

Effect of Pressure on f Number and Isomer Shift for Fe^{57} in Cu , V , and Ti^\dagger

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The effect of pressure to 100 kbar on the Mössbauer resonance has been measured for $\text{Co}^{57}(\text{Fe}^{57})$ in Cu , V , and Ti . Using Bridgman anvils, it is possible to establish the f number as a function of pressure. For Cu the characteristic temperature θ calculated in this way compares closely with that obtained from x-ray Bragg line intensities or room-temperature specific heats. For Ti the comparison with room-temperature specific-heat data is good. For V the θ we obtain compares closely with low-temperature specific-heat values for impure samples, but is low compared with values obtained on very pure samples. The isomer-shift changes with pressure are analyzed briefly in terms of $4s-3d$ electron transfer.

MEASUREMENTS have been made of Mössbauer resonance as a function of pressure to over 100 kbar for $\text{Fe}^{57}(\text{Co}^{57})$ in dilute solution in copper, vanadium, and titanium, which have fcc, bcc, and hcp structures, respectively. The sources, under pressure, were measured with respect to a stainless-steel absorber. This work differs from previous studies on these and similar systems^{1,2} in that Bridgman anvils were utilized. These permit more accurate measurements in the low-pressure region. With this simple geometry, and with appropriate auxiliary data taken in these experiments, it was possible to calculate f numbers as a function of pressure. Sample preparations were the same as those in Refs. 1 and 2. The techniques were otherwise as previously described.³

f NUMBER

It can be shown⁴ that at room temperature the f number can be expressed as

$$f \simeq \exp[-(kTv^2/m)\langle\omega^{-2}\rangle], \quad (1)$$

where

m = mass of decaying atom,

ω = lattice vibrational frequency,

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

and

ν = wave number of the radiation.

For a Debye distribution of frequencies $g(\omega) = (3N/$

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¹ C. K. Edge, R. Ingalls, P. DeBrunner, H. G. Drickamer, and H. Frauenfelder, *Phys. Rev.* **138**, A279 (1965).

² R. L. Ingalls, H. G. Drickamer, and G. DePasquali, *Phys. Rev.* **155**, 165 (1967).

³ P. DeBrunner, R. W. Vaughn, A. R. Champion, J. Cohen, J. A. Moyzis, and H. G. Drickamer, *Rev. Sci. Instr.* **37**, 1310 (1966).

⁴ H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin, Inc., New York, 1964).

$\omega_D^3)\omega^2$, where $\omega_D = k\theta_D/h$, one obtains

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

where $E_r = E_\gamma^2/2mc^2$ is the recoil energy of free nucleus due to decay. It is convenient to consider the logarithmic derivative of (2a):

$$\frac{\partial \ln f}{\partial \ln V} = -\gamma Y, \quad (2b)$$

where

$$\gamma = -\frac{\partial \ln \theta}{\partial \ln V}$$

is the Grüneisen constant, and

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

It should be pointed out that the dependence on $\omega(\langle\omega^{-2}\rangle)$ is the same as for x-ray scattering but differs from the specific heat which goes as $\langle\omega^0\rangle$.

The calculation of f from high-pressure experimental data is discussed in detail elsewhere,⁵ including a thorough discussion of errors. Only an outline is given here.

There have been a number of papers on the evaluation of absolute f numbers from Mössbauer resonance data.⁶⁻¹¹ Here we need only evaluate f at any pressure relative to the value at 1 atm, and the same (298°K) temperature. The area under the curve was obtained

⁵ J. A. Moyzis, Jr., Ph.D. thesis, University of Illinois, 1968 (unpublished).

⁶ S. Margulies and J. R. Ehrman, *Nucl. Instr. Methods* **12**, 131 (1961).

