smaller values of α ($-0.2a_0^3$ mm/sec or less). If such a low value were correct, our qualitative agreement with experiments other than that of bcc iron under pressure would perhaps be worsened. However, here we have found it quite reasonable to adopt a value of $\alpha \sim -0.4a_0^3$ mm/sec. This value is also used in discussing the experimental shifts of Fe^{57} in other metals.[14]

In this work we have again met the interesting question concerning how many $3d$ and $4s$ electrons are in iron. Although the free-atom configuration $3d^74s^1$ gives excellent band-structure results, from a density-of-states point of view, one has $3d^74s^{0.5}4p^{0.5}$. From a Mössbauer-effect standpoint, that is, in terms of $\psi^2(0)$ relative to some free-atom configuration, the effective result is closer perhaps to $3d^{6.5}4s^{1.5}$.

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The author is grateful to H. G. Drickamer, whose keen interest in the pressure dependence of the isomer shift greatly stimulated this calculation. He is greatly indebted to R. W. Vaughan for extensive related computer calculations and to P. Debrunner for helpful comments about the manuscript. He is also pleased to thank J. Callaway, E. Clementi, S. Kobayasi, F. Stern, J. H. Wood, and E. P. Wohlfarth for helpful suggestions and communications.

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Isomer Shift of Fe^{57} in Transition Metals under Pressure*

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Isomer shifts of Fe^{57} in several transition metals have been measured as a function of pressure up to nearly 300 kbar. The host metals studied were Cr, Co, Ni, Nb, Mo, Pd, Ta, W, Pt, and Au. The data are discussed in terms of the volume dependence of (1) the density at the nucleus from $4s$-like conduction electrons and (2) the density at the nucleus from $3s$ core electrons which are shielded by the $3d$-like conduction electrons. Results of the previous paper regarding amount of $4s$ character, n_s, and amount of $3d$ character, n_d, on the iron impurity atom, are used. The data are shown to be consistent with (1) n_s decreasing or n_d increasing, or both, as one goes through each transition-metal series toward more d electrons of the host, and (2) n_s decreasing or n_d increasing, or both, as pressure is applied to the host metal. The degree of the effect (2) is shown to be related to the calibration constant of the isomer shift.

I. INTRODUCTION

THE work reported here represents a continuation of Mössbauer studies of Fe^{57} in transition metals under very high pressure which began with work on iron by Pipkorn *et al.*[1] and continued on titanium, vanadium, and copper by Edge *et al.*[2] The host metals studied here are Cr, Co, Ni, Cu, Nb, Mo, Pd, Ta, W, Pt, and Au. In the present report we are solely concerned with the isomer shifts of Fe^{57} in these hosts. Data for the pressure dependence of the Fe^{57} internal magnetic field in cobalt and nickel, as well as the electric field gradient in cobalt, has been reported earlier[3] together with some preliminary isomer-shift results.

As with Fe, Cu, Ti, and V, our results show that the isomer shift ϵ decreases with increasing pressure corresponding to increasing electron density at the nucleus, $\Psi^2(0)$. Pound *et al.*,[4] in interpreting their original pressure experiment on Fe^{57} in Fe, used a calibration based on free-ion wave functions to show this increase to be consistent with simple scaling of the $4s$ density $\Psi_{4s}^2(0)$ with inverse volume. Although the behavior in bcc vanadium roughly supported this interpretation, the results on hcp Fe, Ti, and fcc Cu showed a much smaller change in $\Psi^2(0)$ with volume[1,2] indicating a possible role of crystal symmetry and host band structure as well as possible complications due to effects of d electron shielding on the $3s$ electron. Indeed, large increases in $\Psi^2(0)$ with pressure have recently been observed in several ionic compounds of Fe in which very little $4s$ density is expected to be present.[5]

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[1] D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **135**, A1604 (1964).

[2] C. K. Edge, R. Ingalls, P. Debrunner, H. G. Drickamer, and H. Faruenfelder, Phys. Rev. **138**, A729 (1965).

