Mössbauer Effect at High Pressure for Fe^{57} in Titanium, Vanadium, and Copper*

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We have measured the effect of pressure to 250 kbar on the isomer shift of Fe^{57} in dilute solution in titanium, vanadium, and copper. These results and previously published data on Fe^{57} in iron indicate that for the bcc metals of the first transition-metal series, the 4s-electron density scales approximately with bulk density. For more closely packed phases the s-electron density changes less rapidly than the bulk density.

I. INTRODUCTION

RECENTLY, Mössbauer experiments with Fe^{57} in iron at high pressure have been done by Pound et al.,[1] Nicol and Jura,[2] and by Pipkorn et al.[3] The isomer-shift data obtained by these authors for the body-centered-cubic (bcc) phase of iron indicate that for a change in lattice parameter up to 2% the only effect of the applied pressure is to scale the Fe^{57} 4s-electron density proportional to the bulk density without affecting the 3d electrons. The experiments reported here show that the same behavior is found for a solid solution of Fe^{57} in bcc vanadium, whereas the solid solutions of Fe^{57} in titanium and in copper show a more complicated behavior.

The isomer shift ϵ is defined as the difference in energy between the centers of gravity of the emission and of the absorption lines.[4] It is here expressed in terms of the Doppler velocity at resonance measured with a stainless steel absorber. As pointed out by Pound et al.[1] The pressure coefficient of the isomer shift consists of a small contribution arising from the change in vibrational energy, which will be neglected, and of a term arising from the change in electron density at the Fe^{57} nucleus,

$$\left(\frac{\partial \epsilon}{\partial p}\right)_T = \text{const}\left(\frac{\partial \psi(0)^2}{\partial (V/V_0)}\right)_T \left(\frac{\partial (V/V_0)}{\partial p}\right)_T. \quad (1)$$

Walker, Wertheim, and Jaccarino[4] have given a relationship between isomer shift and electron density. With their sign convention an increase in s-electron density corresponds to a decrease in isomer shift. If the 4s-electron density scales with volume V, the isomer shift due to the 4s electrons only will vary as[3]

$$\frac{\partial \epsilon}{\partial (V/V_0)} = 0.14 \text{ cm/sec}. \quad (2)$$

II. EXPERIMENT

The method of source preparation was essentially identical with that described by Pipkorn et al.[3] Radioactive Co^{57} was introduced into small foils of the sample metal by plating and diffusion. In all cases the concentration of Co^{57} plus carrier was less than 1%. The absorber used was the same stainless steel foil enriched in Fe^{57} used in the work on iron. The high-pressure cell and Mössbauer spectrometer are also described in detail by Pipkorn et al.[3] The isomer shifts were obtained by computer from a least-squares analysis of the experimental Mössbauer spectra.

III. RESULTS

The isomer shifts at zero pressure for Fe^{57} in the three host metals used in this study are listed in Table I.[5]

TABLE I. Atmospheric-pressure isomer shift for Fe^{57} in various transition metals—relative to stainless steel absorber.

Metal	ϵ_0 (cm/sec)
Ti	-0.0110 ± 0.0004
V	-0.0155 ± 0.0003
Fe	$+0.0086 \pm 0.0005$
Cu	$+0.029 \pm <0.001$

For comparison we also give the isomer shift at zero pressure relative to the same absorber for Fe^{57} in iron.[3] Figure 1 shows the isomer shift versus pressure for Fe^{57} in copper, titanium, and vanadium. Copper crystallizes in the face centered cubic (fcc) structure. Titanium is hexagonal close packed (hcp) at low pressure, but near 80-85 kbars it transforms (quite sluggishly) to a distorted cubic structure.[6] Vanadium crystallizes in the bcc structure as does iron below 130 kbar. At higher pressures iron assumes the hcp structure.

Figures 2 and 3 show the isomer shifts versus fractional volume change for the three host lattices plus that for pure iron. For iron the density data of Clendenen

[1] R. V. Pound, G. B. Benedek, and R. Drever, Phys. Rev. Letters 7, 405 (1961).
[2] M. Nicol and G. Jura, Science 141, 1035 (1963).
[3] D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. 135, A1604 (1964).
[4] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters 6, 98 (1961).

[5] Here we use the sign convention that the velocity is positive when the absorber is moving away from the source. Thus as in conventional experiments with Fe^{57} in which one varies the isomer shift of the absorber, a negative change in the isomer shift indicates increasing s-electron density at the nucleus.
[6] J. C. Jamieson, Science 140, 72 (1963).

and Drickamer[7] obtained from x-ray measurements were used. For the other metals the shock-wave data of Rice, McQueen, and Walsh[8] and of McQueen and Marsh[9] were used. Their data show no discontinuity for titanium so it is not clear whether they had the high-pressure phase or a metastable hcp phase. The volume change at the transition is very probably too small to affect the qualitative discussion given below.