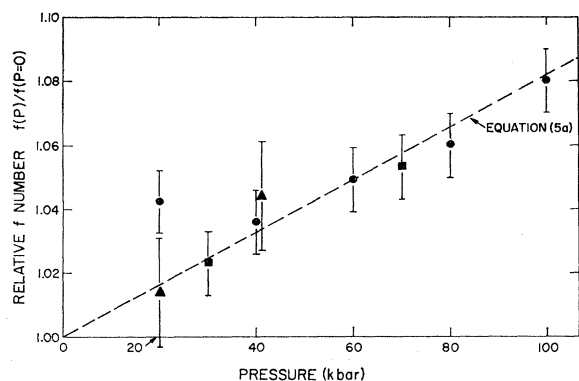
⁷ D. A. Shirley, M. Kaplan, and P. Axel, *Phys. Rev.* **123**, 816 (1961).

⁸ R. M. Housley, N. E. Erickson, and J. G. Dash, *Nucl. Instr. Methods* **27**, 29 (1964).

⁹ R. M. Housley, J. G. Dash, and R. N. Nussbaum, *Phys. Rev.* **136**, A464 (1964).

¹⁰ R. M. Housley, *Nucl. Instr. Methods* **25**, 77 (1965).

¹¹ C. Hohenemser, *Phys. Rev.* **139**, A185 (1965).

FIG. 1. Copper: relative f versus pressure.

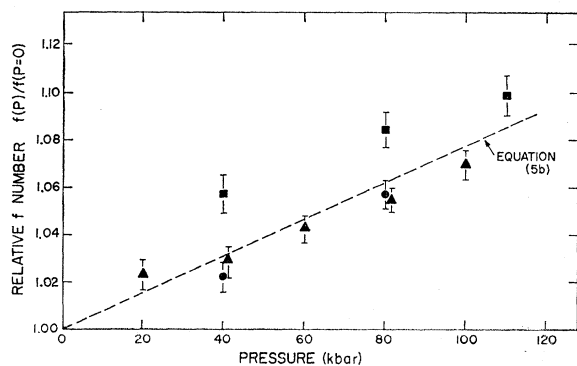
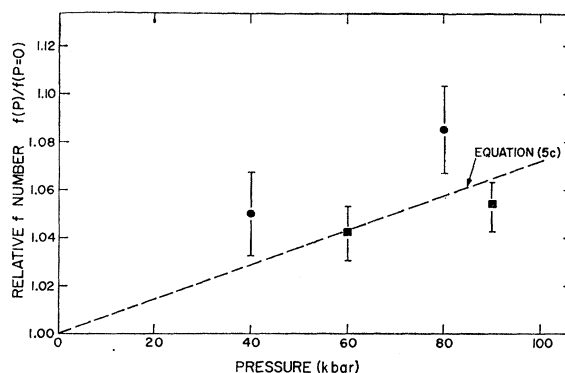
by computer fitting the data to a Lorentzian curve. It was then necessary to correct for the 122-keV γ rays measured by the detector. The ratio of counts was taken with and without a 0.006-in.-thick copper sheet between the source and the absorber. It has been shown⁹ that such an absorber removes all the 14.4-keV γ rays while passing 96% of the high-energy γ rays. The equation for f becomes

$$\frac{f_p}{f_0} = \frac{A_p (1 - \beta_p)}{A_0 (1 - \beta_0)}, \quad (3)$$

where the A 's are the areas mentioned above, and

$$\beta = (1 - \xi)/0.96R. \quad (4)$$

R is the ratio of counts without to with the copper sheet. ξ is a factor of order 0.04–0.05 which corrects for the fact that R is measured over the entire range of velocities including regions where there is finite absorption by the sample. The details of its evaluation are included in Ref. 5. In all cases at least 100 000 counts per channel were accumulated. An error analysis⁵ showed that the greatest error was in the computer fit of the data, excluding conceivable systematic errors such as the possibility that the curves are not truly Lorentzian.

FIG. 2. Vanadium: relative f versus pressure.FIG. 3. Titanium: relative f versus pressure.

