High Pressure Mossbauer Studies
on Iron and Its Dilute Alloys

by

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HIGH PRESSURE MOSSBAUER STUDIES ON IRON
AND ITS DILUTE ALLOYS

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MASTER

The Mössbauer effect has been used to study the effect of very high pressure on dilute alloys of ^{57}Fe in iron, copper, vanadium, and titanium at room temperature.

The pressure dependence of the Mössbauer f number for ^{57}Fe in copper, vanadium, and titanium was studied. Values of the Debye parameter θ and the second inverse moment of the lattice spectrum for the host metals are obtained. The values of θ_{host} for copper, vanadium, and titanium are 309°K, 274°K, and 350°K respectively. The copper value is in excellent agreement with the values of the Debye parameter obtained in X-ray studies which are governed by the same Debye-Waller factor as is the Mössbauer f number. The titanium value is in good agreement with the Debye parameter obtained from room temperature specific heat measurements. For vanadium the value of θ_{host} is in agreement with Debye parameters obtained from specific heat measurements on lower purity vanadium samples and the purity- θ_{host} dependence found in specific heat measurements is also seen here. The values of $\langle w^{-2} \rangle$ for copper, vanadium, and titanium are $1.60 \times 10^{-27} \text{ sec}^2$, $2.57 \times 10^{-27} \text{ sec}^2$, $1.66 \times 10^{-27} \text{ sec}^2$, respectively. The value for copper is in

excellent agreement with results from thermal considerations and X-ray determination of the lattice spectrum. Vanadium again has a discrepancy related to the purity of the sample. No independent $\langle \omega^{-2} \rangle$ exists for titanium.

The pressure dependence of the Mössbauer isomer shift for ^{57}Fe in iron, copper, vanadium, and titanium was studied. An analysis of the data gives a relation between the isomer shift parameter α in $\Delta\varepsilon = \alpha |\Psi(0)|^2$ and the redistribution, with volume, of the conduction electrons between 4s and 3d states represented by $X = \partial n_s / \partial (\ln V) = - \partial n_d / \partial (\ln V)$. For the four metals

$$\alpha(-4.86 + 12.05 X) = Y$$

where $\alpha \equiv [a_0^3 \text{ mm/sec}]$ and $Y = 1.32, 1.54, 0.90$, and 0.83 for iron, vanadium, copper, and titanium respectively. The same qualitative difference in the volume dependence of the isomer shift was seen here as seen in earlier studies; the values for BCC materials are grouped about one number, the values for close-packed materials are grouped about another number and the latter number is significantly lower than the former number. This difference is reflected in the α versus X curves and is interpreted as due to the different importance of s to d electron transfer in the two types of structure.

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I. INTRODUCTION

The Mössbauer effect has been used to study the effect of very high pressure on dilute alloys of ^{57}Fe in iron, copper, vanadium, and titanium at room temperature.

The pressure dependence of the Mössbauer f number for ^{57}Fe in copper, vanadium, and titanium was studied. Values of the Debye parameter θ and the second inverse moment of the lattice spectrum for the host metals are obtained.

The pressure dependence of the Mössbauer isomer shift for ^{57}Fe in iron, copper, vanadium, and titanium was studied. An analysis of the iron data gives a relation between the isomer shift parameter and the redistribution, with volume, of the iron conduction electrons between the 4s and 3d bands. Similar analyses are made for copper, vanadium, and titanium.

II. HISTORY

A. High-Pressure Techniques

The pioneer in the development of modern high pressure techniques was P. W. Bridgman. After a long period of work at lower pressures Bridgman⁽¹⁾ constructed the first apparatus for work above 30 kilobars (1 kilobar = 986.92 atmospheres). This apparatus consisted of a conical cylinder pressed into a conical hole in an outer cylinder which gave outer support to the inner cylinder and thus extended the pressure range able to be achieved. Bridgman⁽²⁻⁵⁾ further developed this technique, usually discussed under the heading of "nested cells", and attained pressures in the 100 kilobar range.

Later Bridgman⁽⁶⁾ developed the use of opposed conical pistons, the so-called "Bridgman anvils". This principle of "massive support" has been modified for use in a variety of experimental situations. For example Jamieson and Lawson⁽⁷⁾ have modified the Bridgman anvils for X-ray work up to 150 kilobars. A study by Myers et al.⁽⁸⁾ of wafer parameters should also be mentioned.

Although Bridgman considered the use of diamond anvils the principal anvil material was Carboloy. More recently diamond anvils have been used in X-ray work by Piermarini and Weir⁽⁹⁾ who report pressures up to 115 kilobars and Owen et al.^(10,11) who report pressures up to 600 kilobars.

The concept of "massive support" has been the starting point for most later developments in the field of very high pressure.

techniques. Drickamer et al. have used a supported version of the Bridgman anvil to achieve pressures up to 600 kilobars. This version has been separately developed for optical studies,⁽¹²⁾ resistance studies,⁽¹³⁾ X-ray studies,⁽¹⁴⁾ and Mössbauer resonance studies.^(15,16)

Hall⁽¹⁷⁾ developed the tetrahedral press where four tetrahedrally opposed pistons bear on a tetrahedral center piece containing the sample under investigation. In a later modification Lloyd et al.⁽¹⁸⁾ replaced the four movable pistons by one movable and three fixed pistons. Pressures of 100 kilobars and temperatures of 3000°K have been achieved.

A cubic press, using six pistons, has been introduced by Houck and Hutton⁽¹⁹⁾ and developed for optical work to 50 kilobars and 1000°C by Owen.⁽²⁰⁾ An interesting independent development of a cubic device has been introduced by Von Platen⁽²¹⁾ who hydraulically drives a segmented spherical piston which encloses a cubic sample space.

A "belt" apparatus developed by Hall,⁽²²⁾ good to 100 kilobars and temperatures of more than 2000°C, has a relatively large volume space because of design considerations allowing a longer piston stroke.

Wittman and Werkman^(23,24) have developed a device that achieves pressures to 100 kilobars. The device has a sample space formed by three parallel axis cylinders and two plane parallel end plates; the pressure is achieved when the cylinders are driven inwards

by a rubber tire inflated to 2.5 kilobars by a high pressure water pump.

A number of books and review articles about very high pressure research are available. (25-32)

Mention should also be made of shock-wave techniques whereby transient high pressures in the megabar range are achieved. (33-35)

B. Mössbauer Effect

Achievement of nuclear gamma-ray resonance was for many years an extremely difficult task. Pollard and Alburger⁽³⁶⁾ found an anomalously large high energy component in the large angle scattering of the 1.38 and 2.76 MeV ^{24}Mg gamma-rays from Mg. This same general effect when Al was used as the target made an interpretation in terms of resonance absorption and reradiation uncertain. More positive results were obtained by Moon⁽³⁷⁾ who brought the 410 keV ^{198}Hg gamma-ray into resonance with a Hg absorber by imparting a high velocity to the source and a corresponding Doppler shift to the source radiation, and by Malmfors⁽³⁸⁾ who achieved an increase in resonance, again for the 410 keV ^{198}Hg gamma-rays, by heating the source to high temperatures and thus greatly increasing the Doppler broadening. These brute force methods made the use of nuclear resonance unproductive as a research tool.

In the late 1950's, Mössbauer,⁽³⁹⁾ in an investigation of the resonant scattering of the 129 keV gamma-ray of ^{191}Ir , found an

increase in the resonance when the source and absorber temperatures were lowered. This unexpected result was explained by Mössbauer using Lamb's⁽⁴⁰⁾ theory on the capture of neutrons by nuclei bound in a crystal, where the possibility of "non-recoil" capture was clearly shown. Within three years of Mössbauer's publication the theory of the Mössbauer effect had been formalized.⁽⁴¹⁻⁴⁴⁾

The big increase in Mössbauer research came when it was found⁽⁴⁵⁻⁴⁸⁾ that ^{57}Fe was a good Mössbauer nucleus, that is the effect at room temperature was large and easily obtained. The availability of ^{57}Co , the parent of ^{57}Fe , and its easy incorporation into many solids, together with the continuing exploitation of new Mössbauer nuclei have made the field of Mössbauer research an extremely active one. Several books^(49,50) and a number of review articles^(51,52,53) are available about the Mössbauer effect.

The first high pressure Mössbauer work was done by Pound et al.⁽⁵⁴⁾ who studied the change of isomer shift of ^{57}Fe in iron up to 3 kilobars at 295°K. Later, Nicol and Jura⁽⁵⁵⁾ studied the change of isomer shift and internal magnetic field of ^{57}Fe in iron up to the BCC to HCP transition at 130 kilobars.

An extensive program of high pressure Mössbauer research is now in progress at this laboratory under the direction of H. G. Drickamer. This work forms one part of that program. Investigations have been made, using the ^{57}Fe Mössbauer nucleus, of the pressure effects in Fe by Pipkorn et al.,⁽¹⁶⁾ Ti, Cu, and V by

Edge et al.,⁽⁵⁶⁾ CoSO_4 and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ by Ingalls et al.,⁽⁵⁷⁾ CoO by Coston et al.,⁽⁵⁸⁾ a number of transition metals by Ingalls et al.,⁽⁵⁹⁾ oxides⁽⁶⁰⁾ and ferrocene⁽⁶¹⁾ by Vaughan and Drickamer, and ionic crystals⁽⁶²⁾ and hemin⁽⁶³⁾ by Champion et al.

III. THEORY

A. The Mössbauer Effect

For optical transitions the recoil of an atom due to emission of radiation does not destroy resonance with another atom since typically the recoil energy (R) of the atom is less than the natural line width of the radiation (Γ). This is not true for nuclear transitions. When $R \gg \Gamma$, see Figure 1, as is true for nuclear transitions, no resonance is possible. Thus for ^{57}Fe ($\tau_{\frac{1}{2}} = 10^{-7}$ sec; $\Gamma = 4.5 \times 10^{-9}$ eV) the recoil energy of the atom upon emission of the 14.4 keV γ -ray is 1.9×10^{-3} eV, thus $R \gg \Gamma$, while for an optical transition of 5000 Å and $\tau_{\frac{1}{2}} = 10^{-8}$ sec ($\Gamma = 4.5 \times 10^{-8}$ eV) $R \simeq 6 \times 10^{-11}$ eV and thus $R \ll \Gamma$.

The Mossbauer effect arises from the experimental fact that for an atom embedded in a solid there exists a finite probability that a nuclear transition will occur without recoil. This recoilless radiation makes it possible to achieve resonance with an atom similarly placed in another solid. Resonance is rarely perfect due to differences of the extra-nuclear environment in the source and absorber. These environmental differences will be discussed below. By relatively low source or absorber velocities, of the order of tenths of millimeters per second, the radiation can be Doppler shifted into resonance and by sweeping over velocities the entire absorption curve can be exhibited.

FIGURE 1. EMISSION AND ABSORPTION LINES OF FREE NUCLEI

In the spectrum of the emitted radiation one can identify the recoilless (no phonon) component of natural line width and recoil components which arise when phonons are emitted. The natural line width of the recoilless radiation arises from the different time scales of the nuclear transitions and atomic vibrations in the lattice. Typically the atom vibrates in the lattice in 10^{-13} seconds while the nucleus decays in 10^{-7} to 10^{-9} seconds. Thus 10^4 to 10^6 lattice vibrations occur during a nuclear decay and the linear Doppler term time averages to zero. There is an important second order effect which shifts the line and will be discussed below.

In Figure 2, drawn from Visscher,⁽⁴¹⁾ a typical γ -ray absorption spectrum is shown. Two features of the spectrum should be noticed. First, the recoilless amplitude at low temperatures is much greater than that of the recoil radiation and decreases with increasing temperature. Second, to achieve a resonance with the recoil radiation would require velocities of hundreds of meters per second. Visscher⁽⁴¹⁾ has pointed out that it is theoretically possible to use this recoil radiation to map out the phonon spectrum but so far no experimental work has been done.

The existence of recoilless radiation with natural line width makes possible the investigation of nuclear environments. The environment can produce shifts and splittings in the recoilless spectrum and a study of the resultant spectrum allows conclusion to be drawn about the environment. There are four basic read-outs in

Figure 2. Schematic Representation of
Nuclear Absorption Spectrum

the Mossbauer effect; (1) the f number, the fraction of emissions or absorptions that occur without recoil; (2) the center shift, due to electron density at the nucleus (isomer shift) and the second order Doppler shift; (3) the magnetic interaction of the nuclear magnetic dipole with the magnetic field at the nucleus; and (4) the quadrupole interaction of the nuclear electric quadrupole moment with the spatial variation of the electric field at the nucleus. These interactions will be discussed in turn in the following sections.

B. f Number

The Mössbauer effect arises from those nuclear transitions in which the lattice is in the same quantum state after the transition as before the transition, i.e., no emitted phonons. Thus one can define the Mössbauer f number for a certain initial lattice state $\{n_s\}$ as

$$f_{\{n_s\}} = |\langle \{n_s\}_g | \mathcal{H}_{\text{int}} | \{n_s\}_e \rangle|^2 \quad (1)$$

where $\{n_s\} \equiv n_s$ phonons in s^{th} lattice mode

$g, e \equiv$ ground and excited states of the nucleus, respectively.

$$\mathcal{H}_{\text{int}} = \text{const}(\tilde{A} \cdot \tilde{p} + \tilde{p} \cdot \tilde{A}). \quad (2)$$

$\tilde{A}$ is expanded in plane waves by the usual process⁽⁶⁴⁾ and it is found^(42,49) that the lattice and nuclear matrix elements can be separated. Then taking a ratio of those transitions in which the

lattice remains in the same state, the Mössbauer transitions, to all transitions, the nuclear matrix elements cancel and one finds that

$$f_{\{n_s\}} = |\langle \{n_s\} | e^{i\vec{k} \cdot \vec{X}_L} | \{n_s\} \rangle|^2 \quad (3)$$

where $\vec{k} \equiv$ wave-vector of the emitted radiation

$\vec{X}_L \equiv$ center-of-mass of the decaying nucleus.

Lipkin⁽⁴²⁾ has given an approximate treatment of this expression which gives the same result as more exact methods and has more direct physical meaning. In this treatment $\vec{X}_L$ is expanded in normal coordinate ξ_s

$$\vec{X}_L = \sum_s a_{LS}(T) \xi_s \quad (4)$$

where the amplitudes a_{LS} are functions of the temperature. Using this expansion the exponential in Eq. (3) is expanded in a series and, assuming that the individual terms are small compared to unity one obtains

$$f_{\{n_s\}} \simeq \exp[-\frac{1}{2} \sum_s \langle \{n_s\} | a_{LS}^2 \xi_s^2 | \{n_s\} \rangle] \quad (5)$$

To obtain the f number for all lattice states one must make a thermal average over all the $\{n_s\}$. This is most simply done by noting that the total potential energy of the lattice in the s^{th} lattice state is equal to one-half of the total energy of that lattice state.

$$E_{\{n_s\}} = (n_s + \frac{1}{2}) \hbar \omega_s \quad (6)$$

where

$$n_s = \frac{1}{e^{\hbar\omega_s/kT} - 1} \quad (7)$$

Thus

$$\frac{1}{2}NM\omega_s^2 \langle \{n_s\} | a_{LS}^2 \xi_s^2 | \{n_s\} \rangle = \frac{1}{2}(n_s + \frac{1}{2})\hbar\omega_s \quad (8)$$

where $M \equiv$ mass of the decaying atom

$N \equiv$ number of lattice atoms.

Combining Eqs. (5) and (8) one obtains

$$f \simeq \exp \left[- \frac{\hbar^2}{2MN} \sum_s \frac{(2n_s + 1)}{\omega_s} \right] \quad (9)$$

The subscript $\{n_s\}$ on f has been dropped since the thermal averaging has been accomplished and the temperature dependence is implicit in the n_s .

Evaluation of the sum in the exponential of Eq. (9) requires knowledge of the phonon spectrum but some information can be obtained from more general considerations.

$$\sum_s \frac{(2n_s + 1)}{\omega_s} = 2 \int_0^\infty \frac{g(\omega)}{\omega} \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right] d\omega \quad (10)$$

where $\beta = 1/kT$. At low temperatures only zero point energy needs to be considered and then

$$\sum_s \frac{(n_s + \frac{1}{2})}{\omega_s} = \langle \omega^{-1} \rangle \quad (11)$$

where

$$\langle \omega^{-1} \rangle = \int \frac{g(\omega)}{\omega} d\omega \quad (12)$$

At high temperature the exponential can be expanded and if the zero point energy is ignored we have

$$\sum_s 2 \frac{(n_s + \frac{1}{2})}{\omega_s} = \frac{2kT}{\hbar} \langle \omega^{-2} \rangle \quad (13)$$

where

$$\langle \omega^{-2} \rangle = \int \frac{g(\omega)}{\omega^2} d\omega. \quad (14)$$

Two characteristics of this treatment should especially be noted. First, the linearity of $\ln f$ in T at high temperature is due only to the harmonic approximation and does not depend on the details of the phonon spectrum. Deviations from this linear behavior have been found, e.g. in Sn by Boyle et al.,⁽⁶⁵⁾ and are due to two quantitatively different considerations. Within the harmonic approximation, modifications must be made to reconcile the harmonic theory formulated for constant volume and the experiment performed at constant pressure. Anharmonic contributions also modify the linear temperature dependence of $\ln f$.

Second, the Mössbauer f number depends mainly on the low frequency part of the phonon spectrum. Since other quantities, such as the specific heat, depend upon different weighting of the phonon spectrum care must be taken in comparing the results of different experiments.

It is usual to assume a Debye spectrum in the evaluation of Eq. (9). Thus

$$g(\omega) = \frac{3N}{3} \omega^2 \quad (15)$$

where

$$\omega_D = \frac{k\theta_D}{h} \quad (16)$$

θ_D = Debye temperature.

In the Debye approximation the Mossbauer f number becomes

$$f = \exp \left[- \frac{6E_r}{k\theta_D} \left\{ \frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x dx}{e^x - 1} \right\} \right] \quad (17)$$

where

$$E_r = \frac{E_\gamma^2}{2Mc^2} \equiv \text{recoil energy of free nucleus due to decay}$$

E_γ $\equiv$ Gamma-ray energy.

From this calculation it is apparent that "good" Mössbauer nuclei will have low recoil energy E_r , due either to large nuclear mass or small E_γ , and large θ_D , i.e. tight lattice binding. θ_D can be determined either by an absolute measurement of f at a single temperature or by the best fit to f measured over a range of temperatures. Both of these measurements have been made and will be discussed below.

The Mössbauer f number will vary with pressure since there is an implicit pressure dependence in θ_D . A portion of this thesis is concerned with the investigation of the pressure dependence of the f number of dilute alloys of ^{57}Fe in Cu, V, and Ti.

C. Center Shift

The experimental fact that Mössbauer resonance very rarely occurs at zero relative velocity between source and absorber is due to two basically different causes, the isomer shift, due to the differences in electron density at the nucleus in source and absorber and the second order Doppler shift, a relativistic effect due to the change of mass of the radiating nucleus due to the gamma-ray emission. In any experiment some method must be devised of separating these two effects.

1. Isomer Shift

The isomer shift is due to the electric monopole interaction between the nuclear charge and the atomic electron density at the nucleus.

The simplest model of the nucleus for the calculation of the isomer shift is that of a uniformly charged spherical nucleus. The difference of the nuclear potential for this spherical nucleus from that of a point charge nucleus is

$$\delta\phi = \begin{cases} \frac{Ze}{R} \left[\frac{3}{2} - \frac{r^2}{2R^2} - \frac{R}{r} \right] & r < R \\ 0 & r > R \end{cases} \quad (18)$$

where $R \equiv$ nuclear charge radius.