[3] H. G. Drickamer, R. L. Ingalls, and C. J. Coston, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press Inc., New York, 1965), p. 313.

[4] R. V. Pound, G. B. Benedek, and R. Drever, Phys. Rev. Letters **7**, 405 (1961).

[5] R. Ingalls, C. J. Coston, G. De Pasquali, H. G. Drickamer, and J. J. Pinajian, J. Chem. Phys. **45**, 1057 (1966); A. R. Champion and R. W. Vaughan (private communication).

In a recent analysis[6] of the isomer shift in iron the above questions have been examined in somewhat more detail than previously. The chief result is that the 4*s* density can be written as

$$\Psi_{4s}^2(0)=n_s\Psi_{\Gamma_1}^2(0)\,, \tag{1}$$

where n_s is the amount of *s* character per atom (referred to here as the "number of *s* electrons") in the combined 3*d*-4*s* band, and $\Psi_{\Gamma_1}^2(0)$ is the density at the nucleus resulting from an electron at the band bottom. It was determined that, for the volumes of interest,

$$\Psi_{\Gamma_1}^2(0)=\text{const}\times V^{-\gamma}\,, \tag{2}$$

with $\gamma\sim 1.25$, independent of crystal structure or symmetry.

In I the shielding effect of the *d*-band electrons on the 3*s* electrons was also considered, with the result that for a given number of *d* electrons n_d (amount of *d* character) in the 4*s*-3*d* band, $\Psi_{3s}^2(0)$ did have a weak volume dependence, increasing with decreasing volume for atomic volumes roughly larger than Fe and decreasing for smaller volumes. For a more regular (Gaussian) density of *d* states, the latter behavior prevailed up to much larger volumes. Of course $\Psi_{3s}^2(0)$ decreased as n_d increased also because of shielding.

In applying the above results to the pressure dependence of iron as originally studied by Pound *et al.*[4] and Pipkorn *et al.*,[1] it was shown[6] that the data could be explained keeping n_s and n_d constant only if α, the proportionality constant in

$$\epsilon=\alpha\Psi^2(0)+\text{const}\,, \tag{3}$$

were considerably smaller than the value originally obtained from free-ion wave functions

$$\alpha\simeq(-0.47\pm0.05)a_0^3\ \text{mm/sec}\,, \tag{4}$$

which raised the question of whether n_s and n_d should in fact be considered constant at all, since theoretical results[7] seem to favor some lowering of the *d* band with respect to the *s* band with decreasing volume. It was then shown that with a change $[V(\partial n_s/\partial V)]_0\simeq 0.1$, accompanied by an equal and opposite change $[V(\partial n_d/\partial V)]_0\simeq -0.1$, the pressure data (as well as other data) could be explained with $\alpha=-0.42\pm0.05\ a_0^3$ mm/sec.

We shall use the above information as a framework for discussing the present experimental data.

II. EXPERIMENT

As in the two previous experiments,[1,2] the metals under study served as hosts for the high-purity Co^{57} source. The source preparation was essentially the same as that reported by Kitchens *et al.*[8] Although variations in zero-pressure isomer shift were common due to slight variations in the preparation, they approached standard values obtained by others (see Table I under $\epsilon_0-\epsilon_{Fe}$) when sufficient care was exercised (e.g., proper heat treatment and sufficient Co^{57} dilution). Small variations in zero-pressure isomer shift showed no effect on the pressure shifts reported in this work. The high-pressure apparatus and Mössbauer spectrometer have been described previously.[1]

TABLE I. Information derived from experimental results of this work and other information relevant to the isomer shift of Fe^{57} in transition metals.