EXPERIMENTAL RESULTS

Experimental plots of relative f versus pressure for Fe⁵⁷ in copper, vanadium, and titanium are shown in Figs. 1–3. One obtains by least squares

$$\text{Cu: } \Delta f/f = (8.14 \pm 0.65) \times 10^{-4} P, \quad (5a)$$

$$\text{V: } \Delta f/f = (7.81 \pm 0.56) \times 10^{-4} P, \quad (5b)$$

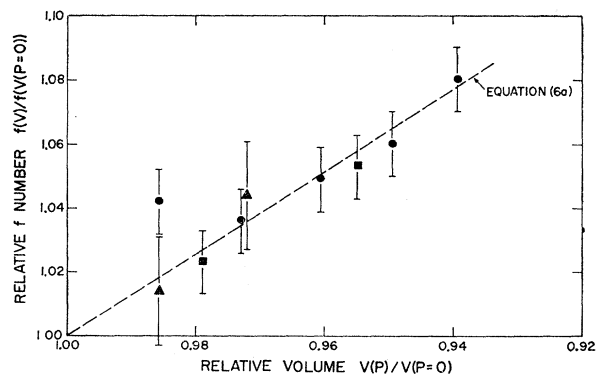
$$\text{Ti: } \Delta f/f = (7.21 \pm 1.39) \times 10^{-4} P \quad (5c)$$

(P is in kbar).

For titanium only a few points were taken because it was necessary to keep the solid solution very dilute to maintain the disordered hcp phase. Further, there is a phase transition at 80–85 kbar. The data were also plotted against volume. (Figure 4 is a typical result.) Again, a linear fit is all that is justified.

The volumetric data were obtained by combining low-pressure compressibilities^{12–14} with shock data^{15,16} in a Murnaghan equation, giving

$$\text{Cu: } V_P/V_0 = [1 + P/234]^{-0.176}, \quad (6a)$$

FIG. 4. Copper: relative f versus $\Delta V/V_0$.

¹² W. C. Overton, Jr., and J. Gaffney, Phys. Rev. **98**, 969 (1955).

¹³ G. A. Alers, Phys. Rev. **119**, 1532 (1960).

¹⁴ E. S. Fisher and C. J. Renken, Phys. Rev. **135**, A482 (1964).

¹⁵ J. M. Walsh, M. H. Rice, R. G. McQueen, and F. L. Yarger, Phys. Rev. **108**, 196 (1957).

¹⁶ R. G. McQueen and S. P. Marsh, J. Appl. Phys. **31**, 1253 (1960).

TABLE I. Grüneisen constant evaluation.

Element	Volume (cm ³ /g)	Compressibility (10 ⁻¹³ dyn/cm ²)	C_v (10 ⁶ erg/g °K)	Thermal expansion coefficient (10 ⁻⁶ /°K)	γ
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 Publishers, Inc., New York, 1963).

^b Reference 12.

^c Reference 13.

^d Reference 14.

^e W. F. Giauque and P. F. Meads, *J. Am. Chem. Soc.* **63**, 1897 (1941).

^f C. T. Anderson, *J. Am. Chem. Soc.* **58**, 564 (1936).

^g Reference 25.

^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).

TABLE II. Results of Mössbauer f -number experiment.

Element	$10^4\alpha^a$	β^b	50 kbar		Atmospheric pressure		$\langle\omega^{-2}\rangle$ (10 ⁻²⁷ sec ²)	f
			θ_f (°K)	θ_{host} (°K)	θ_f (°K)	θ_{host} (°K)		
Cu	8.14±0.65	1.283±0.095	350±14	331±14	327±14	309±14	1.60±0.13	0.684±0.020
V	7.81±0.56	1.380±0.100	268±10	284±11	258±10	274±11	2.57±0.19	0.547±0.024
Ti	7.21±1.39	0.843±0.158	339±35	370±40	321±35	350±40	1.66±0.40	0.674±0.060

^a $\Delta f/f = \alpha P$ (P in kbar).

^b $\Delta f/f = -\beta\Delta V/V$.

$$\text{V: } V_P/V_0 = [1 + P/344]^{-0.222}, \quad (6b) \quad \text{and}$$

$$\text{Ti: } V_P/V_0 = [1 + P/794]^{-0.739} \quad (6c)$$

(P in kbar).