Multiplying this potential difference by the electron density at the nucleus $-e|\psi(0)|^2$ and integrating from $r = 0$ to $r = R$ one obtains the equation for the energy shift due to a finite size nucleus

$$\delta E = \frac{2\pi}{5} Z e^2 |\psi(0)|^2 R^2. \quad (19)$$

Since the excited state of the nucleus will, in general, have a different charge radius than the ground state we have

$$\begin{aligned} \delta E_e - \delta E_g &= \frac{2\pi}{5} Z e^2 |\psi(0)|^2 (R_e^2 - R_g^2) \\ &\simeq \frac{4\pi}{5} Z e^2 R^2 |\psi(0)|^2 \frac{\delta R}{R} \end{aligned} \quad (20)$$

where $\delta R = R_e - R_g$.

In the Mössbauer effect one is interested in the difference in this quantity between the source and absorber. This is the isomer shift and is given by

$$\Delta E = \frac{4\pi}{5} Z e^2 R^2 [|\psi_a(0)|^2 - |\psi_s(0)|^2] \frac{\delta R}{R}. \quad (21)$$

Thus if the electron densities at the nucleus are not the same in the source and absorber the line will not be in resonance at zero relative velocity.

In Eq. (21) we have both electronic and nuclear properties and one can only be extracted if the other is known. Values of $\delta R/R$ are not readily available, in fact the exact meaning of "nuclear charge radius" is not well defined, and values of $|\psi(0)|^2$ for atoms or ions in solids have to be extrapolated from approximate solutions to free atoms or ions.

In ^{57}Fe the excited state has a smaller charge radius than the ground state^(66,67) so that, from Eq. (20) one can see that when $|\psi(0)|^2$ increases the line shifts to lower energies.

Only s electron wave functions overlap the nucleus and thus p,d,... electrons do not contribute directly to the isomer shift. However, as will be discussed in more detail below, the non-s electrons can contribute indirectly to the isomer shift by shielding the s electrons.

A discussion of the evaluation of $|\psi(0)|^2$ has been given by Shirley.⁽⁶⁸⁾ Shirley shows that if $|\psi(0)|^2$ is evaluated non-relativistically the relativistic solution is obtained by modifying Eq. (21) to

$$\Delta E = \frac{4\pi}{5} Ze^2 R^2 S(Z) [|\psi_a(0)|^2 - |\psi_s(0)|^2] \frac{\delta R}{R} \quad (22)$$

where $S(Z)$ is the relativistic correction and has been tabulated by Shirley.⁽⁶⁸⁾ $S(Z) = 1.29$ for ^{57}Fe ($Z = 26$).

A portion of this thesis is concerned with the investigation of the isomer shift of ^{57}Fe in Fe for pressures less than 130 kilobars and of ^{57}Fe in Cu, V, and Ti for pressures up to 100 kilobars.

2. Second Order Doppler Shift

It has been mentioned above that the natural line width of the Mössbauer line is due to the fact that the first order Doppler effect averages to zero over the time of the nuclear decay. The second order Doppler shift, which is proportional to $\langle v^2 \rangle$ does not average to zero and requires discussion. There have been a number of discussions of this effect but the earliest by Josephson⁽⁶⁹⁾ is quite straightforward and will be followed here.

The energy of a nucleus in a lattice can be represented as

$$E = \langle \mathcal{H} \rangle = \left\langle \frac{p^2}{2m} + V \right\rangle \quad (23)$$

where

$\mathcal{H} \equiv$ Hamiltonian of the nucleus.

When the nucleus emits a gamma-ray of energy E_γ it loses mass according to the Einstein relation, $\delta m = -E_\gamma/c^2$, and since this changes the energy of the vibrating nucleus and this energy must come from somewhere, the energy of the gamma-ray changes by the amount

$$\delta E = -\delta \langle \mathcal{H} \rangle = + \frac{\delta m}{m} \left\langle \frac{p^2}{2m} \right\rangle = - \frac{E_\gamma}{mc^2} \left\langle \frac{p^2}{2m} \right\rangle. \quad (24)$$

This is usually written

$$\delta E = - \frac{E_\gamma}{2c^2} \langle v^2 \rangle. \quad (25)$$

It can be shown that the change of the second order Doppler shift with pressure is an order of magnitude less than that of the isomer shift and thus is only of secondary importance in pressure dependence studies.

If we use Eq. (24) and use the Debye theory with

$\langle \text{Kinetic Energy} \rangle = \frac{1}{2} \langle \text{Total Energy} \rangle$ where

$$\langle \text{Total Energy} \rangle = 9k\theta \left[\frac{1}{8} + \left(\frac{T}{\theta} \right)^4 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} \right]. \quad (26)$$

Thus Eq. (24) becomes

$$\delta E = -c \frac{9E_\gamma}{2mc^2} k\theta \left[\frac{1}{8} + \left(\frac{T}{\theta} \right)^4 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} \right] \quad (27)$$

or expressing this in terms of a Doppler velocity $\delta v = \frac{c}{E_\gamma} \delta E$ gives

$$\delta v = -c \frac{9k\theta}{2mc^2} \left[\frac{1}{8} + \left(\frac{T}{\theta}\right)^4 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} \right]. \quad (28)$$

Differentiating this equation with respect to $\ln V$ gives

$$\frac{d(\delta v)}{d(\ln V)} = +c \frac{9k\theta}{2mc^2} \left[\frac{1}{8} + \frac{1}{e^{\theta/T} - 1} - 3\left(\frac{T}{\theta}\right)^4 \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} \right] \quad (29)$$

where

$$\gamma = - \frac{d(\ln \theta)}{d(\ln V)} \quad \text{Grüneisen Constant} \quad (30)$$

Taking $\theta = 467^\circ\text{K}$, $\gamma = 1.6$ for Fe⁽⁷⁰⁾ gives

$$\frac{\delta v}{d(\ln V)} \simeq 8.0 \times 10^{-2} \text{ mm/sec.} \quad (31)$$

At a pressure of 150 kilobars, $\Delta V/V \simeq 7 \times 10^{-2}$ for Fe⁽⁷¹⁾ and this gives $\delta v \simeq 5 \times 10^{-3}$ mm/sec. This is an order of magnitude less than the variation of the isomer shift with pressure at this pressure.

D. Magnetic Dipole Interaction

If a nuclear state has a magnetic moment μ and there exists a magnetic field $\tilde{H}$ at the nucleus which does not average to zero over the nuclear lifetime a nuclear Zeeman effect will result. The formalism is familiar and will only be briefly outlined here.

The interaction Hamiltonian is

$$\mathcal{H} = - \mu \cdot \tilde{H} \quad (32)$$

where

$$\mu = g\mu_n \tilde{I} \quad (33)$$

$g \equiv$ Nuclear g-factor

$\mu_n \equiv$ Nuclear magneton $= e\hbar/2m_n c$

$I \equiv$ Nuclear spin.

The eigenvalues of this Hamiltonian for the nuclear state $|Im_I\rangle$ are

$$E = -g\mu_n H m_I \quad m_I = I, I-1, \dots, -I. \quad (34)$$

For the 14.4 keV γ -ray of ^{57}Fe one has the situation shown in Figure 3a. The labeling of the m_I sublevels and the allowed transitions have been determined as follows. Lemmer et al.⁽⁷²⁾ examined the decay scheme of ^{57}Co and found that the 14.4 keV level of the ^{57}Fe nucleus had $I = 3/2$ and negative parity while the ground state had $I = 1/2$ and negative parity. General considerations⁽⁷³⁾ indicate that the predominant radiation for $\Delta I = 1$ and no parity change must be M1 (magnetic dipole) or E2 (electric quadrupole). Goldhaber and Sunyar⁽⁷⁴⁾ studied the 14.4 keV line and on the basis of the half life of the excited state identified the radiation as predominantly M1. This gives $\Delta m_I = 0, \pm 1$ selection rules and these lines are shown in Figure 3a.

Hanna et al.⁽⁷⁵⁾ studied the polarization of the nuclear Zeeman lines and found that to explain the experimental results the g value of the excited state, g_E , must be opposite in sign to the g value of the ground state, g_G . Since g_G is positive⁽⁷⁶⁾ the M_I lines are properly shown in Figure 3a and since $|g_E| < |g_G|$ ⁽⁷⁵⁾ the lines as numbered in Figure 3a are in terms of decreasing energy.

FIGURE 3. MAGNETIC HYPERFINE SPLITTINGS FOR ^{57}Fe

The same lines are shown in Figure 3b as they appear in a typical run using a single line absorber with a ^{57}Fe in an iron source.

The relative magnitudes of the lines as shown are for a polycrystalline Fe sample with random domain orientation, thus experimentally integrating over the angular dependence of the lines.

The magnetic interaction with the surrounding electrons is of two types. First there is the Fermi contact term⁽⁷⁷⁾ proportional to $|\psi_s(0)|^2$ for unpaired electrons. Second, there is the dipole-dipole interaction for p, d, f, ... electrons. An exhaustive survey of this field has been made by Freeman and Watson⁽⁷⁸⁾ where it has been indicated that the main contribution to $\tilde{H}$ in the ferromagnetic metals comes from the Fermi contact term.

The pressure dependence of this internal magnetic field for ^{57}Fe in iron metal up to the BCC-HCP transition at 130 kilobars is reported in this work in Appendix C.

E. Electric Quadrupole Moment

In discussing the isomer shift in Section III-C we treated the interaction of a spherical nucleus with its environment. In this section the effects of "nuclear shape" will be discussed.

The most direct way of examining these effects is by expanding the electrostatic integral⁽⁷⁹⁾

$$\mathcal{H} = \langle \psi_n \psi_e | \frac{1}{r_{en}} | \psi_n \psi_e \rangle = \langle \psi_n \psi_e | \sum_{\ell=0}^{\infty} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} P_{\ell}(\cos \theta_{en}) | \psi_n \psi_e \rangle \quad (35)$$

where $\Psi_n, \Psi_e \equiv$ nuclear and electronic wave functions. Two important conclusions follow directly from general considerations of this expansion. First, since a nuclear state has a definite parity the nucleus can not have an electric dipole moment and thus no electric dipole interaction with its environment. Second, the n^{th} electric moment of the nucleus averages to zero unless $I \geq n/2$. Thus for the electric quadrupole moment ($n=2$) $I \geq 1$ for a non-zero nuclear quadrupole moment.

It is possible to write the integral in Eq. (35) as a product of integrals dependent upon nuclear and electronic coordinates separately. Thus, for the electric quadrupole interaction

$$\mathcal{H}_Q = \frac{1}{6} \sum_{i,j} \langle \Psi_e | \frac{3x_{ei}x_{ej} - \delta_{ij}r_e^2}{r_e^5} | \Psi_e \rangle \langle \Psi_n | 3x_{ni}x_{nj} - \delta_{ij}r_n^2 | \Psi_n \rangle \quad (36)$$

where i, j label Cartesian axes. The electronic part of $\mathcal{H}_Q$ is a symmetric 2nd order tensor that can be diagonalized and thus reduced to three components. A further reduction to two independent components can be made by using Laplace's equation.

The nuclear integral can be evaluated by using the Wigner-Eckhart theorem⁽⁸⁰⁾ which states that matrix elements of operators that have the same transformation properties are proportional. This allows the $x_i x_j$ integral to be replaced by an $I_i I_j$ integral which is trivial to evaluate for a nuclear state $|I m_I\rangle$.

After considerable algebra one obtains

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} [(3I_z^2 - I^2)v_{zz} + (v_{xx} - v_{yy})(I_x^2 - I_y^2)] \quad (37)$$

where

$$eQ = \langle I, m_I = I | 3z^2 - r^2 | m_I = I, I \rangle . \quad (38)$$

It is usual to make a further simplification of this equation by defining

$$\eta = \frac{v_{xx} - v_{yy}}{v_{zz}} \quad q = \frac{v_{zz}}{e} \quad (39)$$

so that

$$\mathcal{H}_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I^2 + \frac{\eta}{2} (I_+^2 + I_-^2)] \quad (40)$$

where $I_+ = I_x + iI_y$, $I_- = I_x - iI_y$. As I_z appears in $\mathcal{H}_Q$ as a square it is clear that one obtains the same shift for $\pm m_I$. This is shown in Figure 4 for ^{57}Fe where

$$\Delta E = \frac{1}{2} e^2 q Q (1 + \frac{\eta^2}{3})^{\frac{1}{2}} \quad (41)$$

for the $I = 3/2$ excited state.

When the point group of the solid has a single rotation of order three or higher, $\eta \equiv 0$ and $\mathcal{H}_Q$ is further simplified.

The electronic parameter q represents the sum of two contributions. First, there is the contribution due to non-spherical electron distribution of the ion itself and second there is the crystal field contribution.

No quadrupole interactions are studied in this work.

FIGURE 4. ELECTRIC QUADRUPOLE SPLITTING FOR ^{57}Fe

IV. EXPERIMENTAL APPARATUS AND PROCEDURES

A. Introduction

The high pressure Mössbauer equipment used in this work has been described in the literature⁽¹⁶⁾ and is shown in block diagram in Figure.5. The principal advantage of the equipment described is the ability to automatically run two simultaneous high pressure experiments using a single multichannel analyzer.

The gamma rays passing through a moving absorber are detected by a proportional counter, the pulses are amplified, those corresponding to the energy of the Mössbauer line are passed through an energy window, the pulses passed are modulated so that the peak height corresponds to the velocity of the absorber at the time of detection and these modulated pulses are stored in the multichannel analyzer according to their height, thus according to the absorber velocity.

The motion device is a constant acceleration device so that the absorber spends equal time in each velocity interval.

B. Experimental Equipment

1. Proportional Counter

The 14.4 KeV gamma ray is detected by a proportional counter filled with a 90% krypton, 10% methane mixture which serves to enhance the detection of the low energy 14.4 KeV over the higher energy gamma rays also emitted by the source.

The proportional counter is an aluminum tube 35 cm. long, with an 8.9 cm. diameter. Access for the gamma rays is a .08 cm. Be window 2.5 cm. by 7.6 cm.

The high voltage source for the proportional counter is a Fluke 405 High Voltage Power Supply (John Fluke Mfg. Co., Inc., Seattle, Washington). The power supply supplies high voltage for both proportional tubes in the dual set-up shown in Figure 5 and the separate voltages are set by independent voltage dividers.

2. Motion Device

The device is an electromechanical transducer of the double loud-speaker type whose velocity is controlled by a symmetric reference signal and a feedback amplifier. The actual motion device used in this work (Figure 6) is a modification of the device discussed by Kankeleit. (81,82)

The calibration of the motion was determined by use of an iron source and the data of Preston et al.⁽⁸³⁾

The motion device is mounted on an adjustable base which permits use of either a moving source or moving absorber and allows the precise vertical and horizontal alignment necessary in the former case.

3. Electronics

As outlined in Figure 5 a pulse from the proportional counter is amplified in a Hamner model N-384 pre-amplifier (Hamner Electronics co, Inc., Princeton, New Jersey), then by a Hamner model

FIGURE 5. BLOCK DIAGRAM OF HIGH PRESSURE MÖSSBAUER APPARATUS

Figure 6. Construction of Motion Device

N-380 double delay line amplifier. A Hamner model N-686 pulse height analyzer then separates the 14.4 KeV gamma ray from the background.

Since two spectra are being stored in the same multi-channel analyzer it was necessary to construct a routing circuit (schematic in Figure 7) which (1) routes the pulse into the proper half of the multichannel analyzer, and (2) prevents another pulse from entering the system until the pulse being handled is processed.

The pulse is then modulated (schematic of modulator in Figure 7) with the reference signal from the motion device which gives the pulse an amplitude which is a function of the absorber velocity at the time the gamma ray traversed the absorber. This modulated pulse then enters the multichannel analyzer which sorts and stores the modulated pulses. The multichannel analyzer was purchased from Nuclear Data, Inc. of Palatine, Illinois, and consists of an ND-180F analog-to-digital converter, an ND-180M 512 channel memory unit, and an ND-410 display unit.

A highly stable symmetric sawtooth generator and a feedback amplifier (schematics in Figure 8) were built to generate and control the absorber motion. The Philbrick model PR300C low drift 15 volt power supply, model P65AU solid state amplifier, and model P66A solid state booster followers were used in the construction of these circuits (Philbrick Researchers, Inc., Dedham, Massachusetts).

Figure 8. Schematic of Motion and
Control Circuits

Line voltage was controlled by a Sorenson model ACR-300 silicon controlled rectifier (Raytheon Co., Norwalk, Conn.).

4. Sources and Absorbers

a) Sources

The radioactive samples of Cu, V, Fe, and Ti were prepared by electroplating radioactive ^{57}Co (obtained from the Oak Ridge National Laboratory and the New England Nuclear Corp. of Boston, Mass.) onto a strip of the material 1 mil by 10 mils by approximately an eighth of an inch long. This was usually enough material for three high pressure loads. The electroplating medium was 5 ml of an .01% boric acid solution; a Pt anode with a plating voltage of 2 volts was used and this gave a plating current of approximately 15 pamps.

Heat treatment for the Cu, Ti, and Fe consisted of heating the sample after plating at 700°C for 24 hours under vacuum. This treatment was sufficient for diffusion of the activity throughout the sample. A second piece of Fe was preannealed at 1000°C for 30 minutes, plated, heated under vacuum at 700°C for 48 hours and taken to 1000°C for 10 minutes before being cooled. No difference in results was seen in the pressure dependence of the isomer shifts for the two Fe samples.

The V samples needed a more careful heat treatment to obtain reproducible "zero" pressure isomer shift. The samples were preannealed under vacuum at 1400°C for 30 minutes, plated, heated under vacuum at 700°C for 48 hours and taken to 1500°C for 2 minutes. This treatment

gives an isomer shift of ≈ -0.15 mm/sec with respect to ^{57}Fe in iron. This agrees well with the value of Kitchens et al. (84)

b) Absorbers

In the f number study an enriched ^{57}Fe 1.00 mg/cm² $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ absorber was used. This absorber was obtained from the New England Nuclear Corp. (Boston, Mass.).

For the ^{57}Fe isomer shift use was made of an enriched 1.5 mg/cm² ^{57}Fe stainless steel absorber. The enrichment was done by alternately plating ^{57}Fe , then Ni and heating for 24 hours under vacuum at 700°C and repeating until the desired ^{57}Fe density was attained. The Ni plating was necessary to keep the stainless steel foil in a non-magnetic phase.

5. Pressure Generating Apparatus

A Bridgman anvil high pressure device was used in this study rather than the higher pressure Drickamer cell since no pressures higher than 130-140 kilobars were desired.

The anvils consist of work-hardened 1.746 cm diameter carboloy pistons pressed into 4.4 cm diameter hardened steel jackets. The carboloy is work-hardened after being placed in the jacket by pressing a pyrophyllite pellet 0.203 cm in diameter and 0.033 cm thick between two pistons to about 130-150 kilobars and regrinding to the original dimensions. The anvils have a 9° taper and a 0.203 cm diameter flat.

The high pressure cell consists of two such anvils in a close fitting plastic sleeve (see Figure 9). The radioactive source is placed between the flats. The cell is placed in a short stroke hydraulic press with a 11.43 cm diameter piston where a Blackhawk hydraulic pump and Heise Bourdon gauge are used to produce, measure, and control the pressure.

The pressure calibration of this cell was originally determined using the high-pressure X-ray technique of Perez-Albuerne, Forsgren, and Drickamer.⁽¹⁴⁾ The curves shown in Figure 10 result from this work and give the limits of the spread in attainable pressures for any average pressure on the 0.203 cm flat. A periodic check of this calibration was made by making a resistance-pressure run on Bi using the same loading technique as in the radioactive runs. The Bi transitions at 25 kilobars⁽⁸⁵⁾ and 85 kilobars^(4,13,86) were used.

