \left\{ -\frac{3}{2} \frac{E_r}{k' \Theta} \left[1 + \frac{4}{z^2} \int_0^z \frac{x}{e^x - 1} dx \right] \right\} \quad (26)$$

Using the notation of Muir (15) in his tables for computing Mössbauer fractions:

$$Q(z) = \int_0^z \frac{x}{e^x - 1} dx \quad (27)$$

$$P(z) = 1 + \frac{4}{z^2} Q(z) \quad (28)$$

$$\text{and} \quad R(z) = \frac{3}{2k'} P(z) \quad (29)$$

and substituting these expressions into equation (26) produces the following expression:

$$f = \exp \left[- \frac{E_r}{\Phi} R(z) \right] \quad (30)$$

$$\ln f_h = \frac{-E_r}{T} \frac{R(z)}{z} \quad (31)$$

Equation (31) can then be rewritten:

$$\frac{R(z)}{z} = \frac{-\ln f_h \times T}{E_r} \quad (32)$$

or finally

$$\frac{R(z)}{z} = \frac{-\ln f_h \times T}{1.957 \times 10^{-3} \text{eV}} \quad (33)$$

This last equation assumes that the potential energy between atoms in the solid is harmonic. (I.e. that the potential energy is expressible as a quadratic equation.) In order to conform more nearly to conditions in the real solids, the potential energy must be corrected for higher order terms.

$$V = ax^2 + bx^3 + cx^4 \quad (34)$$

Maradudin and Flinn (16) have suggested that this anharmonicity in the potential energy can be taken into account by letting

$$\ln f(T) = (1 + \epsilon(-2)T) \ln f_h(T) \quad (35)$$

$\epsilon(-2)$ is called the anharmonicity parameter. It gives a rough indication of a solid's deviation from harmonic behavior. Therefore (33) becomes

$$\frac{R(z)}{z} = \frac{-\ln f(T)}{(1 + \epsilon T)} \times \frac{T}{1.957 \times 10^{-3} \text{eV}} \quad (36)$$

In obtaining a theoretical fit for the chromium data, a value for the anharmonicity parameter was guessed at and substituted into equation (36). Each chromium f value with its corresponding temperature then produced a value of $R(z)/z$. Values of this ratio for various values of $z = \frac{\Theta}{T}$ have been tabulated (15), so that each value of z corresponds to a Debye temperature (Θ). As a result, one value for the anharmonicity produces a series of Debye temperatures each of which corresponds to a particular f measurement. The "best" theoretical fit to this model is defined as that anharmonicity parameter whose series of Debye temperatures has the least mean square deviation over the range of temperatures measured.

This procedure is illustrated in table III for three values of the anharmonicity parameter. The best fit for the chromium f measurements was found using an $\epsilon(-2)$ of $2 \times 10^{-4-1}$. This choice of parameter gave a series of Debye temperatures whose average value was 438K. A graph of experimental values of $\ln f$ vs T is given in figure 9 with the theoretical points found using the above results.

In work with other metals (1), the Debye temperature derived using the method just described and the Debye temperature of the host were used in estimating changes in force constants which result when an impurity is added to the host. However, the next section describes a better way of determining these changes in force constant.

TABLE III
EFFECTIVE DEBYE TEMPERATURES FOR Fe^{57} IN Cr

TEMPERATURE	DEBYE TEMPERATURE		
	$\epsilon = 1.5 \times 10^{-4} \text{ K}^{-1}$	with $\epsilon = 2.0 \times 10^{-4}$	$\epsilon = 2.5 \times 10^{-4}$
78	440	441.2	442.6
103	437.9	439.3	440.8
120	435.2	436.9	438.5
138	433.5	435.1	436.9
174	435	437.3	439.4
208	437.4	439.9	442.2
251	434.5	437.2	440
294	437.2	440.4	443.6
334	437.2	440.2	443.6
376	435.8	439.5	443.7
413	434.9	439	443.6
453.5	434	438.5	443.1
494.5	432.2	437.1	442.1
543	431.1	436.6	442
593	429.9	435.9	441.8
Mean Debye Temperature:	435.0 ± 2.6	438.3 ± 1.8	441.6 ± 2.0

Figure 9. Graph of $\ln f$ versus K . The dark circles represent experimental points and the line the theoretical fit using the Debye approximation with $\Theta_D = 438\text{K}$ and $\epsilon(-2) = 2 \times 10^{-4} \text{K}^{-1}$. 33