The results for titanium are in serious doubt because it is hard to be sure to what phase the shock data apply. The best fits for f number versus volume then are

$$\text{Cu: } \Delta f/f = (-1.283 \pm 0.095)\Delta V/V, \quad (7a)$$

$$\text{V: } \Delta f/f = (-1.380 \pm 0.100)\Delta V/V, \quad (7b)$$

$$\text{Ti: } \Delta f/f = (-0.843 \pm 0.158)\Delta V/V. \quad (7c)$$

From these results and Eq. (2b) it is possible to evaluate a characteristic temperature which applies to the impurity at some average pressure. Since our data for f/f_0 versus $\Delta V/V_0$ are linear within our accuracy, we obtain a constant value of the product γY . It is reasonable to assume that γ is independent of volume over this range of ΔV . Then we can evaluate an average Y over this pressure range. Our data do not permit a measurement of the change of Y with pressure; thus we obtain a θ which applies, presumably, at 50 kbar. In the first order this can be corrected to apply to the host lattice from the relationship¹⁷

$$\theta_{\text{host}} = (m'/m)^{1/2}\theta_f, \quad (8)$$

where

θ_{host} = characteristic temperatures of the host lattice,
 θ_f = value obtained above,

m, m' = mass of host and impurity atoms.

Finally, it was assumed that these results were characteristic of a pressure of 50 kbar, and they were corrected to 1 atm by

$$\theta_0 = (V_P/V_0)^\gamma \theta_P, \quad (9)$$

where γ is the Grüneisen parameter. Data for evaluation of γ are shown in Table I. In Table II are listed the various θ 's as well as $\langle\omega^{-2}\rangle$.

The comparison of our calculated atmospheric θ 's with those obtained by other methods tests the validity of the assumption that γ is independent of volume in this range.

It is most meaningful to compare our θ_{host} with θ_x evaluated from the variation of Bragg line intensities with temperature. Results for Cu from the literature are listed in Table III and are seen to be in excellent agreement with our value of 309°K. Housley *et al.*,^{9,10} using a black absorber, obtain a value of $f=0.710$ at 297°K. Shiffer *et al.*¹⁸ determined a θ_f from relative f numbers at three temperatures. Their value was $\theta_f=330 \pm 15^\circ\text{K}$, also in agreement with ours (327°K). Specific-heat measurements near room temperature¹⁹ give a $\theta=324^\circ\text{K}$. Salter²⁰ presents a value of

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

¹⁸ J. P. Shiffer, P. N. Parks, and J. Heberle, *Phys. Rev.* **133**, A1553 (1964).

¹⁹ D. L. Martin, *Can. J. Phys.* **38**, 17 (1960).

²⁰ L. S. Salter, *Advan. Phys.* **14**, 1 (1965).

¹⁷ A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 388.

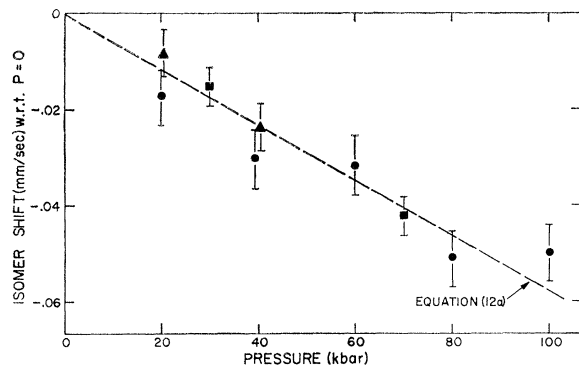


FIG. 5. Copper: change in isomer shift versus pressure.

from thermal data. An integration of Jacobsen's²¹ data on the lattice spectrum of copper gives

$$\langle \omega^{-2} \rangle = 1.59 \times 10^{-27} \text{ sec}^2. \quad (11)$$

Both of these values are in close agreement with our results.