C. Operational Procedures

1. Loading Pressure Cell

A bar of pyrophyllite [$\text{HA}(\text{SiO}_3)_2$] is cut to a rod of .500" diameter on a lathe. The pyrophyllite cylinder is sectioned at right angles to the cylinder axis and the sections are sanded to a height of .0138".

The sanded sections are placed in a 0.500" steel cylinder and using a drill guide an .080" hole is drilled in the center and filled to slight overflowing with a 85% B-15% LiH mixture. This

FIGURE 9. HIGH PRESSURE CELL

Figure 10. Calibration for Bridgman Anvils

mixture is compacted by pressing to 13,000 atmospheres. Using another drill guide a .029" hole is drilled in the center of the .080" B-LiH pellet. The radioactive sample, usually in the form of an arc, is inserted along the edge of the .029" hole (Figure 11) and the hole is filled by a B-LiH pellet whose manufacture is described in the next paragraph. The completed load is then pressed at 15,600 atmospheres and the pyrophyllite is cut away from the .080" B-LiH pellet which is placed in the high pressure cell as shown in Figure 9.

The center piece is made by drilling a .029" hole in a pyrophyllite section sanded to a height of .014", filling the hole with the B-LiH mixture and pressing to 14,300 atmospheres.

2. Data Analysis

The data are read from the multichannel analyzer onto teletype tape using a model 32 Teletype (Teletype Corp., Skokie, Illinois). This teletype tape is used to put the data onto computer cards and the peak locations, widths, and areas are computed using a program originally written by Burton⁽⁸⁷⁾ to fit n Breit-Wigner lines where the exponent of the squared term in the denominator of the Breit-Wigner is allowed to vary.

It is usually necessary, in the extraction of isomer shifts, to make a correction to the peak location for drift arising from changes in dc levels and conversion gain during a pressure run. This is done by correcting the peak location for changes in the center of the velocity spectrum with respect to a specific channel number. This

FIGURE II. HIGH PRESSURE LOAD

correction is determined by observing changes in the half-maximum points on both ends of the spectrum, and normally ranges from 0.1 to 1.5 channels over a run.

V. LATTICE SPECTRUM AND CHARACTERISTIC TEMPERATURE

A. Previous Determinations

1. Copper

a) Mössbauer f number

Housley et al. (88,89) have determined the room temperature Mössbauer f number of Cu using a black absorber. The black absorber is an absorber with a very wide absorption line which is effectively opaque to the Mössbauer line but is partially transparent to the recoil radiation. With such an absorber

$$f = \frac{N_{\infty} - N_0}{N_{\infty}} \quad (42)$$

where N_{∞} is the intensity at "infinite velocity" and N_0 is the intensity at resonance, the background having been subtracted. They obtained $f = 0.710$ for Cu at 297°K.

Schiffer et al. (90) determined a θ_f by taking relative f numbers at three temperatures (82°K, 298°K, 425°K) and fitting the Debye approximation

$$f = \exp \left[- \frac{6E_r}{k\theta} \left\{ \frac{1}{4} + \left(\frac{T}{\theta} \right)^2 \int_0^{\theta/T} \frac{x dx}{e^x - 1} \right\} \right] \quad (43)$$

to these values. The relative f numbers were determined by the expression

$$\frac{f_2}{f_1} = \frac{\alpha_2 \beta_2}{\alpha_1 \beta_1} \quad (44)$$

where α is the fractional depth of the absorption peak and β is the linewidth. They obtained $\theta_f = 330 \pm 15^\circ\text{K}$.

Steyert and Taylor⁽⁹¹⁾ also performed a temperature study of the Mössbauer f number in which a combination of black and regular (Fe-Ti alloy) absorbers were used. Two Cu samples were examined at 293°K and a mean value of $f = 0.721 \pm .016$ was obtained.

b) θ_{host}

The treatment of the effect of thermal vibrations on the intensity of X-rays gives the same formalism as the treatment of the Mössbauer f-number (e.g., see reference 92). Thus a comparison of the θ_{host} obtained in this work can profitably be compared to the θ_x obtained in X-ray studies.

The intensity of an X-ray line can be represented by

$$F_T = F_O e^{-2M} \quad (45)$$

where F_O is the value of intensity obtained by treating the atoms in the solid as stationary and the exponential gives the effect of thermal motion just as in the theory of the Mössbauer f-number.

Five determinations of θ_x for Cu have been made (see Table 1).

Owen and Williams⁽⁹³⁾ did a study of F_T from 293°K to 850°K and, using relative F_T to eliminate all geometric and absorption effects, they obtained $\theta_x = 314^\circ\text{K}$.

Burie⁽⁹⁴⁾ studied the Bragg reflection intensities, proportional to $f^2 e^{-2M}$ where f^2 is the atomic scattering factor, and the temperature diffuse scattering (TDS), proportional to $f^2 (1 - e^{-2m})$ at

Table 1

X-Ray Determinations of the Debye Parameter for Copper

Investigators	Debye Parameter ($^{\circ}\text{K}$)
Owen and Williams ^(a)	314
Burie ^(b)	299
Chipman and Paskin ^(c)	307(327) ^(f)
Flinn <u>et al.</u> ^(d)	322
Graevskaya <u>et al.</u> ^(e)	310

(a) - Reference 93

(b) - Reference 94

(c) - Reference 95

(d) - Reference 96

(e) - Reference 97

(f) - Parenthetical value corrected for one and two phonon generation

a single temperature. A simple ratio then gives a value of e^{-2M} and thus θ_x . He obtained a $\theta_x = 299^\circ\text{K}$.

Chipman and Paskin⁽⁹⁵⁾ measured the intensity of the Bragg reflections at 79°K and related these to room temperature using

$$\theta_{T_0} = \left(\frac{V_{T_1}}{V_{T_0}} \right) \theta_{T_1} \quad (46)$$

They obtained $\theta_x = 307^\circ\text{K}$ from a Debye fit but taking account of the one and two phonon generation terms in the TDS corrected this to a higher 327°K .

Flinn et al.⁽⁹⁶⁾ made X-ray measurements over the temperature range of 4.2°K to 500°K as part of a study correlating X-ray scattering to the elastic properties of the solid and obtained $\theta_x = 322 \pm 22^\circ\text{K}$.

Graevskaya et al.⁽⁹⁷⁾ determined a θ_x of 310°K from intensity measurements concerned with the dependence of θ_x on the annealing duration and temperature in Cu.

A great deal of work has been done on the low temperature specific heat of Cu and a $\theta_{c_v} \simeq 345^\circ\text{K}$ has been firmly established for temperatures near absolute zero. A value of $\theta_{c_v} = 324^\circ\text{K}$ has been determined by Martin⁽¹⁰³⁾ from room temperature measurements. This does not exactly agree with the room temperature values of θ_x but since the two Debye parameters are different weightings of the lattice spectrum complete agreement should not be expected.

c). $\langle \omega^{-2} \rangle$

The general theory of the determination of various moments of the lattice spectrum from thermal data has been thoroughly discussed by Salter.⁽¹⁰⁴⁾ From the data discussed in Salter's paper a value

$$\langle \omega^{-2} \rangle_{\text{therm}} = (1.69 \pm 0.02) \times 10^{-27} \text{ sec}^2 \quad (47)$$

is obtained.

Jacobsen⁽¹⁰⁵⁾ has measured the lattice spectrum of copper using TDS measurements. A numerical integration over Jacobsen's result gives the value

$$\langle \omega^{-2} \rangle_{\text{latt}} = 1.59 \times 10^{-27} \text{ sec}^2. \quad (48)$$

The integration was performed using Simpson's rule over the range of frequencies from 10^{12} sec^{-1} to $\nu_m = 7 \times 10^{12} \text{ sec}^{-1}$ and assuming a quadratic fit from $\nu = 0$ to 10^{12} sec^{-1} . This last assumption was necessary due to the difficulty of reading $g(\nu)$ for $\nu < 10^{12} \text{ sec}^{-1}$ from Jacobsen's graph. This procedure was not completely satisfactory since the low frequency part of the lattice spectrum is important in the determination of inverse moments.

It should be mentioned that neutron diffraction studies of $g(\nu)$ in Cu have been made⁽¹⁰⁶⁻¹⁰⁸⁾ but that they do not agree in detail with one another or with the results of Jacobsen.⁽¹⁰⁵⁾ Thus the value of $\langle \omega^{-2} \rangle_{\text{latt}}$ from this calculation should be viewed with some skepticism.

2. Vanadium

a) θ_{host}

There has been no X-ray determination of the Debye parameter θ_x for vanadium. Therefore the following discussion will be concerned with the determinations of θ_{host} from low temperature specific heat measurements.

The results of these measurements are given in Table 2. It can be seen that there is a large discrepancy among the values obtained by different investigators. No simple explanation of this discrepancy is available.

However, three factors should be mentioned. First, it is possible that impurities are especially important in the determination of θ_{C_v} for vanadium. Thus the two experiments using the highest purity vanadium obtain $380^\circ\text{K}^{(109)}$ and $382^\circ\text{K}^{(110)}$ while the lower impurity results are widely scattered. Although there are not enough data for a good correlation, except for the data of Clusius et al.,⁽¹¹¹⁾ lower purity samples appear to give lower values for θ_{C_v} .

Second, vanadium goes superconducting for temperatures below $5.4^\circ\text{K}^{(110)}$. Thus to measure the specific heat in the normal state below this temperature a magnetic field on the order of five to ten kilogauss must be applied to destroy the superconductivity. This gives a term in C_{normal} which is determined by the interaction between the nuclear magnetic moment and the applied field and which

Table 2

Low Temperature Specific Heat Results for Vanadium

Investigators	Sample Purity(%)	γ ($\frac{\text{millijoules}}{\text{mole} \cdot \text{deg}}$) ^(a)	θ_{C_V} ($^{\circ}\text{K}$)	$\langle \omega^{-2} \rangle (\times 10^{-27} \text{sec}^2)$
Wolcott ^(b)	> 99.98	9.21	380	1.23
Worley <u>et al.</u> ^(c)	Sample 1 - 99.5	9.00	308	1.87
	Sample 2 - 99.8	8.83	273	2.38
Corak <u>et al.</u> ^(d)	$\approx$ 99.8	9.26	338	1.56
Clusius <u>et al.</u> ^(e)	99.5	6.70 ^(g)	425 ^(g)	0.98
Radebaugh and Keesom	> 99.99	9.82	382	1.22

(a) - See Eq. (49)

(b) - Reference 109

(c) - Reference 134

(d) - Reference 135

(e) - Reference 111

(f) - Reference 110

(g) - Experiment performed in temperature range 11-23°K

must be subtracted to get lattice and electronic contributions to the specific heat.

Third, in vanadium at low temperatures the electronic specific heat is quite large compared to the lattice specific heat. In the usual equation for the low temperature specific heat,

$$C = \gamma T + \alpha T^3 \quad (49)$$

$\gamma \simeq 9.82$ millijoules/mole·deg⁽¹¹⁰⁾ for vanadium compared to a value of $\gamma \simeq 0.695$ millijoules/mole·deg⁽⁷⁰⁾ for copper. It is easy to see from Eq. (49) that if the value of γ for vanadium is taken to be lower to agree with earlier investigators the value of θ_{host} must also decrease since α is proportional to $(\theta_{\text{host}})^{-3}$ in the Debye approximation.

b) $\langle \omega^{-2} \rangle$

Salter,⁽¹⁰⁴⁾ in his discussion of thermal data, gives a value

$$\langle \omega^{-2} \rangle_{\text{thermal}} = 1.13 \times 10^{-27} \text{ sec}^2 \quad (50)$$

for vanadium which is based on a value of $\theta_{\text{host}} = 399^\circ\text{K}$ obtained in a low temperature study of the elastic constants of vanadium by Alers.⁽¹¹²⁾ If the value of $\theta_{\text{C}_v} = 382^\circ\text{K}$ obtained in a low temperature specific heat study by Radebaugh and Keesom⁽¹¹⁰⁾ is used a value of $\langle \omega^{-2} \rangle_{\text{thermal}} = 1.21 \times 10^{-27} \text{ sec}^2$ is obtained which does not vary significantly from Salter's value. It should however be noted that $\langle \omega^{-2} \rangle$, as deduced from thermal data, does depend upon

the value chosen for the low temperature Debye parameter θ_{C_v} . The values of $\langle \omega^{-2} \rangle$ corresponding to the various experimental θ_{C_v} are given in Table 2.

$\langle \omega^{-2} \rangle$ has also been obtained from the results of neutron diffraction studies of the vanadium lattice spectrum by doing a numerical integration over the graphed results. Vanadium is a particularly good lattice to study using neutron diffraction since the scattering is almost exclusively incoherent and the vibration spectrum $g(\omega)$ can be drawn directly from the scattering results. (113)

The results of the numerical integrations are given in Table 3. Some other neutron diffraction studies have been made (114-116) but in several of these no correction was made for instrumental resolution. All the reported $g(\omega)$ show the same general two-peak structure. It can be seen that to the accuracy of the rough numerical method used there is a factor of two difference between the highest and lowest values but that they seem to group about a $\langle \omega^{-2} \rangle$ representative of a θ_{host} in the upper three hundreds. The samples used in the study by Chernoplekov et al. (117) exceeded 99.7% purity but no purity was given in the other two works.

As stated before the values of $g(\omega)$ given by the various authors have the least reliability for low ω which are particularly important in the determination of $\langle \omega^{-2} \rangle$.

The values of θ_{host} in Table 3 were obtained by using Salter's treatment (104) in the inverse order and are meant only to

Table 3

Vanadium. $\langle \omega^{-2} \rangle$ from Neutron Diffraction Experiments

Investigators	Sample Purity (%)	$\langle \omega^{-2} \rangle (\times 10^{-27} \text{ sec}^2)$	$\theta_{\text{host}} (^{\circ}\text{K})$
Stewart and Brockhouse ^(a)	-----	1.30	369
Eisenhauer <u>et al.</u> ^(b)	-----	1.08	395
Chernoplekov <u>et al.</u> ^(c)	> 99.7	0.76	483

(a) - A. T. Stewart and B. N. Brockhouse, Revs. Mod. Phys. 30, 250 (1958).

(b) - C. M. Eisenhauer, I. Pelah, D. J. Hughes and H. Palevsky, Phys. Rev. 109, 1046 (1958).

(c) - Reference 117.

give some rough comparison of the neutron diffraction results to the specific heat results.

3. Titanium

a) θ_{host}

There has been only one X-ray determination of the Debye parameter θ_x . Spreadborough and Christian,⁽¹¹⁸⁾ from a study of the temperature variation of the Bragg reflection intensities, obtained a value of $\theta_x = 270 \pm 30^\circ\text{K}$. In the evaluation of their data they used the volume correction of Eq. (46) but for Grüneisen constants of 2, 3, and 4. Since, in Appendix A, we have obtained $\gamma(\text{Ti}) = 1.232$ it is difficult to make a comparison with the value of θ_{host} obtained in their work.

There have been a number of specific heat determinations of the Debye parameter. The studies of most interest for this work are those by Wolcott⁽¹¹⁹⁾ and Johnson and Kothen.⁽¹²⁰⁾ Both groups investigated the specific heat over a wide range of temperature and found that the Debye parameter has a low temperature value of 430°K and decreases as the temperature increases, approaching a room temperature value of 360°K . Two other low temperature specific heat studies also gave a value of approximately 430°K for θ_{C_v} .^(121,122) An earlier study by Estermann et al.⁽¹²³⁾ found a low temperature θ_{C_v} of 280°K but they also obtained a low value for copper ($\theta = 315^\circ\text{K}$) so there may have been a systematic error in their experiment.

b) f Number

Steyert and Taylor, ⁽⁹¹⁾ in a temperature study of the Mössbauer line intensity using a combination of Fe-Ti and black absorbers, obtained a value of $f = 0.47$ for titanium. If Steyert and Taylor's value for f is used in Eq. (43) a value $\theta_r \approx 225^\circ\text{K}$ is obtained; this, using the mass correction discussed below, gives $\theta_{\text{host}} \approx 245^\circ\text{K}$ which is much lower than the room value of θ_{host} obtained from specific heat measurements and discussed in the last section. Thus $f = 0.47$ would seem to be too small a value.

B. Mössbauer f Numbers1. Theory

It was shown in Section III-B that in the Debye approximation the Mössbauer f-number is written

$$f = \exp \left[- \frac{6E_r}{k\theta} \left\{ \frac{1}{4} + \left(\frac{T}{\theta} \right)^2 \int_0^{\theta/T} \frac{x dx}{e^x - 1} \right\} \right] \quad (51)$$

where E_r is the recoil energy of the free nucleus due to the decay and θ is the Debye parameter.

The working formula for this study is obtained by differentiating Eq. (51) with respect to $\ln V$. This gives

$$\frac{\Delta f}{f} = - \gamma Y \frac{\Delta V}{V} \quad (52)$$

where

$$Y = \frac{6E_r}{k\theta} \left[\frac{1}{4} - \frac{1}{e^{\theta/T} - 1} + 3 \left(\frac{T}{\theta} \right)^2 \int_0^{\theta/T} \frac{x dx}{e^x - 1} \right] \quad (53)$$

and

$$\gamma = - \frac{d(\ln \theta)}{d(\ln v)} \quad (54)$$

is the Grüneisen constant. Extraction of the Mössbauer Debye parameter θ_f from γ is discussed in Appendix B where a table of γ vs. θ/T is given. The experimental data give f as a function of pressure; using $P(V)$ data for the elements considered allows f to be known as a function of volume. A least squares fit is then made to the best straight line through a plot of $\Delta f/f$ vs. $\Delta V/V$. From the slope, using an independent value for the Grüneisen constant, one can obtain a value for the Debye parameter θ_f .

This evaluation gives a Debye parameter we shall call θ_f . It represents, in some sense, the interaction of the ^{57}Fe impurity with the host lattice, i.e., θ_f represents the strength of the impurity-host binding. A Debye parameter more representative of the host material may be obtained from the expression

$$\theta_{\text{host}} = \left(\frac{M'}{M} \right)^{\frac{1}{2}} \theta_f \quad (55)$$

where M' is the mass of the ^{57}Fe impurity and M is the host atom mass. Equation (55) results from the observation that the Debye θ is proportional to the lattice wave velocity which is, in turn, proportional to the inverse square root of the atomic mass. (70)

The value of θ_f can be used directly in the evaluation of f at "zero pressure" from Eq. (51) which can then be related to the inverse second moment of the lattice spectrum. We have shown in

Section III-B that

$$f = \exp \left[- \frac{\hbar^2}{MN} \int_0^\infty d\omega \frac{g(\omega)}{\omega} \left\{ \frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1} \right\} \right] \quad (56)$$

which can be written

$$f = \exp \left[- \frac{\hbar^2}{2MN} \int_0^\infty d\omega \frac{g(\omega)}{\omega} \operatorname{ctnh} \frac{\hbar\omega}{2kT} \right] \quad (57)$$

The hyperbolic cotangent can be expanded⁽¹²⁴⁾

$$\operatorname{ctnh} z = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \frac{2}{945} z^5 - \dots + \frac{2^{2n} B_{2n}}{(2n)!} z^{2n-1} + \dots \quad (58)$$

where B_n are the Bernoulli numbers. This expansion is valid for $\theta_D < \pi T$ which is well satisfied for the elements studied in this work.

Keeping only the first three terms of the expansion of Eq.