II. MANNHEIM'S THEORY

The analysis in the previous section was based on the assumption that the chromium was a Debye solid and that the potential energy was nearly harmonic. Nowhere in the discussion was mention made of the fact that the introduction of an impurity atom, such as Co⁵⁷, alters the dynamics of the crystal system. The impurity atom has a different mass than the host, and the force constant between an impurity and host atom will, in general, be different from the force constant between two host atoms. This difference in force constant will affect the mean square displacement of the impurity atom which will in turn affect the Mossbauer fraction. In 1968 Mannheim (5) published a theory which takes into account the mass of the impurity and the change in the force constant.

Our goal in using Mannheim's theory was to produce a theoretical fit to the f measurement data for chromium. The fit was based on two adjustable parameters: 1) anharmonicity ($\epsilon(-2)$) and 2) the force constant ratio ($A_{xx}^{00}/A_{xx}'^{00}$).

For harmonically bound crystals, the mean square displacement for the pure crystal is given by Nussbaum (1) as:

$$\langle x^2 \rangle = \frac{\hbar}{m} \int_0^\infty \left[\frac{1}{2} + \frac{1}{\exp \hbar\omega/kT - 1} \right] \frac{G_h(\omega)}{\omega} d\omega \quad (37)$$

where $G_h(\omega)$ represents the pure crystal phonon frequency spectrum. If an impurity is introduced, $G_h(\omega)$ becomes $G_i(\omega)$. $G_i(\omega)$ is called the "dynamic response function", and it "describes the coupling of the impurity modes to the unperturbed normal modes of the host." (1)

Mannheim, in assuming a harmonically bound crystal and central

forces, arrives at the following expression for $\langle x^2 \rangle$ (5):

$$\begin{aligned} \langle x^2 \rangle = & \frac{\hbar}{M'} \left(\frac{M}{M'} \right) \int_0^{\omega_{\max}} \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega/kT) - 1} \right] \frac{\nu(\omega) d\omega}{\omega \times \left\{ [1 + \rho(\omega)S(\omega)]^2 + \frac{1}{4}\pi^2\omega^2\nu^2(\omega)\rho^2(\omega) \right.} \\ & + \frac{\hbar}{M'} \left(\frac{M}{M'} \right) \frac{1}{\omega_L} \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega_L/kT) - 1} \right] \\ & \times \left[\rho^2(\omega_L)T(\omega_L) + \frac{M}{M'} - [1 + \rho(\omega_L)]^2 \right]^{-1} \end{aligned} \quad (38)$$

where M is the mass of the pure crystal atom, M' the mass of the impurity atom, and $\nu(\omega)$ represents the pure crystal density of states.

The above expression for $\langle x^2 \rangle$ has been simplified by defining

$$\rho(\omega) = \frac{M}{M'} - 1 + \frac{2\omega^2}{\omega_{\max}^2} \left(1 - \frac{A_{xx}^{oo}}{A'_{xx}{}^{oo}} \right) \quad (39)$$

$$S(\omega) = \int \frac{\omega'^2 \nu(\omega'^2) d\omega'^2}{\omega'^2 - \omega^2} \quad (40)$$

and

$$T(\omega) = \omega^4 \int \frac{\nu(\omega'^2)}{(\omega^2 - \omega'^2)^2} d\omega'^2 \quad (41)$$

where $A_{xx}^{oo}/A'_{xx}{}^{oo}$ in equation (39) represents the ratio of the force constant between two host atoms (A_{xx}^{oo}) and the force constant between a host atom and an impurity atom ($A'_{xx}{}^{oo}$).

The second term in equation (38) only contributes to the mean square displacement if there is a localized mode. A localized mode is a mode of vibration which is allowed for the impurity atom (as a result of its mass and the force constant), but which is not allowed for the atoms of the host material. This particular mode of vibration is not coupled to the normal modes of the host system and, therefore, does not

share energy with the host. The condition for a localized mode is:

$$1 + \rho(\omega) S(\omega) = 0 \quad \text{for } \omega > \omega_{\max} \quad (42)$$

This condition was checked in the case of chromium with a Co^{57} impurity and was not satisfied. Therefore, in the analysis of data only the first term in equation (38) was used.