Metal	Crystal structure	Transition series	Atomic volume (a_0^3)[a]	$\epsilon_0-\epsilon_{Fe}$ (mm/sec)[b]	$[V(\partial\epsilon/\partial V)]_0$ (mm/sec)[c]	$\partial\epsilon/\partial P$ (mm/sec kbar)[d]	$\partial\epsilon/\partial P$ (mm/sec kbar)[e]
Titanium[f]	hcp	3*d*	118	−0.19	0.8	4.1×10^{-2}	5.7×10^{-2}
Vanadium[f]	bcc	3*d*	96	−0.17	1.2	5.6	6.4
Chromium	bcc	3*d*	82	−0.16	1.2	3.8	5.4
Iron[g]	bcc	3*d*	80	0.00	1.3	···	6.4
Iron[g]	hcp	3*d*	73[h]	−0.23	0.8	2.1[i]	···
Cobalt	hcp	3*d*	74	−0.03	0.9	4.0	4.0
Nickel	fcc	3*d*	74	−0.00	0.9	3.8	3.8
Copper[f]	fcc	3*d*	80	0.23	0.6	3.4	3.4
Niobium	bcc	4*d*	122	−0.02	1.1	4.8	5.6
Molybdenum	bcc	4*d*	106	0.06	1.1	2.6	3.9
Palladium	fcc	4*d*	100	0.19	0.6	3.1	3.1
Tantalum	bcc	5*d*	122	0.03	1.1	4.0	4.8
Tungsten	bcc	5*d*	107	0.16	1.5	3.0	4.8
Platinum	fcc	5*d*	102	0.36	0.4	1.5	1.5
Gold	fcc	5*d*	115	0.64	0.4	1.8	1.8

[a] Volumes calculated on the basis of atomic weight and density at room temperature and atmospheric pressure as given in *Handbook of Physics and Chemistry* edited by C. D. Hodgeman *et al.* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1965), 46th ed.

[b] Isomer shifts at room temperature and atmospheric pressure compiled from Ref. 8 and R. Segnan (private communication).

[c] Average volume logarithmic derivative (±10%) of the isomer shift for the entire range of the experiment.

[d] Pressure derivative (±10%) of the isomer shift evaluated at 150 kbar.

[e] Pressure derivative (±10%) of the isomer shift evaluated at 50 kbar.

[f] Pressure data taken from Ref. 2.

[g] Pressure data taken from Ref. 1.

[h] Atomic volume at 130 kbar and room temperature.

[i] Pressure derivative (±10%) of the isomer shift evaluated at 200 kbar.

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[6] R. Ingalls, Phys. Rev. **154**, 157 (1967), preceding paper, hereafter referred to as I.

[7] F. Stern, Ph.D. thesis, Princeton University, 1955 (unpublished).

[8] T. A. Kitchens, W. A. Setyert, and R. D. Taylor, Phys. Rev. **138**, A467 (1965).

III. RESULTS AND DISCUSSION

Graphs of the data $\epsilon-\epsilon_0$ (± 0.003 mm/sec) versus pressure are shown in Figs. 1–5, where here ϵ_0 is our zero-pressure isomer shift for a particular run, and results of several runs for each sample have been combined. From our pressure data and available *P-V* data[9,10] we have also obtained graphs of isomer shift versus volume of each host metal. (See also Table I.) Typical such graphs appear in Figs. 6 and 7. From these latter graphs we have then extracted the logarithmic volume derivatives of $[\epsilon(\partial\epsilon/\partial V)]_0$ at zero pressure given in Table I. We also give the atomic volume for each host metal and its crystal symmetry.

From the small range in isomer shifts for the transition metals relative to what one would expect if either the number of *s* or *d* electrons changed by as much as ± 1, it is reasonable to claim that n_s and n_d (if such numbers are still meaningful) are chiefly characteristic of iron. Changes in these numbers are then related to screening and the band structure of the host metal.