(58) we have

$$f = \exp \left[- \frac{\hbar^2}{12MkT} \right] \exp \left[- \frac{kT}{M} \langle \omega^{-2} \rangle \right] \exp \left[\frac{\hbar^4}{720M(kT)^3} \langle \omega^2 \rangle \right] \quad (59)$$

An evaluation of the arguments of the exponentials allows us to simplify this expression further. The first term, for $T = 298^\circ\text{K}$, gives a factor of 0.987. The arguments of the second and third term reduce, at the same temperature to

$$(-2.297 \times 10^{26} \text{ sec}^{-2}) \langle \omega^{-2} \rangle$$

and

$$(1.371 \times 10^{-31} \text{ sec}^2) \langle \omega^2 \rangle.$$

An idea of the relative magnitude of these two terms can be obtained by using the simple Debye model $g(\omega) = \omega^2$. Thus

$$\langle \omega^n \rangle = \frac{\int_0^{\omega_m} \omega^n g(\omega) d\omega}{\int_0^{\omega_m} g(\omega) d\omega} = \frac{3}{n+3} \frac{\omega_m^n}{\omega_m} = \frac{3}{n+3} \left(\frac{k\theta_D}{h} \right)^n \quad (60)$$

For Cu, assuming a $\theta_D \simeq 340^\circ\text{K}$, one obtains

$$\langle \omega^2 \rangle \simeq 1.2 \times 10^{27} \text{ sec}^{-2}$$

$$\langle \omega^{-2} \rangle \simeq 1.5 \times 10^{-27} \text{ sec}^{-2}$$

Using these results it is easy to see that the term involving $\langle \omega^2 \rangle$ is negligible so that we can finally write

$$f = 0.987 \exp[(-2.297 \times 10^{26} \text{ sec}^{-2}) \langle \omega^{-2} \rangle] \quad (61)$$

2. Experimental Method

a) Formalism

The experimental determination of f was first treated in detail by Margulies and Ehrman⁽¹²⁵⁾ who discussed a general expression for the transmission of radiation through a moving absorber as a function of absorber velocity, and by Shirley et al.⁽¹²⁶⁾ who introduced the area method of determining f , a method which will be discussed in detail below. These papers, together with later developments by Housley et al.^(88,89,127) and Hohenemser⁽¹²⁸⁾ were concerned with the determination of absolute f numbers.

In this work the interest is in the change of the Mössbauer f number with pressure and thus the difficulties of obtaining absolute f numbers, discussed by the above authors, are largely by-passed.

To obtain relative f numbers the area method is used. This method will now be discussed.

Let $I_t(E)$ be the total intensity, as a function of energy E , emitted by the source. We can write this as

$$I_t(E) = I_m(E) + I_R(E) + B(E) \quad (62)$$

where

$I_m(E) \equiv$ Mössbauer non-recoil radiation

$I_R(E) \equiv$ Recoil radiation

$B(E) \equiv$ Background .

In the following we shall assume that the background radiation has been subtracted from $I_t(E)$. The experimental method of doing this will be discussed below. Thus we can define

$$I(E) = I_m(E) + I_R(E) \quad (63)$$

where, in the case of ^{57}Fe , $I(E)$ is the intensity of the 14.4 keV radiation. This intensity is processed by a detector system and the final number of counts is given by

$$N = \int dE D(E) I(E) \quad (64)$$

where $D(E)$ is the detector resolution. Adding an absorber and putting the source and absorber into relative motion with a velocity v we obtain

$$N(S) = \int dE D(E) I(E+S) e^{-n\sigma(E)} e^{-n'\sigma'(E)} \quad (65)$$

where

$$S = \frac{v}{c} E_0$$

$n\sigma(E) \equiv$ Resonant absorption

$n'\sigma'(E) \equiv$ Non-resonant absorption.

We can simplify this expression by noting that $I(E)$ is very sharply peaked about E_0 and that $\sigma'(E)$ and $D(E)$ are slowly varying functions of E . Thus to a very good approximation

$$N(S) = D(E_0) e^{-n'\sigma'(E_0)} \int I(E+S) e^{-n\sigma(E)} dE. \quad (66)$$

Using Eq. (63) we can write this

$$N(S) = D(E_0) e^{-n'\sigma'(E_0)} \left[\int I_m(E+S) e^{-n\sigma(E)} dE + \int I_R(E+S) e^{-n\sigma(E)} dE \right]. \quad (67)$$

At this point we can define an experimental f number by the expression

$$fN = \int D(E) I_m(E) dE \simeq D(E_0) \int I_m(E) dE \quad (68)$$

so that we can write the second integral in Eq. (67) as

$$\begin{aligned} D(E_0) \int I_R(E+S) e^{-n\sigma(E)} dE &\simeq D(E_0) \int I_R(E+S) dE \\ &= D(E_0) \left[\int I(E+S) dE - \int I_m(E+S) dE \right] \\ &= N - D(E_0) \int I_m(E+S) dE. \end{aligned} \quad (69)$$

The first equality follows from the fact that by the very nature of the recoil radiation $I_R(E) \neq 0$ only when $\sigma(E) \equiv 0$. Thus

$$N(S) = D(E_0) e^{-n'\sigma'(E_0)} \int I_m(E+S) (e^{n\sigma(E)} - 1) dE + N e^{-n'\sigma'(E_0)}. \quad (70)$$

Next we form the ratio

$$\varepsilon(S) = \frac{N(\infty) - N(S)}{N(\infty)} \quad (71)$$

where

$$N(\infty) = N e^{-n'\sigma'(E_o)} \quad (72)$$

since at "infinite" velocity all Mössbauer resonance is destroyed.

Then

$$\epsilon(S) = \frac{D(E_o)}{N} \int I_m(E+S) (1 - e^{-n\sigma(E)}) dE \quad (73)$$

Integrating $\epsilon(S)$ over all velocities, i.e. taking the area of the resonant curve, gives

$$\int \epsilon(S) dS = f \int (1 - e^{-n\sigma(E)}) dE \quad (74)$$

when we use Eq. (18) and note that $I_m(E+S)$ is symmetric in S and E .

The important thing to note about Eq. (74) is the inclusion of all absorber parameters in the integral separate from the lone source parameter, f , that remains. (The other source parameters such as linewidth and peak position have been normalized out by use of the velocity integration.). Thus if the source is changed in some manner, either by the variation of temperature as in the studies of Steyert and Taylor⁽⁹¹⁾ and Schiffer et al.,⁽⁹⁰⁾ or by pressure as in this study, while keeping the absorber unchanged, the relative change in f_{source} can be obtained by taking a ratio of absorption areas and eliminating all absorber parameters.

b) Data Analysis

In the preceding discussion we have been concerned with the Mossbauer line to the exclusion of background. However,

experimentally one finds that a sizeable background exists consisting of 122 and 136 keV γ -rays involved in the decay of ^{57}Co to ^{57}Fe as well as source X-rays and general non-source background. Periodic checks during runs have shown general non-source background to be several orders of magnitude smaller than source background. Proper setting of the energy window will cut out all radiation below 14.4 keV which, with the solids studied in this work, will remove all X-rays from the source. Thus the highest energy X-rays from Cu are at 9 keV, from V at 5.45 keV and from Ti at 4.95 keV,⁽¹²⁹⁾ and we need consider only the 122 keV and 136 keV radiation.

The " $v=\infty$ " background N_∞ (Figure 12) is actually 14.4 keV radiation plus all the higher energy radiation that appears in the window because it is degraded in energy before entering the proportional counter or is just partially degraded in the proportional counter. Thus we can write

$$N_\infty = H + L \quad (75)$$

where L represents the 14.4 keV radiation and H represents the higher energy radiation.

To eliminate H we take a ratio of the counting rate with source and absorber positioned and in motion as in the experiment, together with the counting rate with the same geometry but with an inserted .006" Cu foil (Figure 13). This foil absorbs essentially all L radiation ($\approx 10^{-5}$ transmission) but only 4% of the H

FIGURE 12. ABSORPTION SPECTRUM—SCHEMATIC

FIGURE 13. BACKGROUND DETERMINATION—EXPERIMENTAL ARRANGEMENT

radiation. (130) The ratio is taken with the absorber in motion and thus some of the L radiation is resonantly absorbed when the .006" Cu foil is not present. Taking all this into consideration we have

$$\text{Ratio} = \frac{H + L(1-X)}{\alpha H} \quad (76)$$

where X is the fraction of L resonantly absorbed and $\alpha = 0.96$ (4% of H absorbed in .006" Cu).

The observed spectrum has an area A (Figure 12) and a certain fraction ξ of this area is contained within the limits $V_1 < V < V_2$ of the spectrum observed in the multi-channel analyzer. In the computer program used to evaluate the spectrum the area is

$$A = \sum_{\text{channels}} \left(\frac{\text{fraction}}{\text{channel}} \right) \quad (77)$$

Thus A is a total fraction of radiation resonantly absorbed, ξA is the fraction of the resonant radiation in the $V_1 < V < V_2$ range, and $\xi A/W$ is the average fraction per channel of resonantly absorbed radiation where W is the width of the multi-channel read-out in channels. Thus

$$XL = \frac{\xi A}{W} N_{\infty} \quad (78)$$

or the fraction of 14.4 keV γ -rays resonantly absorbed is equal to the average fraction per channel absorbed multiplied by the total " $V=\infty$ " level. Inserting this in Eq. (76) gives

$$H = \frac{N_{\infty}}{\alpha R} \left(1 - \frac{\xi A}{W}\right) \quad (79)$$

where we have used the fact that $N_{\infty} = L + H$. Thus we have

$$L = N_{\infty} - H = N_{\infty}(1 - \beta) \quad (80)$$

where $\beta = (1 - \xi A/W)/\alpha R$.

The computer calculates an area based on the N_{∞} and thus

$$\begin{aligned} (\text{Area})_{\text{computer}} &= \int \frac{N_{\infty} - N(v)}{N_{\infty}} dv = (1 - \beta) \int \frac{L_{\infty} - L(v)}{L_{\infty}} \\ &= (1 - \beta)(\text{Area})_{\text{true}} \end{aligned} \quad (81)$$

Writing Eq. (74) as

$$f I_n(\text{abs}) = (\text{Area})_{\text{true}} \quad (82)$$

where $I_n(\text{abs})$ is an integral depending only upon absorber parameters, we see that

$$\frac{f_P}{f_0} = \frac{(\text{Area})_{\text{computer}}(P)}{(\text{Area})_{\text{computer}}(0)} \frac{1 - \beta_0}{1 - \beta_P} \quad (83)$$

where the subscript 0 refers to atmospheric pressure and the subscript P refers to some higher pressure.

To summarize we define a relative f

$$f_R = \frac{(\text{Area})_{\text{computer}}}{1 - \frac{1 - \xi A/W}{\alpha R}} \quad (84)$$

where

$A \equiv$ area of the Lorentzian absorption curve

$\xi \equiv$ fraction of A in the multichannel spectrum

$W \equiv$ width, in channels, of the multichannel spectrum

$\alpha \equiv 0.96$ - fraction of high energy γ -rays that traverse the
.006" Cu insert

$R \equiv$ measured ratio (without Cu insert/with Cu insert).

c) Evaluation of ξ

ξ is approximated by doing the integral

$$\xi = \frac{1}{\pi} \int_{x_1}^{x_2} \frac{dx}{x^2 + 1} \quad x = \frac{2}{\Gamma}(E - E_0) \quad (85)$$

where $x_1 < 0$ and $x_2 > 0$. The values of x_1 and x_2 are obtained by finding the distance from the center of the absorption peak and dividing by the linewidth. Thus

$$|x_1| = \frac{2(p - v_1)}{\Gamma} \quad x_2 = \frac{2(v_2 - p)}{\Gamma} \quad (86)$$

(see Figure 12), where p , v_1 , v_2 , and Γ are given in channels.

This assumes the absorption curve is Lorentzian which is not exactly true. However an error analysis will show that an error of several per cent in ξ has essentially no effect on f_R .

Finally

$$\xi \simeq \frac{1}{\pi} [\arctan x_2 + \arctan |x_1|]. \quad (87)$$

d) Error Analysis

From Eq. (84)

$$\frac{\delta f_R}{f_R} = \left[1 - \frac{\xi A/W}{\alpha R + \frac{\xi A}{W} - 1} \right] \frac{\delta A}{A} = C_A \frac{\delta A}{A} \quad (88a)$$

$$\frac{\delta f_R}{f_R} = \left[1 - \frac{\alpha R}{\alpha R + \frac{\xi A}{W} - 1} \right] \frac{\delta(\alpha R)}{\alpha R} = C_{\alpha R} \frac{\delta(\alpha R)}{\alpha R} \quad (88b)$$

$$\frac{\delta f_R}{f_R} = \left[- \frac{\xi A/W}{\alpha R + \frac{\xi A}{W} - 1} \right] \frac{\delta \xi}{\xi} = C_{\xi} \frac{\delta \xi}{\xi} \quad (88c)$$

$$\frac{\delta f_R}{f_R} = \left[\frac{\xi A/W}{\alpha R + \frac{\xi A}{W} - 1} \right] \frac{\delta W}{W} = C_W \frac{\delta W}{W} \quad (88d)$$

Typical values are

$$\alpha R = 4 ; \xi A = 4 ; W = 100$$

which give $C_A \simeq .99$; $C_{(\alpha R)} \simeq -0.33$; $C_W = -C_{\xi} \simeq .01$. This proves, as stated in the last section, that an error in ξ is relatively unimportant and in the error analysis, errors in ξ and W have been neglected and the second term in C_A , being of the same order, is also neglected. This leaves

$$C_A = 1. \quad C_{\alpha R} = 1 - \frac{\alpha R}{\alpha R + \frac{\xi A}{W} - 1} \quad (89)$$

These expressions also allow us to estimate the number of counts that should be taken in the ratio R to get an error in f_R "wholly" dependent on the area error as evaluated by the computer. We would like to have

$$C_{\alpha R} \frac{\delta(\alpha R)}{\alpha R} \ll C_A \frac{\delta A}{A}.$$

Typically the area A is computed to about 0.7% so that the condition on αR as

$$C_{\alpha R} \frac{\delta(\alpha R)}{\alpha R} \ll 7 \times 10^{-3}$$

or for $C_{\alpha R} \simeq 0.5$, $\frac{\delta(\alpha R)}{\alpha R} \ll 1.5 \times 10^{-2}$. If we take the same number of counts with and without the .006" Cu insert so that the error in each run is $N^{-\frac{1}{2}}$, then

$$\frac{\delta(\alpha R)}{\alpha R} = \sqrt{\frac{2}{N}} \ll 1.5 \times 10^{-2}$$

or $N \gg 10,000$. Typically we have $N \simeq 100,000$ count so this condition is well satisfied and the error in f_R is due almost entirely to the error in the computation of the area by the computer.

C. Experimental Results

1. Introduction

The following sections present the data from the Cu, V, and Ti pressure runs and the characteristic temperatures and lattice moments calculated from this data. In the data tables the area is that computed by Burton's⁽⁸⁷⁾ program previously mentioned; the ratio is the expression

$$R_T = \frac{\alpha R}{1 - \frac{\epsilon A}{W}} = \frac{1}{\beta} \quad (90)$$

and the f numbers are calculated using Eq. (83).

The best straight line fit to the pressure data is given (e.g. see Figure 14). $P(V)$ data for these elements are discussed and the best straight line fit to the plot of $\Delta f/f$ vs. $\Delta V/V$ is given (e.g. see Figure 15). Using Eqs. (52) and (53) and a value of the Grüneisen constant a value of the Debye parameter θ_f is obtained.

This value of θ_f is used to calculate

- 1) a θ_{host} , using Eq. (55), which is more characteristic of the host material, and
- 2) an inverse second moment of the lattice spectrum using Eq. (61).

These values are tabulated in Table 4 and discussed in the sections immediately following.

2. Copper

a) Data

Data for Cu are given in Table 8 of Appendix D and plotted versus pressure in Figure 14. The best straight line fit to the pressure data is

$$\frac{\Delta f}{f} = (8.14 \pm 0.65) \times 10^{-4} P \quad (91)$$

where P is in kilobars.

$P(V)$ data for Cu have been obtained using shock wave techniques by Walsh et al. ⁽¹³¹⁾ in a study going to 500 kilobars and by

FIGURE 14. COPPER RELATIVE f -vs.- PRESSURE

McQueen and Marsh⁽¹³²⁾ in a study going to 3 megabars. There is no significant difference between the two works. Data from the first work are used since the present study is done in the low pressure regions.

The $P(V)$ data were fitted to the Murnaghan equation

$$\frac{V}{V_0} = \left[1 + \frac{P}{234} \right]^{-0.176} \quad (92)$$

by fitting the 100 kilobar result of Walsh et al.⁽¹³¹⁾ to the "zero pressure" compressibility results of Overton and Gaffney.⁽¹³³⁾ Self-consistency was made by checking the fit to the experimental 150 kilobar V_P/V_0 ⁽¹³¹⁾ which agreed with the Murnaghan equation result to within 0.1%.

Using this $P(V)$ expression the straight line fit

$$\frac{\Delta f}{f} = (-1.283 \pm .095) \frac{\Delta V}{V} \quad (93)$$

was obtained. The $f(V)$ data are shown in Figure 15.

From Eq. (52) we see that the slope of the $\Delta f/f$ vs. $\Delta V/V$ fit equals γY where γ is the Grüneisen parameter. Using a value $\gamma = 1.998$ (Appendix A) gives

$$Y = 0.321 \pm .024 \quad (94)$$

which gives (see Appendix B)

$$(\theta_f)_{Cu} = 350 \pm 14^\circ K \quad (95a)$$

FIGURE 15. COPPER RELATIVE f -vs.- VOLUME

and using the mass correction of Eq. (55) gives

$$\theta_{\text{Cu}} = 331 \pm 14^\circ\text{K} . \quad (95b)$$

Since these values are obtained from a linear fit to data over an 100 kilobar range they are probably high. An estimate of the downward correction can be made using the equation

$$\theta_o = \left(\frac{V_p}{V_o} \right)^{\gamma} \theta_p \quad (96)$$

and assuming the values given in Eq. (95) are representative of 50 kilobars, mid-way in the pressure range. Then using the Murnaghan Eq. (92) for V_{50}/V_o gives

$$(\theta_{fo})_{\text{Cu}} = 327 \pm 14^\circ\text{K} \quad (97a)$$

$$(\theta_o)_{\text{Cu}} = 309 \pm 14^\circ\text{K} \quad (97b)$$

where the zero subscripts refer to atmospheric ("zero") pressure.

From Eq. (51), θ_{fo} gives

$$f_{\text{Cu}} = 0.684 \pm .020 \quad (98)$$

and from Eq. (61)

$$\langle \omega^{-2} \rangle_{\text{Cu}} = (1.60 \pm 0.13) \times 10^{-27} \text{ sec}^2. \quad (99)$$

b) Discussion

The results of this work are in excellent agreement with previous results. It is most meaningful to compare the θ_{host} value with the Debye parameter θ_x obtained from studies of the variation

of Bragg line intensities with temperature since both depend upon the Debye-Waller factor. Thus we have obtained $\theta_{\text{host}} = 309^\circ\text{K}$ which falls well in the range of θ_x results which run from 299°K to 322°K and just below the room temperature value of θ_{C_v} obtained by Martin.⁽¹⁰³⁾ Exact agreement between θ_x (and thus θ_f) and θ_{C_v} is not to be expected since they depend upon different weightings of the lattice spectrum.

The value $\theta_f = 327^\circ\text{K}$ for ^{57}Fe in copper obtained here is in good agreement with the value of 330°K obtained by Schiffer et al.⁽⁹⁰⁾ in a temperature study of the Mössbauer f number.

The second inverse moment of the lattice spectrum obtained here, $\langle \omega^{-2} \rangle_f = 1.60 \times 10^{-27} \text{ sec}^2$ agrees to within experimental error with the value of $1.69 \times 10^{-27} \text{ sec}^2$ obtained from thermal data and that of $1.59 \times 10^{-27} \text{ sec}^2$ obtained by a numerical integration over the $g(\omega)$ derived by Jacobsen⁽¹⁰⁵⁾ from an X-ray TDS study.