A more general harmonic analysis for variations of $\langle x^2 \rangle$ with volume, similar to the temperature analysis of Housely and Hess,²² should ultimately be done. A rough use of their analysis can be made as follows, with the aid of the Grüneisen approximation. Differentiating their general expression for $\langle x^2 \rangle$ with respect to $\ln V$ and inserting appropriate constants, one obtains in this approximation

$$\partial \ln f / \partial \ln V = \gamma \ln f - \gamma (2.31 \times 10^{26} \text{ sec}^{-2}) \times [\omega_{jk}^{1/2}(-2) - 5.4 \times 10^{-29} \text{ sec}^2].$$

Using $f=0.71$ at 300°K ,^{9,23} γ from Table I, and our experimental value for $\partial \ln f / \partial \ln V$, one obtains

$$\omega(-2) = 2.72 \times 10^{13} \text{ sec}^{-1}.$$

The high-temperature analysis by Housely and Hess

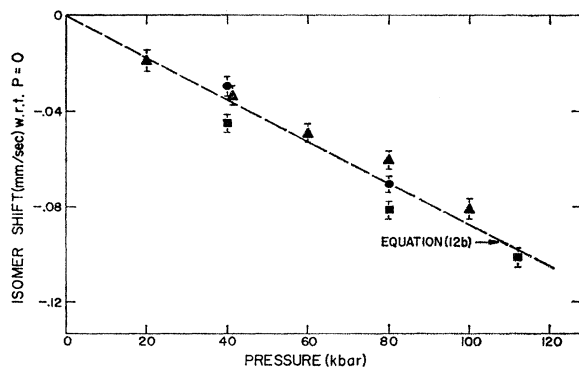


FIG. 6. Vanadium: change in isomer shift versus pressure.

²¹ J. Spreadborough and J. W. Christian, Proc. Phys. Soc. (London) **74**, 609 (1959).

²² R. M. Housley and F. Hess, Phys. Rev. **146**, 517 (1966).

²³ W. A. Steyert and R. D. Taylor, Phys. Rev. **134**, A716 (1964).

TABLE III. X-ray determinations of the Debye parameter for copper.

Investigators	Debye parameter ($^\circ\text{K}$)
a	314
b	299
c	307(327) ^f
d	322
e	310

^a E. A. Owen and R. W. Williams, Proc. Roy. Soc. (London) **A188**, 509 (1947).

^b B. Burje, Acta Cryst. **9**, 617 (1956).

^c D. R. Chipman and A. Paskin, J. Appl. Phys. **30**, 1992 (1959).

^d P. A. Flinn, G. M. McManus, and J. A. Rayne, Phys. Rev. **123**, 809 (1961).

^e Y. I. Graevskaya, V. I. Iveronova, and V. P. Tarasora, Fiz. Tverd. Tela **7**, 1342 (1965) [English transl.: Soviet Phys.—Solid State **7**, 1083 (1965)].

^f Parenthetic value corrected for one- and two-phonon generation.

gives directly

$$\ln f = -2.31 \times 10^{26} \text{ sec}^2 [1/\omega^2(-2) + 5.4 \times 10^{-29} \text{ sec}^2],$$

$$\omega(-2) = 2.56 \times 10^{13} \text{ sec}^{-1},$$

in good agreement with the above value.

A direct comparison of our results with other data for vanadium is more difficult. The values of θ available are from low-temperature specific-heat measurements and are listed in Table IV. It should be kept in mind that vanadium is superconducting below 5.4°K , so that measurements must be made in a field 5–10 kG. Further, a large correction for electronic specific heat is necessary. The results in Table IV show a rather distinct trend with sample purity, with the more impure samples agreeing with our result. This is perhaps reasonable, since our samples contained $\text{Co}^{57}(\text{Fe}^{57})$ impurity. It must be remembered that θ_{c_v} is a distinct function of temperature and may be 50° or more lower at room temperature. The values of $\langle \omega^{-2} \rangle$ depend on the value of θ used.