It can be seen from equation (38) that the dynamic response function $G_1(\omega)$ is represented by:

$$\frac{\nu(\omega)}{[1 + \rho(\omega) S(\omega)]^2 + \frac{1}{4}\pi^2\omega^2 \nu^2(\omega) \rho^2(\omega)} \quad (43)$$

Also, in the case where $A_{xx}^{\infty}/A_{xx}'^{\infty} = 1$ (no change in force constant) and for no mass change, equation (38) reduces to the standard form for $\langle r^2 \rangle$ given in equation (37).

In order to use the theory to analyze Mössbauer f measurements, the only information needed is the pure crystal density of states function. Fortunately, in the case of chromium recent experimental work (see Feldman (3) and Muhlestein (4)) has produced two slightly different density of states functions. Copies of graphs (see figure 10, 11) of these functions were received from Feldman and Muhlestein and used in the calculations based on Mannheim's theory.

The evaluation of the integral $S(\omega)$ (equation 40) involves the expression $\nu(\omega^2)$ which is the pure crystal density of states per unit ω^2 . $\nu(\omega^2)$ is defined by the relation:

$$\int \nu(\omega) d\omega = \int \nu(\omega^2) d\omega^2 \quad (44)$$

or

$$\nu(\omega) = \nu(\omega^2) 2\omega \quad (45)$$

$$\nu(\omega^2) = \frac{\nu(\omega)}{2\omega} \quad (46)$$

Figure 10. Muhlestein's phonon density of states function.

Figure 11. Feldman's phonon density of states function.

For values of ω less than $\omega_{\max}$, $S(\omega)$ is found by taking the principal value of the integral in equation (40). In the numerical integration of this equation using a computer, the problem of singularities is avoided by choosing integer steps for $(\omega')^2$ and half integer steps for ω^2 . In this way $(\omega')^2$ never equals ω^2 .

Graphs of the function $S(\omega)$ for the density of states functions of both Munlestein and Feldman are shown in figure 12. These curves agree in their general behavior with the $S(\omega)$ curves calculated by Mannheim in his analysis of argon (17).

The function $S(\omega)$ was then used in evaluating the integral in equation (38). Values of the mean square displacement were calculated using various force constant ratios. (A force constant ratio greater than one represents a decrease in force constant: ie. the force constant between two Cr atoms is greater than the force constant between a Cr and a Co⁵⁷ atom.)

The calculations of $\langle x^2 \rangle$ in Mannheim's theory are based on the assumption of a harmonic potential. To obtain a fit between theory and the chromium measurements, it was first necessary to apply a correction for anharmonicity. This correction was made by applying the equation:

$$\ln f_h = \frac{\ln f(T)}{1 + \epsilon T} \quad (47)$$

to the experimental f measurements. Each value assumed for the anharmonicity parameter ϵ produced a set of "harmonic" $\ln f_h$ values.

The mean square displacements calculated from Mannheim's theory were transformed into $\ln f_h$ values using the equation

$$-\ln f_h = k^2 \langle x^2 \rangle \quad (48)$$

Figure 12. Graph of $S(\omega)$ versus ω using the phonon density of states of Muhlestein (○) and Feldman (●).

where k is the wave number of the gamma ray. Each force constant ratio produced a set of harmonic $\ln f_h$ values.

The two sets of $\ln f_h$ values, one from assuming different anharmonicity parameters and the other from assuming various force constant ratios, were compared.

For Feldman's density of states function, the best fit to the experimental data was found for a force constant ratio $A_{xx}^{00}/A_{xx}'^{00} = 1.30 \pm 0.07$ and an anharmonicity parameter of $\epsilon = 2.5(\pm 0.5) \times 10^{-4} K^{-1}$. Muhlestein's density of states function produces a best fit with $A_{xx}^{00}/A_{xx}'^{00} = 1.25 \pm 0.06$ and $\epsilon = 3.0(\pm 0.5) \times 10^{-4} K^{-1}$. Interestingly, a similar analysis of vanadium, a body centered cubic metal next to Cr in the periodic table (see Mannheim (18)), produced results indicating an increase in the force constant for Co⁵⁷ impurity. Figures (13, 14) show the comparison between theory and experiment using the two different density of states functions.

The computer programs used in evaluating the integrals in Mannheim's theory are given in the appendix. These programs were written in Basic language for use on a PDP-11 computer.