The Mössbauer f number, $f = 0.684$, lies from 3 to 5% lower than the f numbers previously obtained for ^{57}Fe in copper.^(88,89,91) Better agreement could be obtained by using the value of θ_f obtained directly from the linear fit of $\Delta f/f$ to $\Delta V/V$. This value, $\theta_f = 350^\circ\text{K}$ (Eq. (95a)) gives $f = 0.716$. However, using this value of θ_f , which has been treated here as being representative of a pressure of 50 kilobars destroys the excellent agreement of θ_{host} and $\langle \omega^{-2} \rangle$ with previous results. Thus the use of Eq. (96) to go to an "atmospheric θ_f " is justified.

3. Vanadium

a) Data

Data for V are given in Table 9 of Appendix D and plotted versus pressure in Figure 16. The best straight line fit to the pressure data is

$$\frac{\Delta f}{f} = (7.81 \pm 0.56) \times 10^{-4} P \quad (100)$$

where P is in kilobars.

P(V) data for V have been obtained using shock wave techniques by McQueen and Marsh⁽¹³²⁾ in a study going up to 3 megabars. The P(V) data were fitted to the Murnaghan equation

$$\frac{V_P}{V_0} = \left[1 + \frac{P}{344} \right]^{-0.222} \quad (101)$$

by fitting the 100 kilobar result of McQueen and Marsh to the "zero pressure" compressibility results of Alers.⁽¹¹²⁾ Self-consistency was made by checking the fit to the experimental 200 kilobar V_P/V_0 which agreed with the Murnaghan equation result to within 0.2%.

Using this P(V) expression the straight line fit

$$\frac{\Delta f}{f} = (-1.380 \pm 0.100) \frac{\Delta V}{V} \quad (102)$$

was obtained. The f(V) data are shown in Figure 17. Thus, using $\gamma = 1.257$ (Appendix A),

$$Y = 0.549 \pm .040 \quad (103)$$

which gives (see Appendix B)

$$(\theta_f)_V = 268 \pm 10^\circ \text{K} \quad (104a)$$

FIGURE 16. VANADIUM RELATIVE f -vs.-PRESSURE

FIGURE 17. VANADIUM RELATIVE f -vs.- VOLUME

and the mass correction of Eq. (55) gives

$$\theta_V = 284 \pm 11^\circ\text{K} . \quad (104b)$$

As in the case of copper we can make an adjustment for pressure using Eq. (96) and obtain

$$(\theta_{fo})_V = 258 \pm 10^\circ\text{K} \quad (105a)$$

$$(\theta_o)_V = 274 \pm 11^\circ\text{K} . \quad (105b)$$

From Eq. (51) θ_{fo} gives

$$f_V = 0.547 \pm .024 \quad (106)$$

and from Eq. (61)

$$\langle w^{-2} \rangle_V = (2.57 \pm 0.19) \times 10^{-27} \text{ sec}^2 . \quad (107)$$

b) Discussion

There is an impurity problem for vanadium which makes comparison of results difficult. No determination of the X-ray Debye parameter θ_x exists. Thus, comparison must be made with specific heat θ_{C_V} results.

The value $\theta_{host} = 274^\circ\text{K}$ obtained in this study agrees roughly with the values of θ_{C_V} obtained by Worley et al. ⁽¹³⁴⁾ (273°K, 308°K) and Corak et al. ⁽¹³⁵⁾ (338°K) obtained in low temperature studies of specific heat on lower impurity (99.5-99.8%) vanadium samples. Exact agreement cannot be expected since the Debye parameter is not a constant over all temperatures but is usually less at room temperature than at low temperature. The highest purity ($\sim 99.99\%$)

vanadium gives a low temperature $\theta_{C_v} \simeq 380^\circ\text{K}$ ^(109,110) which is much higher than the 274°K obtained here. The vanadium used in this study was of low purity since it was necessary to diffuse radioactive ^{57}Co into the vanadium to make a Mössbauer source.

This disagreement between low purity and high purity vanadium results is also seen in the results on $\langle \omega^{-2} \rangle$. The value $\langle \omega^{-2} \rangle_f = 2.57 \times 10^{-27} \text{ sec}^2$ here does not agree with the value of $1.21 \times 10^{-27} \text{ sec}^2$ obtained from thermal data based on a $\theta_{C_v} \simeq 380^\circ\text{K}$ but does agree with the $\langle \omega^{-2} \rangle$ derived from the lower purity θ_{C_v} . Rough integration over the results of neutron determinations of $g(\omega)$ gives results characteristic of a Debye parameter in the upper 300's and thus consistent with the high purity θ_{C_v} determinations.

Thus, unlike copper, determination of lattice spectrum moments in vanadium from specific heat and Mössbauer data is very sensitive to impurities in the vanadium.

4. Titanium

a) Introduction

A minimal amount of data was taken for titanium for two reasons. First, as discussed in Section V-C-4, there is some doubt about the $P(V)$ data for titanium. Second, it is possible that even a small addition of ^{57}Co to titanium puts the alloy into a mixed phase $\text{Ti}_2\text{Co} + \alpha$.⁽¹³⁶⁾ A mixed phase would indicate a non-random distribution of Co throughout the titanium lattice and makes the application of the

simple Debye approximation to Δf , Eq. (52), doubtful since we would expect a difference in the Debye parameter θ_f for the two phases and in the pressure dependences of these θ_f .

b) Data

Data for Ti are given in Table 10 of Appendix D and plotted versus pressure in Figure 18. The best straight line fit to the pressure data is

$$\frac{\Delta f}{f} = (7.21 \pm 1.39) \times 10^{-4} P \quad (108)$$

where P is in kilobars.

$P(V)$ data for Ti have been obtained using shock wave techniques by Walsh et al. ⁽¹³¹⁾ in a study going to 500 kilobars and by McQueen and Marsh ⁽¹³²⁾ in a study going to 3 megabars. There is significant disagreement between the two works. A sluggish first-order phase transition from a low pressure hexagonal close-packed structure to a high pressure distorted cubic structure has been reported at 80-85 kilobars. ⁽¹³⁷⁾ It is possible that the discrepancy in $P(V)$ data reflects different rates of attaining this transformation in the shock wave. Using the earlier work and fitting a Murnaghan equation to the 100 kilobar point and the "zero pressure" compressibility data of Fisher and Renken ⁽¹³⁸⁾ gives

$$\frac{V_P}{V_0} = \left[1 + \frac{P}{794} \right]^{-0.739} \quad (109)$$

A self-consistency check made by computing V_{150}/V_0 from Eq. (109) gives a value 0.5% away from the experimental value. Attempts to fit

FIGURE 18. TITANIUM RELATIVE f-vs.-PRESSURE

the data of McQueen and Marsh⁽¹³²⁾ using the atmospheric compressibility value were not successful. It was impossible to fit a Murnaghan equation and using a quadratic fit for the atmospheric compressibility and the 100 kilobar value gave a value approximately 20% away from the experimental value at 200 kilobars.

Using the $P(V)$ expression of Eq. (109) the straight line fit

$$\frac{\Delta f}{f} = (-0.843 \pm 0.158) \frac{\Delta V}{V} . \quad (110)$$

The $f(V)$ data are shown in Figure 19.

Thus, using $\gamma = 1.232$ (Appendix A),

$$Y = 0.342 \pm .064 \quad (111)$$

which gives (see Appendix B)

$$(\theta_f)_{Ti} = 339 \pm 35^\circ K \quad (112a)$$

and the mass correction of Eq. (55) gives

$$\theta_{Ti} = 370 \pm 40^\circ K . \quad (112b)$$

As in the case of copper we can make an adjustment for pressure using Eq. (96) and obtain

$$(\theta_{fo})_{Ti} = 321 \pm 35^\circ K \quad (113a)$$

$$(\theta_o)_{Ti} = 350 \pm 40^\circ K . \quad (113b)$$

From Eq. (51) θ_{fo} gives

$$f_{Ti} = 0.674 \pm .060 \quad (114)$$

FIGURE 19. TITANIUM RELATIVE f -vs.-VOLUME

and from Eq. (61)

$$\langle \omega^{-2} \rangle_{\text{Ti}} = (1.66 \pm 0.40) \times 10^{-27} \text{ sec}^2. \quad (115)$$

c) Discussion

Within the accuracy of the experimental data there is excellent agreement between the value of $\theta_{\text{host}} = 350 \pm 40^\circ\text{K}$ obtained here and the room temperature determinations of $\theta_{\text{C}_v} = 360^\circ\text{K}$.^(119,120) The only determination of the X-ray Debye parameter θ_x , $\theta_x = 270^\circ\text{K}$,⁽¹¹⁸⁾ is obtained from the data by using an incorrect Grüneisen constant and thus comparison with our result is difficult.

The value $f = 0.67$ obtained here for the Mössbauer f number disagrees with the only previous determination of $f = 0.47$ ⁽⁹¹⁾ but the lower value gives an exceptionally low value for θ_{host} when analyzed using Eq. (51) and the mass correction, Eq. (55). Thus the value $f = 0.67$ seems more in line with other data.

No work exists with which to compare our value of $\langle \omega^{-2} \rangle = 1.66 \times 10^{-27} \text{ sec}^2$. Mozer et al.⁽¹³⁹⁾ have obtained some preliminary neutron diffraction results bearing on $g(\omega)$ for titanium but no complete study is available.

D. Conclusion

The discussion of the results for copper indicate that the best agreement is obtained if the value of θ_f obtained from fitting the $\Delta f/f$ data to $\Delta V/V$ is treated as an θ_f representative of the 50 kilobar point and an adjustment to atmospheric pressure is made using Eq. (96). This gives very good agreement in copper with the Debye

parameters θ_x obtained from X-ray intensity measurements, with the $\langle \omega^{-2} \rangle$ obtained from both thermal data and an X-ray determination of $g(\omega)$, and with previous f number values. Since copper seems to be a good standard,⁽⁸⁹⁾ the adjustment to atmospheric pressure was made systematically throughout the vanadium and titanium analysis since it works well for copper.

The copper results are consistent with a θ_{host} of 310-320°K at room temperature and a $\langle \omega^{-2} \rangle$ of $1.60-1.70 \times 10^{-27} \text{ sec}^2$.

The vanadium result ($\theta_{\text{host}} = 274^\circ\text{K}$) agrees roughly with the low temperature specific heat θ_{host} obtained from lower purity vanadium ($\theta \simeq 380^\circ\text{K}$). There seems to be an impurity problem here which is not well understood at present.

The results for titanium agree very well with results of the specific heat determinations of the Debye parameter and seem to indicate a value of $\theta_{\text{host}} \simeq 350-360^\circ\text{K}$ at room temperature. There is disagreement with the only previous f number determination for titanium by Steyert and Taylor⁽⁹¹⁾ but that value gives an exceptionally low θ_{host} .

The results of this study are tabulated in Table 4; the explanation of the table headings is given in Section V-C-1.

Table 4

Results of Mössbauer f Number Experiment

Element	$\alpha (\times 10^{-4})$	β	50 kilobar		Atmospheric		$\langle \omega^{-2} \rangle$	f
	from $\Delta f/f = \alpha P$ (P in kbars)	from $\Delta f/f = -\beta \Delta V/V$	$\theta_f (^{\circ}\text{K})$	$\theta_{\text{host}} (^{\circ}\text{K})$	$\theta_f (^{\circ}\text{K})$	$\theta_{\text{host}} (^{\circ}\text{K})$	($\times 10^{-27} \text{sec}^2$)	
Cu	8.14 ± 0.65	$1.283 \pm .095$	350 ± 14	331 ± 14	327 ± 14	309 ± 14	1.60 ± 0.13	$0.684 \pm .020$
V	7.81 ± 0.56	$1.380 \pm .100$	268 ± 10	284 ± 11	258 ± 10	274 ± 11	2.57 ± 0.19	$0.547 \pm .024$
Ti	7.21 ± 1.39	$0.843 \pm .158$	339 ± 35	370 ± 40	321 ± 35	350 ± 40	1.66 ± 0.40	$0.674 \pm .060$

VI. ISOMER SHIFT

A. Introduction

We have seen in Section III-C that the energy shift of the nuclear levels due to the finite size of the nucleus can be written

$$\Delta\epsilon = \alpha |\Psi(0)|^2 \quad (116)$$

where $|\Psi(0)|^2$ is the total s electron density at the nucleus and α is a scaling parameter containing electronic and nuclear parameters. Experimentally it is the difference in $\Delta\epsilon$ between materials that is measured and comparison between isomer shifts must always be made with respect to a common material.

A determination of α can be made by comparing the isomer shifts of ferric and ferrous salts measured by De Benedetti et al.⁽⁶⁶⁾ and Walker et al.⁽⁶⁷⁾ and the ionic wave functions computed by Watson.⁽¹⁴⁰⁾ Experimentally

$$\Delta\epsilon(\text{Fe}^{2+}) - \Delta\epsilon(\text{Fe}^{3+}) \simeq 0.90 \text{ mm/sec.} \quad (117)$$

Using the free ion wave functions of Watson⁽¹⁴⁰⁾ who obtained

$$|\Psi_{2+}(0)|^2 - |\Psi_{3+}(0)|^2 \simeq -1.9 a_0^{-3} \quad (118)$$

gives

$$\alpha \simeq -0.47 a_0^3 \text{ mm/sec.} \quad (119)$$

This procedure has been criticized by Simanek and Sroubek⁽¹⁴¹⁾ who argue that the large increases in $|\psi(0)|^2$ on going from the ferrous to the ferric salts can be explained by an increase in the amount of 4s-bonding and that overlap distortion is a more important contribution to $|\psi(0)|^2$ than is the 3d shielding that gives Watson's result (Eq. 118) for free ions.

Since this treatment has not been applied to metallic iron we shall use the value of α in Eq. (119) to get an approximate idea of the electronic configuration of iron. Various investigators (e.g. refs. 62,66) have found

$$\Delta\varepsilon(\text{Fe}^{2+}) - \Delta\varepsilon(\text{Fe}_{\text{metal}}) \simeq 1.3 \text{ mm/sec} \quad (120)$$

which, using the value of α in Eq. (119), gives

$$|\psi_{\text{Fe}_{\text{metal}}}(0)|^2 - |\psi_{\text{Fe}^{2+}}(0)|^2 \simeq 2.7 a_0^{-3}. \quad (121)$$

This value of $\Delta|\psi(0)|^2$ indicates that metallic iron has a $3d^7 4s$ configuration. This can be shown in two ways. First, De Benedetti et al.⁽⁶⁶⁾ have found that the experimental isomer shift for metallic iron lies midway between the theoretical values derived for the $3d^6 4s^2$ and $3d^8$ configurations. Second, Walker et al.⁽⁶⁷⁾ have used the Fermi-Segré-Goudsmit^(142,143) (FSG) formalism to obtain a plot of $\Delta\varepsilon$ versus the amount of s-electron character in various $3d^n$ configurations. The experimental isomer shift of iron gives agreement with the $3d^7 4s^x$ line on this plot at $x = 1.0$.

This study will investigate the change of $|\Psi(0)|^2$ at the ^{57}Fe nucleus in Fe, Cu, V, and Ti as a function of pressure. The change in $\Delta\epsilon$ can be written

$$d(\Delta\epsilon) = d(\Delta\epsilon)_L + d(\Delta\epsilon)_B \quad (122)$$

$d(\Delta\epsilon)_L$ representing simple volume scaling where $|\Psi(0)|^2$ increases due to compression of the s-electron wave functions without change of shape while $d(\Delta\epsilon)_B$ represents the transfer of electrons into or out of the s-like states in the s-d conduction band.

A value of $d(\Delta\epsilon)_L$ can be obtained quite simply from the calculations of Walker et al. ⁽⁶⁷⁾ Addition of a 4s-electron to the $3d^7$ configuration at constant volume decreases the isomer shift by 1.4 mm/sec. Reversing the argument, holding $3d^7 4s$ constant and changing the volume, gives

$$\frac{d(\Delta\epsilon)_L}{d(\ln V)} = 1.4 \text{ mm/sec.} \quad (123)$$

Explicit expressions for $d(\Delta\epsilon)_L$ and $d(\Delta\epsilon)_B$ due to Ingalls ⁽¹⁴⁴⁾ will be discussed below.

Iron has a BCC structure at room temperature and atmospheric pressure. Shock wave, ⁽¹⁴⁵⁾ resistance, ⁽¹³⁾ and Mössbauer ⁽¹⁵⁾ measurements have revealed a phase transition at 130 kilobars and room temperature. This high pressure phase has been shown to be HCP. ^(7,146) In this study we are interested in the isomer shift in BCC iron and thus pressures of 130 kilobars or greater were achieved primarily for calibration purposes.

At atmospheric pressure copper is FCC, vanadium is BCC, and titanium is HCP. Copper and vanadium retain their atmospheric structures to the highest pressures reported in this study⁽⁵⁶⁾ while titanium has a phase transition to a distorted cubic structure at 80 to 85 kilobars.⁽¹³⁷⁾

B. Iron

1. Theory

The following formalism is due to Ingalls⁽¹⁴⁴⁾ and any parameters quoted without reference may be found in that paper.

Since we are interested in the pressure dependence of $|\Psi(0)|^2$, only the 4s and 3s-electron contributions are considered. The 4s electrons are affected in a direct way since they are itinerant and thus can be expected to scale with volume. The 1s, 2s, and 3s electrons are not directly affected by small volume changes but the 3s electrons are indirectly affected by the changes in 3d electron wave functions.

The 4s contribution can be written

$$|\Psi_{4s}(0)|^2 = \int_0^{E_F} N_s(E) |\Psi_s(0,E)|^2 dE \quad (124)$$

where $N_s(E)$ is the number of s-states in the 3d-4s conduction band.

Ingalls performed a modified tight binding calculation of the 4s wave functions at $\Gamma_1(k \equiv 0)$ for several volumes and found

$$|\Psi_{\Gamma_1}(0)|^2 = 7.1 a_o^{-3} \quad \text{for } V = 80 a_o^3 \quad (125)$$

and

$$|\Psi_{\Gamma_1}(0)|^2 = \text{const } V^{-\gamma} \quad (126)$$

where $\gamma \simeq 1.25$. With the assumption that $|\Psi_s(0, E)|^2$ equals $|\Psi_{\Gamma_1}(0)|^2$, the decrease in the s-like nature of the conduction band being completely represented by the decrease in $N_s(E)$ as k increases, Ingalls obtained

$$|\Psi_{4s}(0)|^2 = n_s |\Psi_{\Gamma_1}(0)|^2 \quad (127)$$

where $n_s = 0.53$ is the number of s-electrons per iron atom.