In order to obtain a basis for discussion we use the results of I, which show the dependence of the isomer shift on atomic volume Ω as well as n_s and n_d for a metal having the density-of-states curve of bcc iron.[11] If n_s+n_d are kept constant at the value of 7.52 for bcc paramagnetic iron, one may calculate, from I, curves of $\Psi^2(0)-\Psi_{\mathrm{Fe}}^2(0)$ versus n_s, n_d, and Ω (Fig. 8), where $\Psi_{\mathrm{Fe}}^2(0)$ is the density at the nucleus in *ferromagnetic* bcc iron at atomspheric pressure. Proceeding further, we arbitrarily adopt the reasonable calibration constant[6] $\alpha=-0.4a_0^3$ mm/sec in order to place on the same graph, versus volume, the experimental data in Table I, i.e., $\epsilon-\epsilon_{\mathrm{Fe}}$ and its volume dependence. Such a procedure enables one to correlate in some sense the relation between isomer shift, volume, and relative amounts of *s* and *d* character. To our knowledge it is the only attempt to relate the pressure dependence of ϵ, as well as ϵ_0 itself, to volume. We shall discuss the shortcomings of this procedure below. For each transition series (i.e., 3*d*, 4*d*, 5*d*) one first notes the general trend[12] toward greater isomer shift as the number of *d* electrons on the host increases. The method of displaying the data here would suggest that, simultaneously, a very small percentage of *s* character is transferred to *d*. This could be related to the general lowering of the *d* band with respect to the

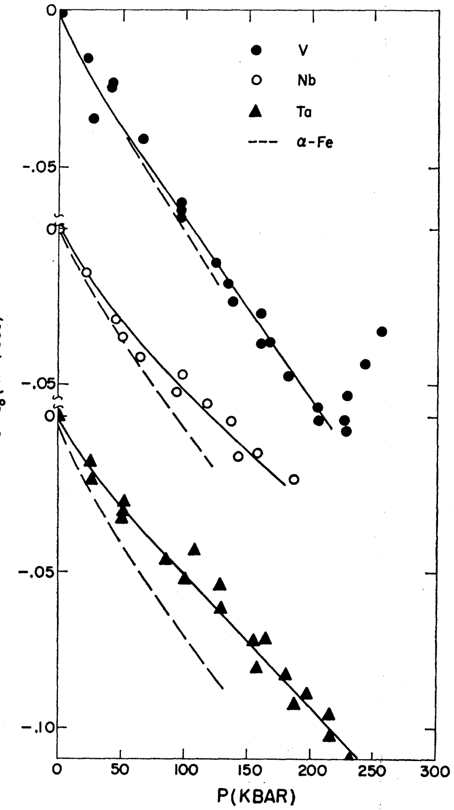

FIG. 1. Isomer shift versus pressure for Fe^{57} in V, Nb, and Ta.

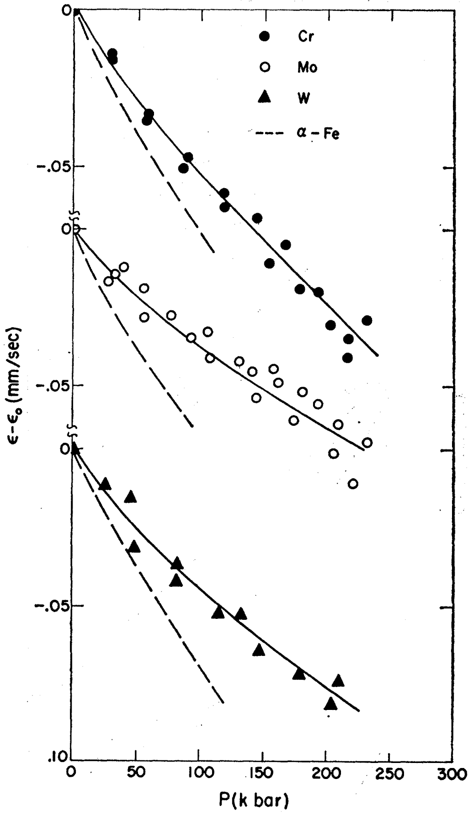

FIG. 2. Isomer shift versus pressure for Fe^{57} in Cr, Mo, and W.

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[9] 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.