Figure 13. Graph of $\ln f$ versus temperature (K). (●) represents experimental points and (○) theoretical points calculated from Mannheim's theory and using Feldman's density of states.⁴ The fit is based on a force constant ratio of 1.30 and an anharmonicity parameter of $2.5(-.5) \times 10^{-4} \text{ K}^{-1}$.

Figure 14. Graph of $\ln f$ versus temperature (K). (●) represent experimental points and (○) theoretical points calculated from Mannheim's theory and using Muhlestein's density of states. The fit is based on a force constant ratio of 1.25 and an anharmonicity parameter of $3.0(^{+1.5}_{-1.5}) \times 10^{-4} \text{ K}^{-1}$.

SUMMARY AND CONCLUSIONS

I. SUMMARY

A single crystal chip of chromium was doped with Co^{57} and used as a Mössbauer source. The Mossbauer fraction was then measured over a range of temperatures from 78K to 792K. Because of uncertainty in the blackness correction, C_B , f values above 600K were not used in the analysis of results.

The f values were analyzed using two theories. Assuming that chromium is a Debye solid, the data could be fit using a Debye temperature of 438K and an anharmonicity parameter of $2 \times 10^{-4} \text{K}^{-1}$. The data was also analyzed by applying Mannheim's theory which takes into account the mass of the impurity and the possibility of a change in force constant. Using two different phonon density of states functions, results were obtained which were in excellent agreement.

For Muhlestein's frequency spectrum a fit to experimental data was made using a force constant ratio of $1.25^{+.06}$ and an anharmonicity parameter of $3.0 (\pm .5) \times 10^{-4} \text{K}^{-1}$.

Feldman's spectrum gave a fit for a force constant ratio of $1.30(\pm .07)$ and an anharmonicity parameter of $2.5 (\pm .5) \times 10^{-4} \text{K}^{-1}$.

II. CONCLUSIONS

In attempting to compare the results presented in this thesis with other experimental work done with chromium, one finds that very little f measurement data is available. One recent measurement (Qaim (19)) gives a room temperature f value of $.76^{+}.02$. This compares with our room temperature value of $.793^{+}.008$.

The purpose in analyzing the data in terms of the Debye approximation was to obtain a characteristic Debye temperature which could serve as a comparison with other experimental work. The Debye temperature found in fitting f measurement data at high temperatures corresponds to the -2 moment. There is a marked difference between the values for the Debye temperature thus obtained (438K) and the corresponding host Debye temperature using the phonon density of states function (see Appendix B and figure 15)*. This difference is reflected in the decrease in force constant found using Mannheim's theory.

*Of the two curves shown in figure 15, the one based on Feldman's data seems to agree more nearly with other experimental work. Recent measurements (20) of low temperature elastic constants give a $\Theta_D(-3)$ of 592K, and heat capacity data (4) has produced a value of 478K for $\Theta_D(2)$.

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APPENDIX A

MEASUREMENT OF THE INTERNAL MAGNETIC FIELD IN CHROMIUM

Chromium has interesting magnetic properties which could affect the f measurements. Above approximately 310K chromium is paramagnetic. Below this temperature it is antiferromagnetic. At 120K, called the "spin flip" temperature, indications are that the electron spins reorient themselves at right angles to their previous orientation.

The fact that this antiferromagnetic state exists made it necessary to determine the magnitude of any internal magnetic field.

This internal magnetic field, if large enough, could produce hyperfine splitting of the Fe^{57} nuclear levels. The result of such splitting could produce resonant gamma rays whose energy would be shifted such that they could not be absorbed by the black absorber. This in turn would make any f measurements using our technique invalid.

Low temperature heat capacity work in the range of 0.06K to 1.2K has been done by Ho and Phillips (21). Their work places an upper limit on the magnitude of the internal magnetic field in chromium at 13kOe. A field of this size would indeed have a negligible effect on the accuracy of any f measurements.

This observation is consistent with the results of Herbert et.al. (22). They observed a slightly broadened single line at 4.2K. As the

temperature of the sample was increased, this broadening decreased. By the time 100K was reached, the broadening had disappeared and the width of the single line was the same as it was at high temperatures.

In order to check these measurements, a line shape measurement was made at 114K with the chromium and a natural iron absorber. The results agreed with Herbert's in that the width of the line was the same as its room temperature value.