For titanium, there is a value of $\theta_x = 270 \pm 30^\circ\text{K}$ from x-ray intensities.²¹ These authors used Grüneisen constants of 2, 3, and 4 in their calculations. Since we find a value of $\gamma = 1.23$, a direct comparison is difficult. Wolcott²⁴ and Johnson and Kothen²⁵ have made C_v

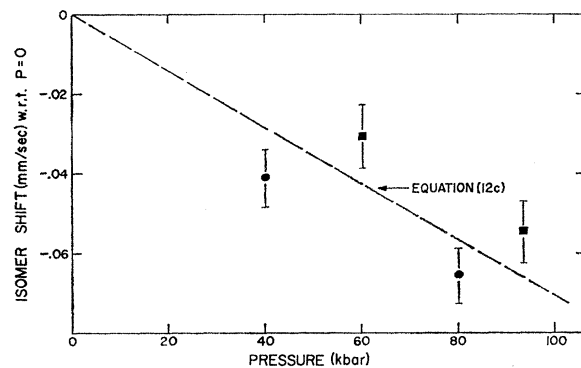


FIG. 7. Titanium: change in isomer shift versus pressure.

²⁴ N. M. Wolcott, Phil. Mag. **2**, 1246 (1957).

²⁵ N. L. Johnson and C. W. Kothen, J. Am. Chem. Soc. **75**, 3101 (1953).

TABLE IV. Low-temperature specific-heat results for vanadium.

Investigators	Sample purity (%)	γ (mJ/mole deg)	θ_{C_v} (°K)	$\langle\omega^{-2}\rangle$ (10^{-27} sec 2)
a	>99.98	9.21	380	1.23
b	Sample 1 99.5	9.00	308	1.87
	Sample 2 99.8	8.83	273	2.38
c	\approx 99.8	9.26	338	1.56
d	99.5	6.70 ^f	425 ^f	0.98
e	>99.99	9.82	382	1.22

^a N. M. Wolcott, in *Conférence de Physique des Basses Températures* (Institute International du Froid, Paris, 1955).

^b R. D. Worley, M. W. Zemansky, and H. A. Boorse, *Phys. Rev.* **99**, 447 (1955).

^c W. S. Corak, B. B. Goodman, C. B. Satherwaite, and A. Wexler, *Phys. Rev.* **102**, 656 (1956).

^d K. Clusius, P. Franzosini, and V. Piesbergen, *Z. Naturforsch.* **15a**, 728 (1960).

^e R. Radebaugh and P. H. Keesom, *Phys. Rev.* **149**, 209 (1966).

^f Experiment performed in temperature range 11–23°K.

measurements over a wide temperature range. At low temperatures they obtain $\theta=430^\circ\text{K}$ and near room temperature a value of 360°K , in very good agreement with our results.

The results for these three metals demonstrate that, to a good approximation, γ is independent of density at least to 100 kbar, which validates the Grüneisen equation of state over this range and permits the prediction of θ as a function of pressure to 100 kbar at least.

ISOMER SHIFT

In addition to the f -number data discussed above, the change in isomer shift with pressure was measured. The energy shift of the nuclear levels due to the finite size of the nucleus can be written⁴

$$\Delta\epsilon = \alpha |\psi(0)|^2,$$

where $|\psi(0)|^2$ is the total s electron density at the nucleus and α is a scaling parameter whose evaluation is discussed below.

Figures 5–7 show plots of isomer shift versus pressure, which are, within our accuracy, linear. The equations for the least-squares fit are

$$\text{Cu: } \Delta(\Delta\epsilon) = (-5.78 \pm 0.28) \times 10^{-4} P \text{ mm/sec, (12a)}$$

$$\text{V: } \Delta(\Delta\epsilon) = (-8.71 \pm 0.33) \times 10^{-4} P \text{ mm/sec, (12b)}$$

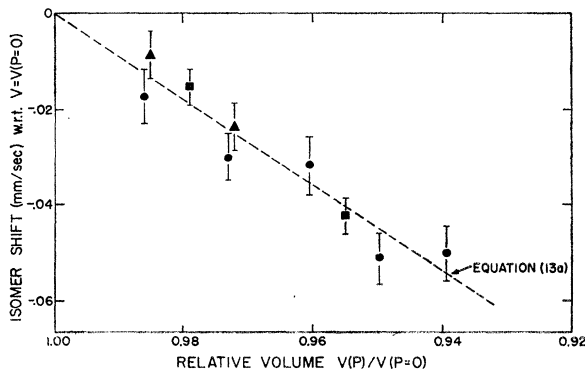


FIG. 8. Copper: change in isomer shift versus $\Delta V/V_0$.