The dotted lines in Figs. 2 and 3 represent the isomer shifts calculated using the slope from Eq. (2), which was obtained assuming the Fe^{57} $4s$-electron-density scales with bulk density. Although this assumption is
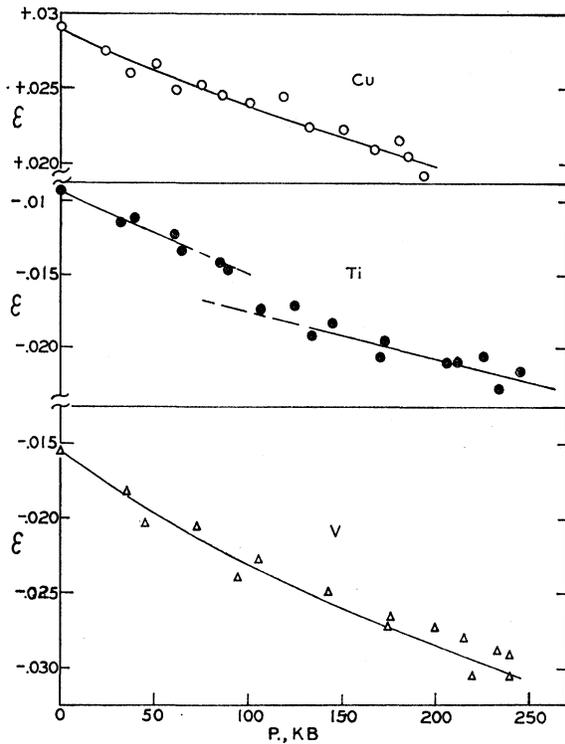

FIG. 1. Isomer shift versus pressure for Fe^{57} in copper, titanium, and vanadium.

only a first approximation, some interesting qualitative conclusions can be drawn comparing this calculated slope with those actually observed. Metals crystallizing in the bcc structure, namely, vanadium and iron in the low-pressure phase, show an Fe^{57} $4s$-electron density which scales with bulk density at least below 100–150 kbar. On the other hand, the closer packed materials, namely copper, and the hcp phases of titanium and iron show a slower rate of increase of Fe^{57} $4s$-electron density than predicted from the scaling assumption.

[7] R. L. Clendenen and H. G. Drickamer, J. Phys. Chem. Solids (to be published).

[8] M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

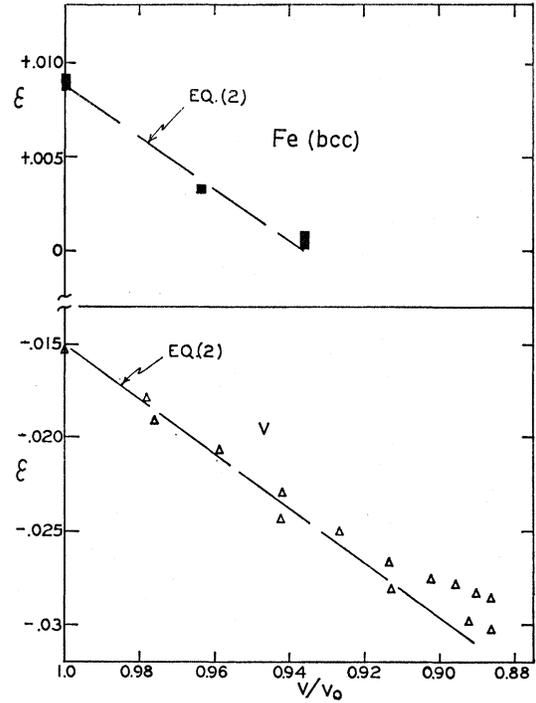[9] R. G. McQueen and S. P. Marsh, J. Appl. Phys. **31**, 1253 (1960).

FIG. 2. Isomer shift versus V/V_0 for Fe^{57} in vanadium and bcc iron.