APPENDIX B

THE MOMENTS OF THE FREQUENCY SPECTRUM

The density of states functions of Feldman and Muhlestein were used to calculate the moments of the frequency spectrum. The n^{th} moment is given by

$$\omega_n = \int \omega^n \nu(\omega) d\omega \quad (49)$$

where $\nu(\omega)$ is the density of states function.

In order to obtain quantities with the same order of magnitude, weighted moments are defined. These are given by the relation:

$$\langle \omega_n \rangle = \left\{ \frac{n+3}{3} \omega_n \right\}^{1/n} \quad (50)$$

The expression:

$$\hbar \langle \omega_n \rangle = k \Theta_n \quad (51)$$

is then used to find the Debye temperature associated with the n^{th} moment.

Graphs of Debye temperature vs. n are given in figure 15. Also included is the computer program used in calculating these moments.

Figure 15. Graph of weighted Debye temperature $\langle \Theta_D \rangle_n$ versus n where n represents the n^{th} moment of the frequency spectrum. (a) represent calculation based on Fialkow's spectrum and (b) calculations based on Muhlstein's spectrum.

APPENDIX C

The appendix lists the programs used and explains the procedure followed in applying Mannheim's theory to the chromium f measurements.

The first step involved describing the density of states function by a set of piecewise continuous functions. These functions were then used in evaluating the $S(\omega)$ integral:

$$S(\omega) = \frac{\int \omega'^2 \gamma(\omega'^2) d\omega'^2}{(\omega'^2 - \omega^2)} \quad (52)$$

Making use of equation (46), $S(\omega)$ can be written as:

$$S(\omega) = \frac{\int \gamma(\omega') d\omega}{(1 - \omega^2/\omega'^2)} \quad (53)$$

The following program for evaluating this integral was used with Feldman's phonon density of states function.

```

5 DIM G(210)                                     establishes array for G(ω)
10 FOR N=1 TO 90
12 LET W=N/30
15 LET G(N)=4.7778*W*W
18 NEXT N
20 FOR N=91 TO 126
22 LET W=N/30
25 LET G(N)=149.78/(4.908-W)-35.49
28 NEXT N
30 FOR N=127 TO 144
32 LET W=N/30
35 LET G(N)=53.56/(5.0743-W)+114.74
38 NEXT N
40 FOR N=145 TO 147
42 LET W=N/30

```

```

45 LET G(N)=214*W-717.2
48 NEXT N
50 FOR N=148 TO 159
52 LET W=N/30
55 LET G(N)=29.85/(W-4.77)+101.77
58 NEXT N
60 FOR N=160 TO 171
62 LET W=N/30
65 LET G(N)=1637.5*W*W-18100*W+50090.6
68 NEXT N
70 FOR N=172 TO 189
72 LET W=N/30
75 LET G(N)=278.11/(7.115-W)-74.05
78 NEXT N
80 FOR N=190 TO 195
82 LET W=N/30
85 LET G(N)=6400*W*W-83260*W+270790
88 NEXT N
200 FOR I=0 TO 300
205 LET J=I+.5
210 LET S=0
220 FOR N=1 TO 195
240 LET D=J/N
250 LET S=S+G(N)/(1-D*D)
260 NEXT N
270 LET S=S/(5611.6*3)
300 PRINT J/30,S
310 NEXT I
320 END
READY

```

ω
offsets ω to prevent denominator from becoming zero

$$S(\omega) = \frac{G(\omega') d\omega'}{1 - (\omega/\omega')^2}$$

Normalize $G(\omega)$
Change to PRINT S then turn on tape punch. You get $S(\omega)$ tape.

Next the values of $S(\omega)$ obtained from the above program were used in evaluating the integral of equation (38):

```

1 DIM S(66): DIM M(9,19)
2 FOR N=0 TO 65
3 LETS(N)=EXP(N)
4 NEXT N
5 LET H=1.0545E-34
6 LET K=1.38054E-23
7 LET C1=.91246
8 LET F=6.5
9 LET C=H*C1/.946E-25
10 LET D=.02
20 LET D2=D/4
23 LET L2=0: LET T2=0
25 FOR L=1.2 TO 1.4 STEP .05
37 LET L2=L2+1
38 FOR T=0 TO 800 STEP 50
39 LET E=0: LET E1=0: LET E2=0: LET E3=0: LET E4=0: LET E5=0: LET E6=0: LET E7=0: LET E8=0
40 FOR X=0 TO 30 STEP D2

```

$S(\omega)$ and data readout array
Reads in $S(\omega)$ tape

Mass ratio (M/M')