$$\text{Ti: } \Delta(\Delta\epsilon) = (-7.10 \pm 1.10) \times 10^{-4} P \text{ mm/sec (12c)}$$

(P in kbar). As shown in Fig. 8 for copper, the change in compressibility with pressure is sufficiently small that within our accuracy the data are also linear in volume, giving

$$\text{Cu: } \Delta(\Delta\epsilon) = (0.90 \pm 0.04) \Delta V/V \text{ mm/sec, (13a)}$$

$$\text{V: } \Delta(\Delta\epsilon) = (1.54 \pm 0.06) \Delta V/V \text{ mm/sec, (13b)}$$

$$\text{Ti: } \Delta(\Delta\epsilon) = (0.83 \pm 0.12) \Delta V/V \text{ mm/sec. (13c)}$$

These values check rather well previously published results^{1,2} over a larger pressure range with less data concentrated in the low-pressure region. They also illustrate (as do the recently published iron data²⁶) the already observed trend^{1,2} for the bcc phases to show measurably greater change in isomer shift with volume than the close-packed materials.

Walker *et al.*²⁷ have presented an analysis which gives a value for α of $-0.47a_0^3$ mm/sec ($a_0 \equiv$ Bohr radius). Others^{28,29} have suggested that α is considerably

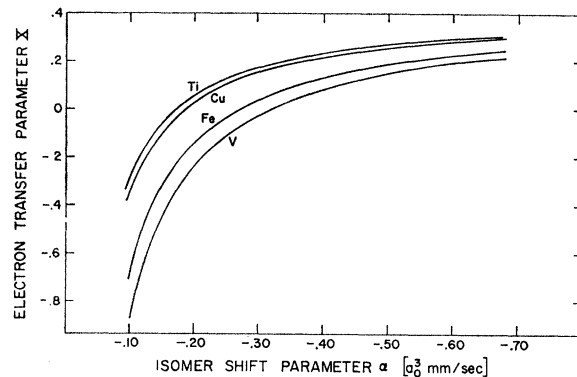


FIG. 9. α versus X for Fe^{57} in transition metals.

²⁶ J. A. Moyzis, Jr., and H. G. Drickamer, *Phys. Rev.* **171**, 389 (1968).

²⁷ L. R. Walker, G. K. Wertheim, and V. Jaccarina, *Phys. Rev. Letters* **6**, 98 (1961).

²⁸ V. I. Gol'danski, in *Proceeding of the Dubna Conference on the Mössbauer Effect* (Consultants Bureau Enterprises, Inc., New York, 1963), pp. 17–19.

²⁹ J. Danon, in *Applications of the Mössbauer Effect in Chemistry and Solid State Physics* (International Atomic Energy Agency, Vienna, 1966), p. 89.

smaller in magnitude, as low as $-0.20a_0^3$ mm/sec. Ingalls³⁰ has given an analysis for Fe⁵⁷ in iron which takes into account both scaling in the 4s part of the conduction band and $s \rightarrow d$ (or $d \rightarrow s$) transfer of electrons in the 4s-3d band, changing the shielding of the 3s electrons. His results can be put in the form²⁶

$$d(m\epsilon)/d \ln V = \alpha[-4.86 + 12.05X], \quad (14)$$

where $X = dN_s/d \ln V$ is the change in number of 4s electrons with fractional volume change in the 4s-3d band. This is assumed in first order to be equal to $-\partial N_a/\partial \ln V$.

It is not obvious that this relationship should apply to Fe⁵⁷ in dilute solution in other metals. We shall here

³⁰ R. Ingalls, Phys. Rev. **155**, 157 (1967).

assume that it does. For Fe⁵⁷ dissolved in a number of first-row transition metals the isomer shifts cluster around that for metallic iron in a band quite narrow compared, say, with the difference between ferrous and ferric ion isomer shifts, giving a sort of zeroth-order validity to this assumption. In Fig. 9 are the plots of α versus X including our recently published data for iron. The grouping of close-packed and bcc systems is obvious. For iron, Stern's³¹ calculations indicate a positive value for X . In any case, it is quite clear that if there is no $s \leftrightarrow d$ transfer in one structure, it must occur in the other, and that, in general, the close-packed systems have a greater tendency for s -to- d electron transfer.