The 3s contribution is approximated by using the proportionality found by Watson⁽¹⁴⁰⁾ and Clementi⁽¹⁴⁷⁾ between the density of 3s electrons at the nucleus and $\langle nu_m^2 \rangle$

$$|\Psi_{3s}(0)|^2 = \beta \langle nu_m^2 \rangle \quad (128)$$

where u_m is the maximum of the radial wave function in the wave function

$$\Psi_d(\mathbf{r}) = Y_{\ell m}(\theta, \phi) \frac{u(r)}{r} \quad (129)$$

and

$$\langle nu_m^2 \rangle = \int_0^{E_F} N_d(E) u_m^2(E) dE \quad (130)$$

with $\beta = -5.5 a_0^{-2}$. The integral in Eq. (130) is performed up to the respective Fermi energy in each half of the band (spin up and spin down) using the linear relationship between $u_m^2(E)$ and E discussed by Ingalls.⁽¹⁴⁴⁾

Thus for the 3s and 4s contributions we have

$$|\Psi(0)|^2 = n_s |\Psi_{\Gamma_1}(0)|^2 + \beta \langle nu_m^2 \rangle \quad (131)$$

Taking the volume derivative of Eq. (130) gives

$$\begin{aligned} \frac{d|\Psi(0)|^2}{d(\ln V)} &= -n_s \gamma |\Psi_{\Gamma_1}(0)|^2 + \beta \frac{\partial \langle nu_m^2 \rangle}{\partial (\ln V)} \\ &+ |\Psi_{\Gamma_1}(0)|^2 \frac{\partial n_s}{\partial (\ln V)} + \beta \frac{\partial \langle nu_m^2 \rangle}{\partial n_d} \frac{\partial n_d}{\partial (\ln V)}. \end{aligned} \quad (132)$$

Here we see the expression for $d(\Delta\epsilon)_L$, due to volume scaling, and $d(\Delta\epsilon)_B$, due to $s \leftrightarrow d$ electron transfer, mentioned in the introduction

$$\frac{d(\Delta\epsilon)_L}{d(\ln V)} = \alpha \left[-n_s \gamma |\Psi_{\Gamma_1}(0)|^2 + \beta \frac{\partial \langle nu_m^2 \rangle}{\partial (\ln V)} \right] \quad (133)$$

$$\frac{d(\Delta\epsilon)_B}{d(\ln V)} = \alpha \left[|\Psi_{\Gamma_1}(0)|^2 \frac{\partial n_s}{\partial (\ln V)} + \beta \frac{\partial \langle nu_m^2 \rangle}{\partial n_d} \frac{\partial n_d}{\partial (\ln V)} \right]. \quad (134)$$

Using the values of $|\Psi_{\Gamma_1}(0)|^2$, n_s , γ , and β mentioned above

and

$$\frac{\partial \langle nu_m^2 \rangle}{\partial (\ln V)} = 0.03 a_o^{-1} \quad (135)$$

$$\frac{\partial \langle nu_m^2 \rangle}{\partial n_d} = 0.9 a_o^{-1} \quad (136)$$

gives

$$\frac{d(\Delta\epsilon)_L}{d(\ln V)} = -4.86\alpha \text{ mm/sec} \quad (137)$$

$$\frac{d(\Delta\epsilon)_B}{d(\ln V)} = \alpha \left[7.1 \frac{\partial n_s}{\partial (\ln V)} - 4.95 \frac{\partial n_d}{\partial (\ln V)} \right] \text{ mm/sec} \quad (138)$$

where $\alpha \equiv [a_o^3 \text{ mm/sec}]$.

Equation (137) can be viewed as an alternative to Eq. (123), which gave a rough value of $d(\Delta\epsilon)/d(\ln V)$ from volume scaling alone, and will be used in this work instead of Eq. (123). To obtain agreement between Eq. (123) and Eq. (137) we would need $\alpha = -0.35 \text{ a}_0^3 \text{ mm/sec}$ which is significantly different from the value of $\alpha = -0.47 \text{ a}_0^3 \text{ mm/sec}$ found above. This is not important since we will later treat α as a variable.

2. Experimental Data

a) Previous Work

Two previous studies have been concerned with the pressure dependence of the isomer shift of ^{57}Fe in Fe. Pound et al.,⁽⁵⁴⁾ in a study to 3 kilobars, found

$$\frac{\Delta\epsilon}{\Delta P} = (-7.98 \pm 0.31) \times 10^{-4} \frac{\text{mm/sec}}{\text{kbar}} \quad (139)$$

Pipkorn et al.,⁽¹⁵⁾ of this laboratory, in a study to 250 kilobars found general agreement with this value. No systematic investigation of the low pressure BCC phase of iron was made in that study, the primary concern being the BCC $\rightarrow$ HCP transition at 130 kilobars and the pressure dependence of the isomer shift of the HCP phase.

b) Present Study

In the present study of iron the main emphasis is on the pressure dependence of the isomer shift in the low pressure BCC phase. To obtain the best accuracy only the two inner peaks of the six-line magnetic spectrum of iron were examined.

The experimental points are given in Table 11 in Appendix D and plotted in Figure 20. $P(V)$ data for iron has been reported by Ho-Kwang Mao et al. ⁽¹⁴⁸⁾ who found

$$\frac{V_P}{V_0} = \left(1 + \frac{P}{275}\right)^{-0.169} \quad (140)$$

for the BCC phase of iron. Using this equation the data are plotted versus volume in Figure 21.

It can be seen from Figures 20 and 21 that for pressures above 60 kilobars there exists a region where the change of the isomer shift with pressure becomes non-linear and it has been necessary to fit the data with a quadratic function in pressure and volume. Below 60 kilobars there is no obvious departure from linearity.

Below 60 kilobars a least squares fit of the data to a linear dependence on pressure and volume give

$$d(\Delta\epsilon) = (-8.26 \pm 0.92) \times 10^{-4} P \text{ mm/sec} \quad (141)$$

where P is in kilobars, and

$$d(\Delta\epsilon) = (1.47 \pm 0.17) \frac{\Delta V}{V} \text{ mm/sec.} \quad (142)$$

The quadratic fit of all the data below the BCC $\rightarrow$ HCP transition at 130 kilobars gives essentially the same results. Thus

$$d(\Delta\epsilon) = (-8.00 \pm 1.10) \times 10^{-4} P + (1.65 \pm 1.10) \times 10^{-6} P^2 \frac{\text{mm}}{\text{sec}} \quad (143)$$

and

$$d(\Delta\epsilon) = (1.38 \pm 0.22) \frac{\Delta V}{V} + (2.69 \pm 4.53) \left(\frac{\Delta V}{V}\right)^2 \frac{\text{mm}}{\text{sec}} \quad (144)$$

FIGURE 20. IRON ISOMER SHIFT — vs. — PRESSURE

FIGURE 21. IRON ISOMER SHIFT -vs.-VOLUME

These results are in excellent agreement with the results of Pound et al.⁽⁵⁴⁾ and Pipkorn et al.⁽¹⁵⁾ and there is no need to discuss the analysis of these two previous experiments separately.

Each pressure run with iron was self-calibrating; the calibration was made by obtaining the BCC $\rightarrow$ HCP transition at 130 kilobars. The transition is sluggish but a paramagnetic single peak is clearly present for pressures above 130 kilobars (see Figure 22).

From the three pressure runs we obtain

$$\Delta\epsilon(\text{HCP}, P=146 \text{ kbars}) - \Delta\epsilon(\text{BCC}, P=0) = -.244 \pm .014 \text{ mm/sec} \quad (145)$$

which agrees with the value of about -0.25 mm/sec obtained by Pipkorn et al.⁽¹⁵⁾

3. Discussion

If we assume that the number of electrons in the 3d-4s conduction band of iron is a constant we can combine Eqs. (137) and (138) and get

$$\frac{d(\Delta\epsilon)}{d(\ln V)} = -4.86\alpha + 12.05\alpha X \quad (146)$$

where

$$X = \frac{\partial n_s}{\partial(\ln V)} = - \frac{\partial n_d}{\partial(\ln V)} \quad (147)$$

Equation (146), together with the experimental value of the change of the isomer shift with volume, gives a relation between the isomer shift parameter α and the s to d electron transfer.

CHANNEL NUMBER (3.23 x 10⁻² mm/sec/channel)

FIGURE 22. IRON P=134 KILOBAR SPECTRUM

Experimentally we have obtained

$$\left. \frac{d(\Delta\varepsilon)}{d(\ln V)} \right|_{V=V_0} = (1.38 \pm 0.22) \text{ mm/sec.} \quad (148)$$

A correction for the change of the second order Doppler shift with volume can be made by using the discussion of Section III-C-2. There a rough value of this change was obtained by using a Debye parameter $\theta = 467^\circ\text{K}$ for iron. This Debye parameter is characteristic of iron at low temperature. A better value of $d(v)/d(\ln V)$ due to the second order Doppler shift can be obtained by using a Debye parameter of $\theta = 420^\circ\text{K}$ ⁽¹⁴⁹⁾ which is a better approximation to the room temperature value. Using Eq. (29) we obtain

$$\frac{d(v_{\text{second order}})}{d(\ln V)} = 6 \times 10^{-2} \text{ mm/sec.} \quad (149)$$

Thus, for the isomer shift alone we have

$$\frac{d(\Delta\varepsilon)}{d(\ln V)} = (1.32 \pm 0.22) \text{ mm/sec.} \quad (150)$$

Combining Eqs. (146) and (150) gives

$$-4.86\alpha + 12.05\alpha X = 1.32 \quad (151)$$

where $\alpha \equiv [a_0^3 \text{ mm/sec}]$. If $\alpha = -0.47 a_0^3 \text{ mm/sec}$ we have $X = +0.17$ and thus a transfer of electrons from the s to the d part of the conduction band. Qualitatively Stern⁽¹⁵⁰⁾ has found that as the volume decreases the d band drops in energy with respect to the s band making an s to d electron transfer energetically favorable and justifying the sign of X.

However no quantitative estimate can be drawn from this argument and thus Eq. (151) has been used to make the α vs. X plot shown in Figure 23. An independent α and/or X determination would thus give α and X directly. From Stern's⁽¹⁵⁰⁾ work one expects $X > 0$ so that this portion of Figure 23 would be the physically meaningful region.

It can be seen from Figure 23 that for $X = 0$, no s to d electron transfer occurring, $\alpha \simeq -0.28 a_0^3$ mm/sec. This value is certainly not outside the range of possible α values. In fact some authors^(151,152) have obtained values of $\alpha = -0.2 a_0^3$ mm/sec or less using chemical or molecular orbital arguments. Here we have obtained a relationship between the isomer shift parameter α and the s to d electron transfer parameter X that any independent measurements of α or X must satisfy.

C. Cu, V, and Ti

1. Theory

Ingalls et al.⁽⁵⁹⁾ have used the formalism derived for ^{57}Fe in iron⁽¹⁴⁴⁾ in a study of the pressure dependence of the Mössbauer f number discussed in Section V. These data supplement, and to some degree correct, the previous isomer shift data of Edge et al.⁽⁵⁶⁾ for the same elements.

The use of the same formalism depends upon the assumption that the total number of outer electrons (s plus d) characteristic

FIGURE 23. IRON α -vs.- X

of the ^{57}Fe impurity is the same as that for ^{57}Fe in iron. Plausibility can be given to this assumption by noting that the zero pressure isomer shifts for ^{57}Fe in the first series of the transition metals are grouped rather closely compared to the changes in isomer shift when either an s or d electron is added to an atom. Thus for Cu, V, and Ti the zero pressure isomer shifts differ from that of ^{57}Fe in iron by less than .22 mm/sec (see below) while the addition of an s electron gives an isomer shift change of approximately 1.5 mm/sec⁽⁶⁷⁾ and an addition of a d electron (e.g., ferric to ferrous) gives an isomer shift change of approximately 0.9 mm/sec.^(66,67)

2. Experimental Data

a) Previous Work

Two previous studies of the pressure dependence of the isomer shift for ^{57}Fe in transition metals have been made in this laboratory. Edge et al.⁽⁵⁶⁾ studied Cu, V, and Ti to 250 kilobars and found a quantitative difference between the isomer shift for close-packed and BCC structures. The $d(\Delta\epsilon)/d(\ln V)$ for the BCC V and Fe, Fe data having been taken by Pipkorn et al.,⁽¹⁵⁾ were greater than for the close-packed Ti and Cu.

Ingalls et al.⁽⁵⁹⁾ investigated eleven other transition metals to 250 kilobars and found the same behavior for open and closed structures.

b) Present Study

The pressure dependence of the isomer shift of ^{57}Fe in Cu, V, and Ti is studied to 100 kilobars. The zero pressure isomer shifts ($\Delta\epsilon_0$) with respect to ^{57}Fe in iron have also been measured. For copper $\Delta\epsilon_0$ agrees well with the previous results of Edge et al. ⁽⁵⁶⁾ and Kitchens et al. ⁽⁸⁴⁾ The vanadium $\Delta\epsilon_0$ obtained here agree with Kitchens et al. ⁽⁸⁴⁾ but not with Edge et al.; ⁽⁵⁶⁾ the consistency in results in the three vanadium runs made in this study confirms the value of the former work. For titanium the two pressure runs using two different titanium samples give somewhat different values for $\Delta\epsilon_0$, which may be due to the phase difficulty discussed in Section V-C-4a, but the values are close to that obtained by Edge et al. ⁽⁵⁶⁾

For copper the data are given in Table 12 in Appendix D and plotted versus pressure in Figure 24. A least squares analysis gives

$$d(\Delta\epsilon) = (-5.78 \pm 0.28) \times 10^{-4} \text{ P mm/sec} \quad (152)$$

where P is in kilobars. The copper data are plotted in Figure 25 versus volume using P(V) data for copper ^(131,132) discussed in Section V-C-2a. A least squares analysis gives

$$\frac{d(\Delta\epsilon)}{d(\ln V)} = 0.90 \pm 0.04 \text{ mm/sec.} \quad (153)$$

For vanadium the data are given in Table 13 and plotted versus pressure in Figure 26. A least squares analysis gives

$$d(\Delta\epsilon) = (-8.71 \pm 0.33) \times 10^{-4} \text{ P mm/sec} \quad (154)$$

FIGURE 24. COPPER ISOMER SHIFT—vs.—PRESSURE

FIGURE 25. COPPER ISOMER SHIFT - vs. - VOLUME

FIGURE 26. VANADIUM ISOMER SHIFT -vs.-PRESSURE

where P is in kilobars. The vanadium data are plotted in Figure 27 versus volume using $P(V)$ data for vanadium (132) discussed in Section V-C-ea. A least squares analysis gives

$$\frac{d(\Delta\epsilon)}{d(\ln V)} = 1.54 \pm 0.06 \text{ mm/sec} . \quad (155)$$

For titanium the data are given in Table 14 and plotted versus pressure in Figure 28. A least squares analysis gives

$$d(\Delta\epsilon) + (-7.10 \pm 1.10) \times 10^{-4} P \text{ mm/sec} \quad (156)$$

where P is in kilobars. The titanium data are plotted versus volume in Figure 29 using $P(V)$ data for titanium⁽¹³¹⁾ discussed in Section V-C-4b. A least squares analysis gives

$$\frac{d(\Delta\epsilon)}{d(\ln V)} = 0.83 \pm 0.12 \text{ mm/sec} . \quad (157)$$

3. Discussion

First it should be noted that we obtain the same quantitative difference in the volume coefficient of the isomer shift as found by Edge et al.⁽⁵⁶⁾ and Ingalls et al.⁽⁵⁹⁾ Thus for the open BCC structures of vanadium and iron we have

$$\text{Fe} \quad \frac{d(\Delta\epsilon)}{d(\ln V)} = 1.38 \text{ mm/sec} \quad (158)$$

$$\text{V} \quad \frac{d(\Delta\epsilon)}{d(\ln V)} = 1.54 \text{ mm/sec} \quad (159)$$

while for the close-packed structures, Cu and Ti, we obtain the lower values

$$\text{Cu (FCC)} \quad \frac{d(\Delta\epsilon)}{d(\ln V)} = 0.90 \text{ mm/sec} \quad (160)$$

$$\text{Ti (HCP)} \quad \frac{d(\Delta\epsilon)}{d(\ln V)} = 0.83 \text{ mm/sec} . \quad (161)$$

FIGURE 27. VANADIUM ISOMER SHIFT -vs.- VOLUME

FIGURE 28. TITANIUM ISOMER SHIFT -vs.- PRESSURE

FIGURE 29. TITANIUM ISOMER SHIFT -vs.-VOLUME

The values given in Eq. (159) to (161) can be used in Eq. (146) to obtain α versus X relations as has already been done for iron in Figure 23. (No correction is made here for the pressure coefficient of the second order Doppler effect.) The interpretation of the α versus X relation for ^{57}Fe in iron has already been discussed in Section VI-B-3. For ^{57}Fe in other transition metals the interpretation is less direct since the relation of X , the change of the number of s and d electrons characteristic of the ^{57}Fe impurity, to the host band structure is obscure. There is no reason why the number of s and d electrons should not change independently making the assumption

$$\frac{dn_s}{d(\ln V)} = \frac{dn_d}{d(\ln V)} \quad (162)$$

invalid.

However we have assumed here, for the purposes of discussion, that Eq. (162) is valid since this allows us to use Eq. (146)

$$\frac{d(\Delta E)}{d(\ln V)} = \alpha[-4.86 + 12.05 X] \text{ mm/sec}$$

to obtain the α vs. X curves for copper, vanadium, and titanium which can be compared with one another and with the results for iron. These curves are plotted in Figure 30 together with the iron curve of Figure 23 and show that no matter what the interpretation of X is for the transition metals, if $X \simeq 0$ for the BCC structures $X \neq 0$ for the close-packed structures (or vice-versa) and some electron redistribution with pressure between s and d states is indicated.

ISOMER SHIFT PARAMETER α [mm/sec]

FIGURE 30. ^{57}Fe IN TRANSITION METALS α -vs.- X

Ingalls⁽⁵⁹⁾ represented the isomer shift-volume relations for all the transition metals on a single graph by assuming an $\alpha \simeq -0.4 \text{ a}_0^3 \text{ mm/sec}$. Since the value of α is far from settled Figure 30 gives the same type of information in a somewhat more general form. Thus Ingalls states that if the BCC structures have no s to d electron transfer ($X \simeq 0$), then the close-packed systems must have $X > 0$. This is easily seen from Figure 30 for when α is chosen so that $X \simeq 0$ for the BCC iron and vanadium, $X > 0$ for the close-packed copper and titanium.

D. Conclusion

The data on the volume coefficient of the isomer shift of ^{57}Fe in Fe, Cu, V, and Ti, together with the formalism by Ingalls^(144,59) allow one to derive a relation between the isomer shift parameter and the transfer of electron from s to d character with volume. This relation is plotted in Figure 30 for the four metals studied.

The qualitative difference in the value of the volume coefficient of the isomer shift for BCC and close-packed metals noted by others^(56,59) has also been found in this work. This difference indicates that if volume scaling of the s electron density (no s to d electron transfer) exists for metals of one type of structure, it is necessary that some s to d electron transfer exist for metals of the other structure.

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APPENDIX A. GRUNEISEN CONSTANT

A. Theory

The Gruneisen constant is defined by

$$\gamma = - \frac{d(\ln \theta)}{d(\ln V)} \quad (163)$$

where θ is the Debye temperature. The values of γ used in this work are obtained by evaluating the expression

$$\gamma = \frac{\alpha V}{\chi C_v} \quad (164)$$

where $\alpha \equiv$ Thermal expansion coefficient

$V \equiv$ Volume

$\chi \equiv$ Compressibility

$C_v \equiv$ Specific heat at constant volume .

The following development shows the connection between Eqs. (163) and (164).

Thermodynamic pressure is defined⁽¹⁵³⁾ as

$$P = - \left(\frac{\partial A}{\partial V} \right)_T \quad (165)$$

where $A = E - TS = -kT \ln Z$ is the Helmholtz free energy and

$$Z = \sum_i e^{-E_i/kT} \quad (166)$$

is the partition function, the sum over i being the sum over all energy states. In the harmonic approximation, in which the lattice is represented by a set of uncoupled harmonic oscillators

(corresponding to the normal modes)

$$Z = \prod_{i=1}^{3N} \frac{e^{h\nu_i/kT}}{e^{h\nu_i/kT} - 1} \quad (167)$$

where each term in the product represents one of the normal modes (the $T = 0$ term which does not contribute to the thermal pressure we are considering has been neglected). Thus

$$P = \frac{1}{V} \sum_{i=1}^{3N} \gamma_i \frac{h\nu_i}{(e^{h\nu_i/kT} - 1)} \quad (168)$$

where

$$\gamma_i = \frac{d(\ln \nu_i)}{d(\ln V)} \quad (169)$$

is the Grüneisen parameter for the i^{th} normal mode.