ω
Constant (n/M')(M/M')
Step size for integration

Sets array for data readout
Force constant ratio

Temperature


```

50IFX=OGOTO4500
60 LET Z=4.7778*X*X
65GOSUB3000
70 IF(X+D2)>3 GO TO 90
80LETZ=2*Z
90LETE=E+Z
100NEXTX
110 LET W=(E*D2)/2

```

First Function
Goes to calculation of function

The same process in steps 40 through 110 is repeated for each of the functions that are used to describe the phonon density of states.

```

780 LET W=W+W1+W2+W3+W4+W5+W6+W7
790LETT2=T2+1
800LETM(L2,T2)=W*C*.5326E22
805 PRINT L,T,M(L2,T2)
810NEXTT
815LETT2=0
820 NEXT L
830 END
900 FOR L2=1 TO2
910 FOR T2=1 TO 5
920PRINTL2,(T2*50)-50,M(L2,T2)
930NEXTT2
940NEXTL2
950END

```

Sums up pieces of integral

$$\langle x^2 \rangle k^2$$

Prints out results

```

3000IFT=OGOTO4000
3005 LET X1=EXP((H*X*1E13)/(K*T))
3010LETY1=1/(X1-1)
3020LETZ1=.5+Y1
3030 LET R=X*X
3035 LET P=C1-1+(2*R/(F*F))*(1-L)
3040 LET R1=INT(10*X)
3045 IF R1+.5<=10*X GO TO 3064
3050 LET R2=R1-1
3055 IF R2=0 THEN LET R2=0
3060 LET Q=(S(R1)-S(R2))*(10*X-R1+.5)+S(R2)
3062 GOTO 3070
3064 LET R2=R1:LET R1=R2+1
3066 LET Q=(S(R1)-S(R2))*(10*X-R1+.5)+S(R2)
3070LETN1=Z1*Z
3080 LET D1=(1+P*Q)*(1+P*Q)
3090 LET D3=X*Z*P*1.5708/.56116E3
3100 LET D4=X*(D1+D3*B3)
3110LETZ=N1/D4
3120RETURN
4000LETZ1=.5
4010GOTO3030
4500 LET Z=T*K*4.778/(H*.56116E29)
4510GOTO90
4520END

```

Calculates $\left[\frac{1}{2} + 1/\exp\left[\frac{h\omega}{kT}\right] - 1 \right]$

Calculates $\rho(\omega)$ see eq. (39)
Interpolates between values of $S(\omega)$

Calculates $G(\omega) \left[\frac{1}{2} + 1/\exp\left[\frac{h\omega}{kT}\right] - 1 \right]$
Calculates terms in denominator

Calculates integral function

The last program in this appendix was the program used to calculate the moments of the frequency spectrum. Again, this is illustrated using Feldman's density of states.

```

1 PRINT " N ";" NTH MOMENT", "WGT. MOMENT",,"DEBYE THETA":PRINT
2 LET H=1.0545E-34
3 LET K=1.38054E-23
4 FOR N=-2.6 TO -2.9 STEP -.1           Range of N (moment) values
5 IF N=OGOTO820
6 LET D=.02                               Stop size
7 LET D2=D/4                             Initial step size
8 LET E=0:LETE1=0:LETE2=0:LETE3=0:LETE4=0:LETE5=0:LETE6=0:LETE7=0
9 LET E8=0
10 FOR X=0 TO 3 STEP D2                   First function
11 IF X=0 THEN GOTO100
12 LET Z=4.778*(X↑(N+2))
13 IF X+D2>3 GO TO 90
14 LET Z=2*Z
15 LET E=E+Z
16 NEXT X
17 LET W=(E*D2*1E13)/2

```

Steps 40-110 are repeated for the other functions describing the density of states function.

```

780 LET W=W+W1+W2+W3+W4+W5+W6+W7
785 LET W=W*(1E13↑N)

```

Calculate total integral. If $N=0$ this is $\int G(\omega) d\omega$. Then you must stop at 789. .56116E16 is $\int G(\omega) d\omega$. Calculates weighted moments ($N \neq 0$) Converts to $\Theta_D(N)$

```

786 LET W=W/.56116E16
790 LET M=(((N+3)*W)/3)↑(1/N)
800 LET Q=(H*M)/K
810 PRINT N;W,M,Q
820 NEXT N
900 END

```