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

[11] J. H. Wood, Phys. Rev. **126**, 517 (1962); J. F. Cornwell and E. P. Wohlfarth, J. Phys. Soc. Japan **17**, 32, Suppl. B-1 (1962).

[12] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **4**, 98 (1961).

s band of the host as shown by Mattheiss,[13] although we can neither eliminate the possibility that the d character alone increases nor that the s character alone decreases.

The effect of volume is quite apparent in such a diagram, although it raises the question as to what volume is really meaningful (if any) for iron dissolved in some host. Here we have necessarily used the host volume as a parameter. The fact that elements in a given column of the periodic table do not exactly fall in a column here might suggest that the effective volume for iron in the $4d$ and $5d$ metals should actually be smaller than the host volume. However, our constraint on the total number of s and d character could have brought about this result.

Figure 8 would also suggest that, for each element, there is a transfer from s to d character as the volume decreases. As shown in Sec. I in discussing the results[6] on Fe, the amount of such a transfer is related to the calibration constant α. If α were $\simeq -0.3a_0{}^3$ mm/sec the pressure curves for the bcc structure in Fig. 8 would approach the vertical (i.e., no s-to-d transfer). If it were reduced even further to $\alpha \simeq -0.2\ a_0{}^3$ mm/sec then the pressure data for the close-packed structure (fcc and hcp) would approach the vertical but one would then assign a d-to-s transfer with pressure for the bcc cases.

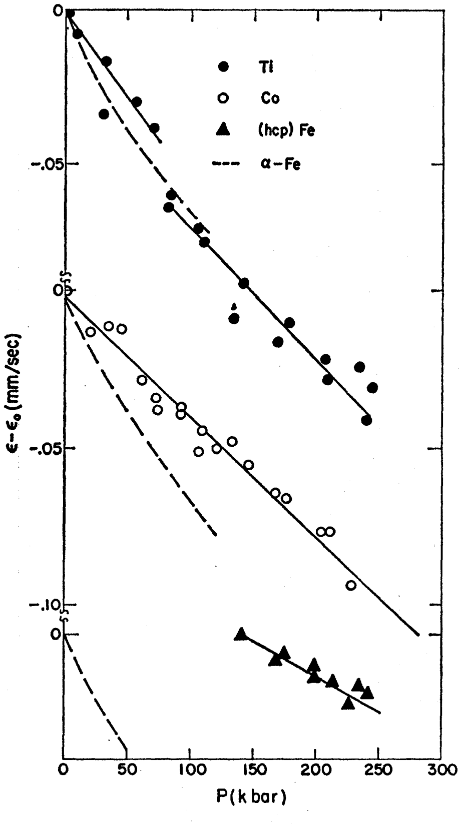

FIG. 3. Isomer shift versus pressure for Fe^{57} in Ti, Co, and Fe (hcp).

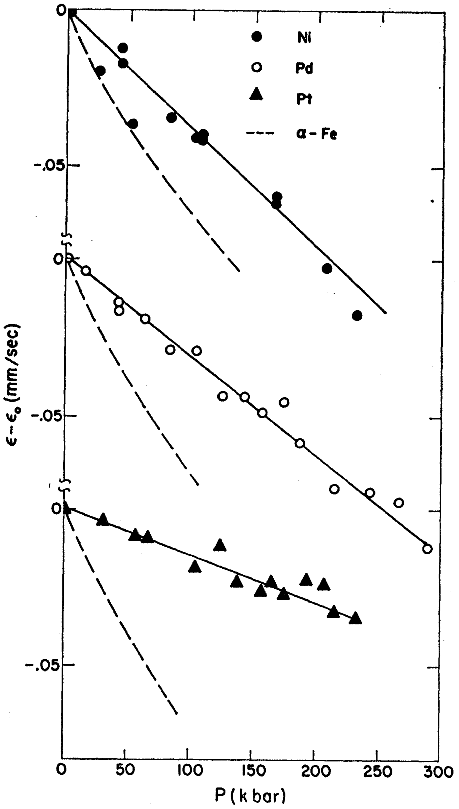

FIG. 4. Isomer shift versus pressure for Fe^{57} in Ni, Pd, and Pt.