Next we use the expression

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (170)$$

and

$$\left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_P = 1 \quad (171)$$

to obtain

$$\alpha = \chi \left(\frac{\partial P}{\partial T} \right)_V \quad (172)$$

Taking the temperature derivative of Eq. (168) gives

$$\alpha = \frac{\chi}{V} \sum_{i=1}^{3N} \gamma_i k \frac{(h\nu_i/kT)^2 e^{h\nu_i/kT}}{(e^{h\nu_i/kT} - 1)^2} \quad (173)$$

When we note that the specific heat C_v is given by

$$C_v = \sum_{i=1}^{3N} k \frac{(h\nu_i/kT)^2 e^{h\nu_i/kT}}{(e^{h\nu_i/kT} - 1)^2} \quad (174)$$

and assume $\gamma_i = \gamma$ for all i , where γ is called the Grüneisen constant, we have

$$\alpha = \frac{\chi \gamma C_v}{V} \quad (175)$$

which is just Eq. (164).

To show that Eqs. (163) and (164) are compatible it is sufficient to note that if

$$\frac{d(\ln \nu_i)}{d(\ln V)} = \text{constant}$$

for all i , then we can evaluate the constant by using any frequency ν_i , in particular the maximum frequency in the Debye spectrum, ν_m . Then since $\nu_m \propto \theta_D$ we have Eq. (163).

When it is not possible to assume that all γ_i have the same value it is still possible to get the form of Eq. (164) if we define a mean Grüneisen parameter

$$\bar{\gamma} = \frac{\sum \gamma_i k \frac{(h\nu_i/kT)^2 e^{h\nu_i/kT}}{(e^{h\nu_i/kT} - 1)^2}}{C_v} \quad (176)$$

Then Eq. (173) becomes

$$\bar{\gamma} = \frac{\alpha V}{\chi C_v} \quad (177)$$

Other forms for the Grüneisen constant have been proposed. Slater^(153,154) has shown that

$$\gamma = -\frac{2}{3} - \frac{V}{2} \frac{(\partial^2 P / \partial V^2)_T}{(\partial P / \partial V)_T} \quad (178)$$

so that γ can be obtained directly from $P(V)$ data. This result has been questioned by Dugdale and MacDonald⁽¹⁵⁵⁾ who made an evaluation of γ in a study of compressibility and obtained

$$\gamma = -1 - \frac{V}{2} \frac{(\partial^2 P / \partial V^2)_T}{(\partial P / \partial V)_T} \quad (179)$$

Gilvarry⁽¹⁵⁶⁾ made a study of the agreement between Slater's γ Eq. (178) and Eq. (164) for a number of solids and finds good agreement that would be partially destroyed if Eq. (179) is used.

Recently Pastine⁽¹⁵⁷⁾ has criticized both of the above treatments and has derived a more complicated expression for γ in terms of the volume derivatives of pressure and the Poisson's ratio.

Since Eq. (164) is used for the evaluation of γ in this work this controversy is essentially by-passed.

B. Evaluation of γ

The parameters used in the evaluation of γ using Eq. (164) are listed in Table 5 with the relevant references. The following comments about these parameters will supplement this table.

- 1) Volume - Calculated directly from lattice dimensions.
- 2) Compressibility - Determined from ultrasonic study of

elastic constants.

3) Specific Heat - The experiments determined C_p . C_v was evaluated using the expression⁽¹⁶³⁾

$$C_v = C_p - \frac{\alpha^2 VT}{\chi} . \quad (179)$$

4) Thermal Expansion Coefficient. $\alpha_l = l^{-1} dl/dT$ was determined in the references cited. The value of α given is

$$\alpha = 3\alpha_l . \quad (180)$$

Table 5

Grüneisen Constant Evaluation

Element	Volume (cm ³ /gm)	Compressibility (10 ⁻¹³ dynes/cm ²)	C _v (10 ⁶ ergs/gm °K)	Thermal Expansion Coefficient (10 ⁻⁶ /°K)	Y
Cu	0.1119 ^(a)	7.510 ^(b)	3.737 ^(e)	50.1 ^(h)	1.998
V	0.1660 ^(a)	6.447 ^(c)	4.764 ^(f)	23.25 ⁽ⁱ⁾	1.257
Ti	0.2220 ^(a)	9.31 ^(d)	5.168 ^(g)	26.7 ^(j)	1.232

(a) - R.W.G. Wyckoff, Crystal Structures (Interscience).

(b) - Reference 133

(c) - Reference 112

(d) - Reference 138

(e) - W. F. Giauque and P. F. Meads, J. Amer. Chem. Soc. 63, 1897 (1941).

(f) - C. T. Anderson, J. Amer. Chem. Soc. 58, 564 (1936).

(g) - Reference 120

(h) - F. C. Nix and D. MacNair, Phys. Rev. 60, 597 (1941).

(i) - G. K. White, Cryogenics 2, 292 (1962).

(j) - E. S. Greiner and W. C. Ellis, Trans. AIME 180, 657 (1949).

APPENDIX B. EVALUATION OF γ

In Section V-B-1 it is seen that

$$\frac{\Delta f}{f} = - \gamma \gamma \frac{\Delta V}{V} \quad (181)$$

where γ is the Grüneisen parameter and

$$\gamma = \frac{6E_r}{k\theta} \left[\frac{1}{4} - \frac{1}{e^{\theta/T} - 1} + 3 \left(\frac{T}{\theta} \right)^2 \int_0^{\theta/T} \frac{x dx}{e^x - 1} \right] \quad (182)$$

Multiplying both sides of Eq. (182) by the temperature T gives the expression

$$TY = \frac{6E_r}{kx} \left[\frac{1}{4} - \frac{1}{e^x - 1} + \frac{3}{x^2} \int_0^x \frac{\alpha d\alpha}{e^\alpha - 1} \right] \quad (183)$$

where the right hand side of Eq. (183) depends on the temperature and θ only in the ratio $x = \theta/T$.

Evaluation of TY was made at intervals of 0.01 in x from $x = 0.15$ to $x = 7.00$ and are given in Table 6. The evaluation of the Debye integral

$$Q(x) = \int_0^x \frac{\alpha d\alpha}{e^\alpha - 1} \quad (184)$$

was made using the tabulated values of Holm. (158)

To obtain the Debye parameter θ_f from γ it is necessary to multiply γ by the temperature of the experiment, the value of TY then gives the value of x from Table 6 and this gives the value of θ_f .

Table 6
Values of $Q(x)$ and $TY(x)$

x	$Q(x)$	$TY(x)$
.15	.144469	11749.366699
.16	.153714	10326.588501
.17	.162913	9147.533081
.18	.172062	8159.265015
.19	.181165	7322.967712
.20	.190222	6608.996155
.21	.199232	5994.555054
.22	.208196	5462.000549
.23	.217113	4997.364014
.24	.225984	4589.593811
.25	.234809	4229.770691
.26	.243588	3910.658173
.27	.252321	3626.335632
.28	.261009	3371.939026
.29	.269652	3143.408447
.30	.278249	2937.335114
.31	.286802	2750.895050
.32	.295309	2581.644623
.33	.303772	2427.554352
.34	.312191	2286.864441
.35	.320565	2158.054230
.36	.328894	2039.821518
.37	.337180	1931.053711
.38	.345422	1830.758240
.39	.353620	1738.076462
.40	.361775	1652.262024
.41	.369886	1572.646088
.42	.377954	1498.650299
.43	.385979	1429.756973
.44	.393962	1365.511597
.45	.401901	1305.495636
.46	.409798	1249.353455
.47	.417653	1196.758102
.48	.425465	1147.412781
.49	.433235	1101.057999
.50	.440964	1057.459503
.51	.448650	1016.396637
.52	.456295	977.681656
.53	.463899	941.138535
.54	.471461	906.604774
.55	.478983	873.940262
.56	.486463	843.007469
.57	.493903	813.690155
.58	.501302	785.875298
.59	.508660	759.461761

x	Q(x)	TY(x)
.60	.515979	734.360306
.61	.523257	710.481651
.62	.530495	687.749069
.63	.537693	666.090141
.64	.544852	645.439583
.65	.551971	625.734047
.66	.559051	606.917938
.67	.566092	588.938263
.68	.573094	571.746048
.69	.580057	555.295708
.70	.586981	539.545052
.71	.593867	524.455833
.72	.600715	509.991398
.73	.607524	496.116539
.74	.614295	482.800476
.75	.621028	470.013420
.76	.627724	457.728546
.77	.634382	445.918850
.78	.641003	434.560852
.79	.647586	423.630878
.80	.654132	413.108349
.81	.660641	402.973171
.82	.667114	393.207127
.83	.673550	383.791744
.84	.679949	374.710316
.85	.686312	365.947796
.86	.692639	357.489307
.87	.698930	349.320881
.88	.705185	341.429314
.89	.711404	333.802139
.90	.717588	326.428139
.91	.723737	319.296150
.92	.729850	312.395130
.93	.735928	305.715614
.94	.741971	299.248165
.95	.747979	292.983826
.96	.753953	286.914566
.97	.759892	281.031868
.98	.765797	275.328518
.99	.771668	269.797249
1.00	.777505	264.431145
1.01	.783307	259.223419
1.02	.789077	254.168379
1.03	.794812	249.259871
1.04	.800514	244.492287
1.05	.806183	239.860247
1.06	.811818	235.358618
1.07	.817422	230.983110
1.08	.822992	226.728472
1.09	.828529	222.590424

x	Q(x)	TY(x)
1.10	.834034	218.564703
1.11	.839506	214.647243
1.12	.844946	210.834501
1.13	.850355	207.122528
1.14	.855731	203.507847
1.15	.861075	199.987038
1.16	.866387	196.556837
1.17	.871669	193.214520
1.18	.876919	189.956795
1.19	.882137	186.780884
1.20	.887325	183.684046
1.21	.892481	180.663647
1.22	.897608	177.717527
1.23	.902703	174.842932
1.24	.907768	172.037626
1.25	.912803	169.299385
1.26	.917807	166.626057
1.27	.922781	164.015799
1.28	.927726	161.466497
1.29	.932640	158.976284
1.30	.937525	156.543324
1.31	.942380	154.165842
1.32	.947206	151.842436
1.33	.952003	149.571228
1.34	.956771	147.350714
1.35	.961510	145.179379
1.36	.966220	143.055758
1.37	.970902	140.978683
1.38	.975555	138.946592
1.39	.980180	136.958244
1.40	.984776	135.012371
1.41	.989344	133.107750
1.42	.993885	131.243410
1.43	.998398	129.418049
1.44	1.002883	127.630615
1.45	1.007340	125.880060
1.46	1.011769	124.165350
1.47	1.016172	122.485642
1.48	1.020548	120.839900
1.49	1.024897	119.227215
1.50	1.029218	117.646696
1.51	1.033512	116.097486
1.52	1.037781	114.578916
1.53	1.042023	113.090032
1.54	1.046239	111.630097
1.55	1.050428	110.198352
1.56	1.054591	108.794063
1.57	1.058728	107.416645
1.58	1.062840	106.065322
1.59	1.066926	104.739455
1.60	1.070986	103.438396

x	Q(x)	TY(x)
1.61	1.075020	102.161519
1.62	1.079030	100.908360
1.63	1.083015	99.678201
1.64	1.086975	98.470517
1.65	1.090909	97.284750
1.66	1.094818	96.120359
1.67	1.098704	94.976930
1.68	1.102564	93.853882
1.69	1.106400	92.750751
1.70	1.110212	91.667061
1.71	1.113999	90.602338
1.72	1.117763	89.556267
1.73	1.121503	88.528294
1.74	1.125220	87.518026
1.75	1.128912	86.525064
1.76	1.132580	85.548992
1.77	1.136226	84.589492
1.78	1.139848	83.646159
1.79	1.143447	82.718628
1.80	1.147023	81.806546
1.81	1.150576	80.909562
1.82	1.154107	80.027453
1.83	1.157615	79.159775
1.84	1.161100	78.306243
1.85	1.164563	77.466540
1.86	1.168003	76.640371
1.87	1.171421	75.827472
1.88	1.174818	75.027555
1.89	1.178192	74.240341
1.90	1.181544	73.465553
1.91	1.184874	72.702925
1.92	1.188184	71.952303
1.93	1.191472	71.213328
1.94	1.194739	70.485789
1.95	1.197984	69.769447
1.96	1.201208	69.064062
1.97	1.204411	68.369457
1.98	1.207593	67.685382
1.99	1.210754	67.011630
2.00	1.213895	66.347989
2.01	1.217015	65.694252
2.02	1.220115	65.050281
2.03	1.223194	64.415826
2.04	1.226253	63.790714
2.05	1.229292	63.174759
2.06	1.232311	62.567777
2.07	1.235310	61.969639
2.08	1.238289	61.380137
2.09	1.241249	60.799115
2.10	1.244189	60.226402
2.11	1.247109	59.661840

x	Q(x)	TY(x)
2.12	1.250011	59.105330
2.13	1.252894	58.556661
2.14	1.255757	58.015698
2.15	1.258601	57.482301
2.16	1.261426	56.956319
2.17	1.264233	56.437650
2.18	1.267020	55.926133
2.19	1.269789	55.421639
2.20	1.272540	54.924040
2.21	1.275272	54.433205
2.22	1.277986	53.949042
2.23	1.280682	53.471411
2.24	1.283359	53.000196
2.25	1.286019	52.535282
2.26	1.288660	52.076549
2.27	1.291285	51.623941
2.28	1.293892	51.177296
2.29	1.296481	50.736522
2.30	1.299053	50.301517
2.31	1.301607	49.872175
2.32	1.304144	49.448423
2.33	1.306664	49.030143
2.34	1.309167	48.617247
2.35	1.311653	48.209641
2.36	1.314122	47.807228
2.37	1.316574	47.409947
2.38	1.319010	47.017695
2.39	1.321429	46.630387
2.40	1.323831	46.247940
2.41	1.326217	45.870269
2.42	1.328587	45.497331
2.43	1.330941	45.129011
2.44	1.333279	44.765242
2.45	1.335601	44.405947
2.46	1.337907	44.051051
2.47	1.340197	43.700505
2.48	1.342472	43.354217
2.49	1.344731	43.012124
2.50	1.346974	42.674156
2.51	1.349202	42.340244
2.52	1.351414	42.010341
2.53	1.353612	41.684373
2.54	1.355794	41.362276
2.55	1.357961	41.043989
2.56	1.360113	40.729450
2.57	1.362251	40.418628
2.58	1.364374	40.111436
2.59	1.366482	39.807826
2.60	1.368575	39.507739
2.61	1.370654	39.211119
2.62	1.372718	38.917932

x	Q(x)	TY(x)
2.63	1.374769	38.628108
2.64	1.376804	38.341599
2.65	1.378826	38.058355
2.66	1.380833	37.778322
2.67	1.382827	37.501465
2.68	1.384806	37.227731
2.69	1.386772	36.957071
2.70	1.388724	36.689440
2.71	1.390662	36.424790
2.72	1.392587	36.163103
2.73	1.394499	35.904306
2.74	1.396397	35.648366
2.75	1.398282	35.395240
2.76	1.400153	35.144883
2.77	1.402012	34.897268
2.78	1.403857	34.652348
2.79	1.405690	34.410081
2.80	1.407509	34.170431
2.81	1.409315	33.933358
2.82	1.411109	33.698840
2.83	1.412890	33.466826
2.84	1.414659	33.237285
2.85	1.416415	33.010181
2.86	1.418158	32.785477
2.87	1.419890	32.563154
2.88	1.421609	32.343166
2.89	1.423315	32.125483
2.90	1.425010	31.910072
2.91	1.426692	31.696900
2.92	1.428363	31.485951
2.93	1.430022	31.277179
2.94	1.431669	31.070560
2.95	1.433304	30.866061
2.96	1.434928	30.663661
2.97	1.436540	30.463327
2.98	1.438140	30.265029
2.99	1.439729	30.068738
3.00	1.441306	29.874426
3.01	1.442871	29.682068
3.02	1.444427	29.491657
3.03	1.445970	29.303149
3.04	1.447503	29.116526
3.05	1.449025	28.931759
3.06	1.450536	28.748824
3.07	1.452036	28.567697
3.08	1.453526	28.388352
3.09	1.455004	28.210768
3.10	1.456471	28.034918
3.11	1.457927	27.860780
3.12	1.459374	27.688353
3.13	1.460811	27.517596

x	Q(x)	TY(x)
3.14	1.462237	27.348491
3.15	1.463652	27.181017
3.16	1.465058	27.015154
3.17	1.466453	26.850879
3.18	1.467838	26.688172
3.19	1.469213	26.527012
3.20	1.470577	26.367379
3.21	1.471931	26.209254
3.22	1.473276	26.052631
3.23	1.474611	25.897482
3.24	1.475937	25.743789
3.25	1.477253	25.591535
3.26	1.478559	25.440701
3.27	1.479856	25.291268
3.28	1.481143	25.143220
3.29	1.482421	24.996539
3.30	1.483689	24.851207
3.31	1.484947	24.707206
3.32	1.486198	24.564540
3.33	1.487439	24.423175
3.34	1.488670	24.283097
3.35	1.489893	24.144293
3.36	1.491107	24.006747
3.37	1.492312	23.870441
3.38	1.493508	23.735363
3.39	1.494695	23.601496
3.40	1.495873	23.468825
3.41	1.497042	23.337336
3.42	1.498203	23.207024
3.43	1.499355	23.077869
3.44	1.500499	22.949859
3.45	1.501635	22.822980
3.46	1.502762	22.697217
3.47	1.503880	22.572559
3.48	1.504991	22.448990
3.49	1.506093	22.326500
3.50	1.507186	22.205074
3.51	1.508271	22.084699
3.52	1.509349	21.965377
3.53	1.510419	21.847082
3.54	1.511481	21.729808
3.55	1.512535	21.613541
3.56	1.513581	21.498271
3.57	1.514619	21.383984
3.58	1.515650	21.270671
3.59	1.516672	21.158319
3.60	1.517687	21.046917
3.61	1.518694	20.936454
3.62	1.519694	20.826931
3.63	1.520687	20.718326
3.64	1.521672	20.610633

x	Q(x)	TY(x)
3.65	1.522650	20.503840
3.66	1.523621	20.397938
3.67	1.524584	20.292917
3.68	1.525540	20.188766
3.69	1.526489	20.085475
3.70	1.527430	19.983035
3.71	1.528364	19.881437
3.72	1.529292	19.780678
3.73	1.530212	19.680743
3.74	1.531126	19.581625
3.75	1.532033	19.483314
3.76	1.532933	19.385802
3.77	1.533826	19.289080
3.78	1.534712	19.193138
3.79	1.535591	19.097969
3.80	1.536464	19.003564
3.81	1.537330	18.909913
3.82	1.538189	18.817017
3.83	1.539042	18.724861
3.84	1.539889	18.633439
3.85	1.540729	18.542744
3.86	1.541563	18.452766
3.87	1.542391	18.363499
3.88	1.543212	18.274935
3.89	1.544027	18.187066
3.90	1.544835	18.099884
3.91	1.545637	18.013383
3.92	1.546434	17.927568
3.93	1.547225	17.842416
3.94	1.548010	17.757924
3.95	1.548788	17.674086
3.96	1.549561	17.590896
3.97	1.550327	17.508345
3.98	1.551087	17.426428
3.99	1.551842	17.345138
4.00	1.552590	17.264468
4.01	1.553332	17.184412
4.02	1.554067	17.104954
4.03	1.554797	17.026106
4.04	1.555521	16.947855
4.05	1.556240	16.870196
4.06	1.556953	16.793121
4.07	1.557661	16.716626
4.08	1.558363	16.640704
4.09	1.559059	16.565349
4.10	1.559750	16.490556
4.11	1.560435	16.416318
4.12	1.561117	16.342643
4.13	1.561792	16.269510
4.14	1.562463	16.196920