³¹ F. Stern, Ph.D. thesis, Princeton University (unpublished).

Reflectance and $1/\epsilon$ Resonance of Beryllium in the Far Ultraviolet

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The reflectance of evaporated Be layers has been measured after 3-min exposure to ambient pressures of $\leq 3 \times 10^{-7}$ Torr, for the wavelength range of 480–1200 Å, for a spread of angles between 20° and 80°. These values give n and k by calculation; also, from these ϵ_1 , ϵ_2 , $\text{Re}(1/\epsilon)$, and $\text{Im}(1/\epsilon)$. The last two functions show good agreement with an inverted Drude-Sellmeier resonance formula. The center frequency of the resonance falls at 18.4 ± 0.1 eV, corresponding to the natural plasma-resonance frequency of a free-electron gas with 2.0 electrons per atom; this confirms a 1948 prediction by A. Bohr. The half-width of the resonance is measured as 4.7 ± 0.1 eV; this value is also obtained, within $\pm 10\%$, from a sum-rule approximation, and is thought to represent an upper limit of the systematic error. This value corresponds to a decay time (for intensity) of the plasma oscillation of about 1.3×10^{-16} sec. An Argand-diagram display of the data is given, and the "longitudinal" Kramers-Kronig relationship is demonstrated.

I. INTRODUCTION

NUMEROUS studies of the "plasmon" dielectric excitation in solids by fast-electron energy losses¹⁻⁸ have shown the collective, or many-electron, nature of this phenomenon. In a 1948 paper on proton stopping, Bohr⁹ proposed that beryllium should exhibit a simple form of this "longitudinal" dielectric resonance, in which two conduction electrons per atom would form an ideal free-electron gas resonating at 18 eV.

The present measurement appears to confirm Bohr's prediction in considerable detail. The electron-gas resonance, whose center turns out to lie at 18.4 eV (corresponding to the integral number 2 electrons per atom, within $\pm 2\%$, when all errors of the comparison are considered), may be accurately fitted with an inversion of the semiclassical Drude-Sellmeier functions in a manner previously suggested by Fano^{10,11} and by LaVilla and Mendlowitz.¹²

These measurements show a significant improvement over previous¹² Be optical data in the far ultraviolet. Measurement of reflectances at a number of incident angles permits the optical constants to be determined independently at each wavelength. The full spectral range of the free-electron-gas resonance is covered. The vacuum conditions have been improved, so that surface-contamination effects have been greatly reduced.

¹ L. Marton, J. Arol Simpson, H. A. Fowler, and N. Swanson, Phys. Rev. **126**, 182 (1962).

² H. Raether, *Ergeb. Exakt. Naturw.* **38**, 84 (1965).

³ J. Hubbard, Proc. Phys. Soc. (London) **A68**, 976 (1955).

⁴ H. Frohlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955); P. Nozières and D. Pines, Phys. Rev. **109**, 762 (1958); D. Bohm and D. Pines, *ibid.* **92**, 609 (1953); D. Pines, *ibid.* **92**, 626 (1953).

⁵ L. Marton, L. B. Leder, and H. Mendlowitz, *Advan. Electron. Electron Phys.* **7**, 183 (1955), especially pp. 225 ff.

⁶ N. Swanson, J. Opt. Soc. Am. **54**, 1130 (1964).

⁷ R. H. Ritchie, Phys. Rev. **106**, 874 (1957).

⁸ N. Swanson and C. J. Powell, Phys. Rev. **145**, 195 (1966).

⁹ A. Bohr, Kgl. Danske Videnskab. Selskab, *Mat.-Fys. Medd.* **14**, 19 (1948).

¹⁰ U. Fano, Phys. Rev. **103**, 1202 (1956).

¹¹ U. Fano, *Ann. Rev. Nucl. Sci.* **13**, 1 (1963), especially pp. 17-19.

¹² R. E. LaVilla and H. Mendlowitz, *Appl. Opt.* **4**, 955 (1965).