In considering these results one must bear in mind that metals of the iron transition series possess the fol-
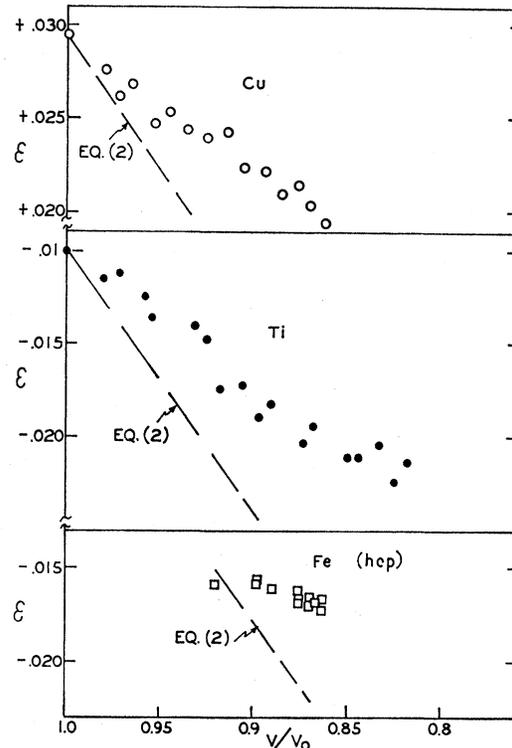

FIG. 3. Isomer shift versus V/V_0 for Fe^{57} in copper, titanium, and hcp iron.

lowing characteristics: They all have a rather broad 4s band overlapped by a narrow 3d band. The numbers of electrons which can be accommodated are two per atom for the 4s band and ten per atom for the 3d band, so that the density of allowed energy states is much higher in the 3d than in the 4s band. For these metals, the Fermi level lies somewhere within the 3d band. Thus, owing to the large difference in the density of states between the two bands, a small movement of the 3d band with respect to the 4s band caused by high pressure could result in a substantial redistribution of the electronic population. Therefore, the conclusion from the results is that in the bcc structure, for first-row transition metals, the relative positions and relative widths of the bands arising from the s and d atomic levels are independent of density, at least for modest density changes. For the closer packed metals apparently there is a relative lowering of the d band with increasing density so that there is some transfer of electrons from the s band to the d band, which slows the rate of increase of s-electron density at the nucleus.

Anharmonic Lattice in One Dimension: Energy Shift and Lifetime of an Excitation

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The self-energy and lifetime of a long-wavelength one-dimensional phonon are calculated by Van Hove's resolvent operator formalism using the first anharmonic term. The results are valid for zero temperature.

THE problem considered here is that of a one-dimensional anharmonic lattice. The dependences of the lifetime and energy shift of a phonon on the wave vector (at long wavelength) have been obtained by the resolvent operator method. The results are valid at zero temperature. The corresponding results for high temperatures have been obtained by Maradudin.[1] Thus, the results of this note supplement the results of Maradudin. His results indicate that at high temperatures the lifetime of all phonons is the same. But here we find that at zero temperature the lifetime of a phonon is a function of the wave vector.

The notation used is the same as that of Van Hove[2] and Hugenholtz.[3]

The Hamiltonian for the harmonic lattice without zero-point energy is

$$H_0 = \int_{-\pi/a}^{\pi/a} dk\, A_k{}^\dagger A_k \omega_k ,$$

where $A_k{}^\dagger$ and A_k are the usual creation and annihilation operators for phonons, and

$$\omega_k = (4\alpha/m)^{1/2} |\sin\tfrac{1}{2}ka| .$$

We assume that a, the interatomic distance, is small and that we can take

$$\omega_k = A |k| ,$$

where

$$A = (\alpha a^2/m)^{1/2}.$$

The first anharmonic term is

$$V^{(3)} = \int_{-\pi/a}^{\pi/a} dk_1 \int_{-\pi/a}^{\pi/a} dk_2 \int_{-\pi/a}^{\pi/a} dk_3\, C_{k_1,k_2,k_3} (A_{k_1} + A^\dagger{}_{-k_1})$$

$$\times (A_{k_2} + A^\dagger{}_{-k_2})(A_{k_3} + A^\dagger{}_{-k_3})\delta(k_1 + k_2 + k_3) ,$$

where

$$C_{k_1 k_2 k_3} = \frac{\beta a^3}{i 3!} \left(\frac{1}{8m^3 \omega_{k_1} \omega_{k_2} \omega_{k_3}} \right)^{1/2} k_1 k_2 k_3$$

and α, β are force constants. The diagonal part of the resolvent is given by

$$D_k(z) = \frac{1}{\omega_k - G_k(z) - z} .$$

The definition of these has been given by Van Hove and Hugenholtz. Here we evaluate the function approximately by considering the simplest diagram which contributes to it, i.e., the diagram of Fig. 1. We have left out a large number of diagrams and we work in

[1] A. A. Maradudin, Phys. Letters 2, 298 (1962).
[2] L. Van Hove, Physica 21, 901 (1955); L. Van Hove, in *Frontiers in Physics* (W. A. Benjamin, Inc., New York, 1961).
[3] N. M. Hugenholtz, Physica 23, 481 (1957).