x	Q(x)	TY(x)
4.15	1.563129	16.124866
4.16	1.563789	16.053342
4.17	1.564445	15.982344
4.18	1.565095	15.911867
4.19	1.565740	15.841903
4.20	1.566380	15.772451
4.21	1.567015	15.703502
4.22	1.567646	15.635062
4.23	1.568272	15.567115
4.24	1.568894	15.499660
4.25	1.569510	15.432690
4.26	1.570122	15.366203
4.27	1.570728	15.300192
4.28	1.571330	15.234654
4.29	1.571928	15.169583
4.30	1.572520	15.104976
4.31	1.573108	15.040827
4.32	1.573686	14.977112
4.33	1.574263	14.913863
4.34	1.574837	14.851063
4.35	1.575406	14.788708
4.36	1.575971	14.726793
4.37	1.576531	14.665314
4.38	1.577088	14.604267
4.39	1.577641	14.543648
4.40	1.578190	14.483452
4.41	1.578735	14.423676
4.42	1.579294	14.364401
4.43	1.579839	14.305490
4.44	1.580379	14.246982
4.45	1.580914	14.188875
4.46	1.581445	14.131164
4.47	1.581971	14.073846
4.48	1.582492	14.016917
4.49	1.583008	13.960374
4.50	1.583520	13.904213
4.51	1.584027	13.848430
4.52	1.584499	13.792893
4.53	1.584982	13.737795
4.54	1.585460	13.683069
4.55	1.585934	13.628709
4.56	1.586404	13.574714
4.57	1.586870	13.521078
4.58	1.587331	13.467800
4.59	1.587788	13.414876
4.60	1.588240	13.362303
4.61	1.588688	13.310078
4.62	1.589155	13.258289
4.63	1.589608	13.206803
4.64	1.590058	13.155661
4.65	1.590506	13.104859

x	Q(x)	TY(x)
4.66	1.590950	13.054394
4.67	1.591392	13.004264
4.68	1.591831	12.954465
4.69	1.592267	12.904994
4.70	1.592700	12.855847
4.71	1.593130	12.807024
4.72	1.593551	12.758493
4.73	1.593972	12.710293
4.74	1.594391	12.662408
4.75	1.594807	12.614835
4.76	1.595221	12.567571
4.77	1.595632	12.520614
4.78	1.596041	12.473960
4.79	1.596447	12.427607
4.80	1.596850	12.381552
4.81	1.597251	12.335793
4.82	1.597660	12.290367
4.83	1.598061	12.245210
4.84	1.598459	12.200340
4.85	1.598854	12.155755
4.86	1.599247	12.111452
4.87	1.599637	12.067429
4.88	1.600024	12.023683
4.89	1.600408	11.980211
4.90	1.600790	11.937013
4.91	1.601142	11.893996
4.92	1.601515	11.851324
4.93	1.601885	11.808917
4.94	1.602251	11.766773
4.95	1.602615	11.724890
4.96	1.602976	11.683265
4.97	1.603334	11.641896
4.98	1.603689	11.600782
4.99	1.604041	11.559919
5.00	1.604390	11.519306
5.01	1.604736	11.478940
5.02	1.605066	11.438778
5.03	1.605400	11.398882
5.04	1.605731	11.359228
5.05	1.606059	11.319815
5.06	1.606385	11.280639
5.07	1.606707	11.241700
5.08	1.607027	11.202995
5.09	1.607344	11.164523
5.10	1.607659	11.126281
5.11	1.607970	11.088267
5.12	1.608279	11.050480
5.13	1.608585	11.012918
5.14	1.608888	10.975579
5.15	1.609189	10.938461
5.16	1.609487	10.901563

x	Q(x)	TY(x)
5.17	1.609782	10.864882
5.18	1.610074	10.828417
5.19	1.610363	10.792166
5.20	1.610650	10.756127
5.21	1.610934	10.720299
5.22	1.611221	10.684698
5.23	1.611503	10.649297
5.24	1.611784	10.614103
5.25	1.612062	10.579115
5.26	1.612337	10.544331
5.27	1.612611	10.509749
5.28	1.612882	10.475367
5.29	1.613152	10.441185
5.30	1.613419	10.407200
5.31	1.613684	10.373411
5.32	1.613946	10.339815
5.33	1.614207	10.306413
5.34	1.614465	10.273202
5.35	1.614722	10.240181
5.36	1.614976	10.207348
5.37	1.615227	10.174701
5.38	1.615477	10.142240
5.39	1.615725	10.109963
5.40	1.615970	10.077868
5.41	1.616213	10.045954
5.42	1.616455	10.014223
5.43	1.616695	9.982670
5.44	1.616934	9.951294
5.45	1.617170	9.920094
5.46	1.617404	9.889069
5.47	1.617637	9.858218
5.48	1.617867	9.827539
5.49	1.618096	9.797031
5.50	1.618323	9.766692
5.51	1.618548	9.736521
5.52	1.618771	9.706517
5.53	1.618993	9.676679
5.54	1.619212	9.647005
5.55	1.619430	9.617494
5.56	1.619646	9.588145
5.57	1.619859	9.558957
5.58	1.620071	9.529928
5.59	1.620282	9.501057
5.60	1.620490	9.472344
5.61	1.620696	9.443786
5.62	1.620902	9.415385
5.63	1.621105	9.387137
5.64	1.621307	9.359043
5.65	1.621507	9.331100
5.66	1.621706	9.303307
5.67	1.621903	9.275665

x	Q(x)	TY(x)
5.68	1.622099	9.248171
5.69	1.622293	9.220824
5.70	1.622485	9.193623
5.71	1.622676	9.166568
5.72	1.622865	9.139656
5.73	1.623052	9.112888
5.74	1.623238	9.086262
5.75	1.623422	9.059777
5.76	1.623605	9.033431
5.77	1.623786	9.007225
5.78	1.623966	8.981156
5.79	1.624144	8.955224
5.80	1.624320	8.929428
5.81	1.624764	8.904313
5.82	1.624930	8.878768
5.83	1.625094	8.853356
5.84	1.625256	8.828076
5.85	1.625416	8.802925
5.86	1.625573	8.777904
5.87	1.625729	8.753011
5.88	1.625882	8.728245
5.89	1.626033	8.703607
5.90	1.626183	8.679093
5.91	1.626330	8.654705
5.92	1.626475	8.630441
5.93	1.626618	8.606300
5.94	1.626759	8.582281
5.95	1.626897	8.558383
5.96	1.627034	8.534606
5.97	1.627169	8.510949
5.98	1.627301	8.487410
5.99	1.627432	8.463990
6.00	1.627560	8.440686
6.01	1.627686	8.417499
6.02	1.627853	8.394506
6.03	1.627998	8.371590
6.04	1.628143	8.348791
6.05	1.628286	8.326106
6.06	1.628428	8.303535
6.07	1.628570	8.281078
6.08	1.628710	8.258733
6.09	1.628850	8.236499
6.10	1.628989	8.214376
6.11	1.629126	8.192364
6.12	1.629263	8.170461
6.13	1.629399	8.148666
6.14	1.629534	8.126980
6.15	1.629667	8.105400
6.16	1.629800	8.083927
6.17	1.629932	8.062559
6.18	1.630063	8.041297

x	Q(x)	TY(x)
6.19	1.630194	8.020138
6.20	1.630323	7.999083
6.21	1.630451	7.978131
6.22	1.630578	7.957281
6.23	1.630705	7.936532
6.24	1.630830	7.915884
6.25	1.630954	7.895336
6.26	1.631078	7.874887
6.27	1.631201	7.854537
6.28	1.631322	7.834285
6.29	1.631443	7.814131
6.30	1.631563	7.794073
6.31	1.631681	7.774111
6.32	1.631799	7.754245
6.33	1.631916	7.734473
6.34	1.632032	7.714795
6.35	1.632147	7.695211
6.36	1.632261	7.675720
6.37	1.632374	7.656321
6.38	1.632487	7.637014
6.39	1.632598	7.617799
6.40	1.632708	7.598673
6.41	1.632818	7.579637
6.42	1.632926	7.560691
6.43	1.633033	7.541833
6.44	1.633140	7.523064
6.45	1.633246	7.504382
6.46	1.633350	7.485787
6.47	1.633454	7.467278
6.48	1.633557	7.448856
6.49	1.633658	7.430518
6.50	1.633759	7.412266
6.51	1.633859	7.394097
6.52	1.633958	7.376012
6.53	1.634056	7.358011
6.54	1.634153	7.340092
6.55	1.634250	7.322255
6.56	1.634345	7.304499
6.57	1.634439	7.286825
6.58	1.634532	7.269231
6.59	1.634625	7.251717
6.60	1.634716	7.234282
6.61	1.634807	7.216927
6.62	1.634896	7.199650
6.63	1.634985	7.182451
6.64	1.635072	7.165329
6.65	1.635159	7.148284
6.66	1.635245	7.131316
6.67	1.635330	7.114424
6.68	1.635414	7.097607
6.69	1.635497	7.080866

x	Q(x)	TY(x)
6.70	1.635579	7.064199
6.71	1.635660	7.047606
6.72	1.635740	7.031387
6.73	1.635819	7.014641
6.74	1.635897	6.998268
6.75	1.635974	6.981968
6.76	1.636051	6.965739
6.77	1.636126	6.949581
6.78	1.636201	6.933495
6.79	1.636274	6.917479
6.80	1.636347	6.901533
6.81	1.636418	6.885657
6.82	1.636489	6.869850
6.83	1.636559	6.854111
6.84	1.636628	6.838442
6.85	1.636695	6.822840
6.86	1.636762	6.807306
6.87	1.636828	6.791839
6.88	1.636893	6.776439
6.89	1.636957	6.761105
6.90	1.637021	6.745837
6.91	1.637083	6.730634
6.92	1.637144	6.715497
6.93	1.637204	6.700425
6.94	1.637264	6.685416
6.95	1.637322	6.670472
6.96	1.637380	6.655592
6.97	1.637436	6.640774
6.98	1.637492	6.626020
6.99	1.637546	6.611328
7.00	1.637600	6.596698

APPENDIX C. MAGNETIC FIELD

The data obtained in this study bearing on the pressure dependence of the internal magnetic field of ^{57}Fe in iron agree very well with previous determinations.^(15,159) The data are given in Table 7 and plotted versus pressure in Figure 31 and versus volume in Figure 32. A least squares fit to the data gives the dependences

$$\frac{d(\ln H)}{dP} = (-1.85 \pm 0.28) \times 10^{-4} / \text{kbar} \quad (185)$$

$$\frac{d(\ln H)}{d(\ln V)} = 0.36 \pm 0.05 . \quad (186)$$

Lister and Benedek,⁽¹⁵⁹⁾ in a nuclear magnetic resonance study to a pressure of 65 kilobars, found

$$\frac{d(\ln H)}{dP} = (-1.69 \pm 0.05) \times 10^{-4} / \text{kbar} \quad (187)$$

and, in a Mössbauer study mentioned previously in connection with the pressure dependence of the isomer shift, Pipkorn et al.⁽¹⁵⁾ obtained data that agree with this dependence.

Benedek,⁽¹⁶⁰⁾ in an analysis of the Mössbauer and nuclear magnetic resonance data obtained in these pressure studies, showed that independent determination of the change with volume of spin-up and spin-down s-electron density at the ^{57}Fe nucleus was possible. This is due to the fact that the isomer shift gives the sum of the two spin densities, while the magnetic field, via the Fermi-contact

Table 7

Iron. Internal Magnetic Field Data Points

Pressure (kilobars)		H/H ₀
Run #1	0	1.000
	20	0.989 ± .011
	40	1.001 ± .011
	60	0.981 ± .012
	80	0.987 ± .011
	104	0.967 ± .012
	122	0.970 ± .012
Run #2	0	1.000
	30	0.983 ± .009
	70	0.994 ± .009
	90	0.986 ± .009
	119	0.974 ± .010
Run #3	0	1.000
	30	1.005 ± .010
	70	0.985 ± .010
	90	0.981 ± .009
	112	0.994 ± .009

FIGURE 31. IRON INTERNAL MAGNETIC FIELD—vs.—PRESSURE

FIGURE 32. IRON INTERNAL MAGNETIC FIELD—vs.—VOLUME

term, gives the difference. Benedek concluded that the spin-up and spin-down densities changed with volume at essentially the same rate. Thus he obtained

$$\frac{\partial [|\Psi(0)|^2 + |\bar{\Psi}(0)|^2]}{\partial (\ln V)} = -2.7 a_0^{-3} \quad (188)$$

from the volume dependence of the isomer shift and

$$\frac{\partial [|\Psi(0)|^2 - |\bar{\Psi}(0)|^2]}{\partial (\ln V)} = -0.12 a_0^{-3} \quad (189)$$

from the volume dependence of the internal magnetic field. The isomer shift value, Eq. (188), was obtained by assuming a value for the isomer shift parameter derived from ferric-ferrous isomer shift differences.

The exact values given in Eqs. (188) and (189) can be disputed using the analysis of the isomer shift in Section 6. Thus the probability of 4s to 3d electron transfer with volume in iron makes the value in Eq. (189) uncertain since the principal contribution to the volume dependence of the difference of spin-up and spin-down densities comes from the 4s electrons. Also the interdependence of the isomer shift parameter α and the s to d electron transfer parameter $X = \partial n_s / \partial (\ln V)$ makes the value in Eq. (188) uncertain.

However it seems unlikely that X could be large enough to change the basic argument that the spin-up and spin-down densities change with volume at essentially the same rate.

APPENDIX D. TABULATED EXPERIMENTAL DATA

Tables 8 through 10 give the Mössbauer f number data for Cu, V, and Ti, respectively. The area is that calculated by the computer using Burton's⁽⁸⁷⁾ program and is given by Eq. (77). The ratio is given by Eq. (90). $f(P)/f(P=0)$ is calculated using Eq. (83).

Tables 11 through 14 give the Mössbauer isomer shift data for Fe, Cu, V, and Ti, respectively. The isomer shifts ($\Delta\epsilon$) are given with respect to the isomer shift at atmospheric pressure. The atmospheric values of the isomer shift ($\Delta\epsilon_0$) are also given for each pressure run with respect to ^{57}Fe in iron.

Table 8

Copper. Mössbauer f Number Data Points

	P(kilobars)	Area	Ratio	f(P)/f(P=0)
Run #1	0	4.2789	5.1935	-----
	20	4.0420	3.7327	1.042 $\pm$.010
	40	3.9029	3.4561	1.036 $\pm$.010
	60	3.8604	3.2709	1.049 $\pm$.010
	80	3.7884	3.0728	1.060 $\pm$.010
	100	3.8071	2.9862	1.080 $\pm$.010
Run #2	0	6.3330	3.0056	-----
	30	5.5780	2.3499	1.023 $\pm$.010
	70	5.4510	2.1991	1.053 $\pm$.010
Run #3	0	6.5916	3.1191	-----
	20	5.8914	2.4929	1.014 $\pm$.017
	40	5.9023	2.3964	1.044 $\pm$.017

Table 9

Vanadium. Mössbauer f Number Data Points

	P(kilobars)	Area	Ratio	f(P)/f(P=0)
Run #1	0	8.6792	5.0252	-----
	40	8.2677	4.3813	1.022 $\pm$.006
	80	8.2929	3.9816	1.057 $\pm$.006
Run #2	0	8.6324	6.6222	-----
	40	8.5732	4.9387	1.057 $\pm$.008
	80	8.5682	4.4909	1.084 $\pm$.007
	110	8.5575	4.2676	1.099 $\pm$.008
Run #3	0	8.8714	7.1403	-----
	20	8.7869	5.9634	1.023 $\pm$.006
	40	8.7716	5.7573	1.029 $\pm$.006
	60	8.8420	5.6092	1.043 $\pm$.005
	80	8.8888	5.4474	1.055 $\pm$.005
	100	8.9711	5.3350	1.070 $\pm$.006

Table 10

Titanium. Mössbauer f Number Data Points

	P(kilobars)	Area	Ratio	$f(P)/f(P=0)$
Run #1	0	4.4006	6.4314	-----
	40	4.3584	4.9132	$1.050 \pm .017$
	80	4.3496	4.3402	$1.085 \pm .018$
Run #2	0	3.8241	5.5506	-----
	60	3.6168	3.9103	$1.042 \pm .011$
	90	3.5404	3.5754	$1.054 \pm .011$

Table 11

Iron. Isomer Shift Data Points

	P(kilobars)	$\Delta\epsilon$ (mm/sec)
Run #1	0	-----
	20	-.012 $\pm$.011
	40	-.029 $\pm$.011
	60	-.053 $\pm$.012
	80	-.054 $\pm$.011
	104	-.055 $\pm$.012
	122	-.089 $\pm$.012
Run #2	0	-----
	30	-.032 $\pm$.009
	70	-.046 $\pm$.010
	90	-.054 $\pm$.010
	119	-.070 $\pm$.010
Run #3	0	-----
	30	-.017 $\pm$.010
	70	-.044 $\pm$.010
	90	-.064 $\pm$.010
	112	-.065 $\pm$.009

Table 12

Copper. Isomer Shift Data Points

	P(kilobars)	$\Delta\varepsilon$ (mm/sec)	$\Delta\varepsilon_0$ (mm/sec)
Run #1	0	-----	+22.1
	20	-.017 $\pm$.006	
	40	-.030 $\pm$.006	
	60	-.032 $\pm$.006	
	80	-.051 $\pm$.006	
	100	-.050 $\pm$.006	
Run #2	0	-----	+22.0
	30	-.015 $\pm$.004	
	70	-.042 $\pm$.004	
Run #3	0	-----	+20.1
	20	-.008 $\pm$.005	
	40	-.024 $\pm$.005	

Table 13

Vanadium. Isomer Shift Data Points

	P(kilobars)	$\Delta\epsilon$ (mm/sec)	$\Delta\epsilon_0$ (mm/sec)
Run #1	0	-----	-15.8
	40	-.030 $\pm$.003	
	80	-.070 $\pm$.003	
Run #2	0	-----	-15.4
	40	-.045 $\pm$.003	
	80	-.081 $\pm$.003	
	110	-.101 $\pm$.003	
Run #3	0	-----	-15.3
	20	-.019 $\pm$.003	
	40	-.033 $\pm$.003	
	60	-.049 $\pm$.003	
	80	-.061 $\pm$.003	
	100	-.081 $\pm$.003	

Table 14

Titanium. Isomer Shift Data Points

	P(kilobars)	$\Delta\epsilon$ (mm/sec)	$\Delta\epsilon_0$ (mm/sec)
Run #1	0	-----	+16.1
	40	$-.041 \pm .007$	
	80	$-.066 \pm .007$	
Run #2	0	-----	-22.6
	60	$-.031 \pm .008$	
	90	$-.055 \pm .008$	

VITA

Joseph Andrew Moyzis, Jr., was born October 21, 1931, in Chicago, Illinois, and graduated from Lane Technical High School in that city in June, 1949. He entered the University of Illinois in September, 1949, and, after four years of service in the U. S. Navy from January, 1951, to January, 1955, obtained his B.A. in physics in August, 1957.

Mr. Moyzis entered graduate school at the University of Illinois in September, 1957, and received his M.S. in physics in June, 1958. Since that time he has worked for a year and a half with a low energy nuclear physics group at the University of Illinois Betatron and for three years at Cornell Aeronautical Laboratory of Buffalo, New York, where he engaged in optical systems and high temperature gas studies, before entering the high pressure research group under Professor H. G. Drickamer at the University of Illinois to do thesis work for his Ph.D. in physics.

Mr. Moyzis received a University of Illinois fellowship for the 1957-58 academic year and has since worked under a combination of research and teaching assistantships.