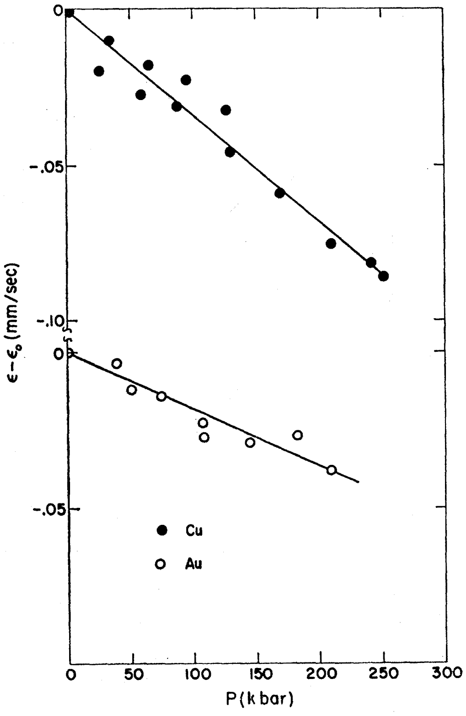

FIG. 5. Isomer shift versus pressure for Fe^{57} in Cu and Au.

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[13] L. F. Mattheiss, Phys. Rev. 134, A970 (1964).

As mentioned in Sec. I, strict analysis using free-ion wave function favors a value $\alpha = -0.47a_0^3$ mm/sec. However, some authors[13–15] have used chemical and molecular orbital arguments to show that α could conceivably reach values like $\sim -0.2a_0^3$ mm/sec or less. We must thus regard the calibration problem, as well as the question of *s*-to-*d* transfer, as still open.

There is the basic question remaining concerning the applicability of the calculation for pure bcc iron to the impurity problem of Fe^{57} in another metal. Certainly, on the basis of the rigid-band model one might argue in favor of its use for dilute concentrations of other transition metals *in iron*. Perhaps it is also still somewhat reasonable to use it for Fe^{57} in other body-centered lattices. The similarity of the volume dependence of the Fe^{57} isomer shift in the bcc hosts supports this to some extent (see Fig. 6). On the other hand, for all close-packed structures (hcp and fcc, including hcp iron) the volume dependences are similar to each other (Fig. 7) but significantly smaller than in the bcc structures. As mentioned in Sec. I, such behavior suggests an effective

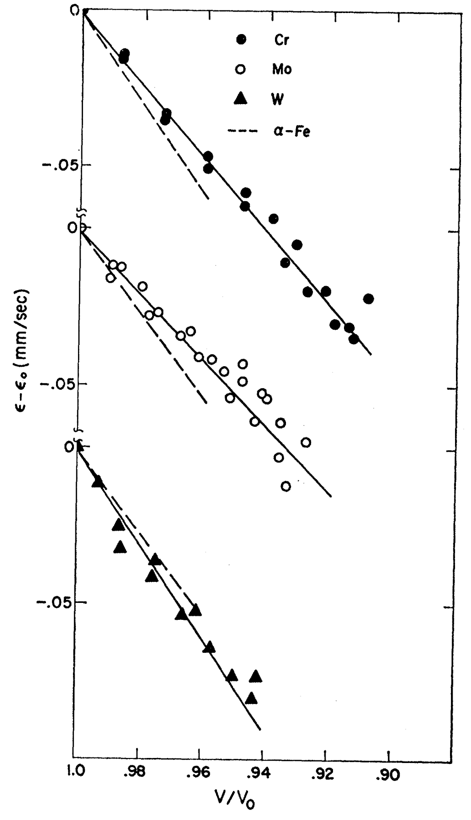

FIG. 6. Isomer shift versus V/V_0 for Fe^{57} in Cr, Mo, and W.

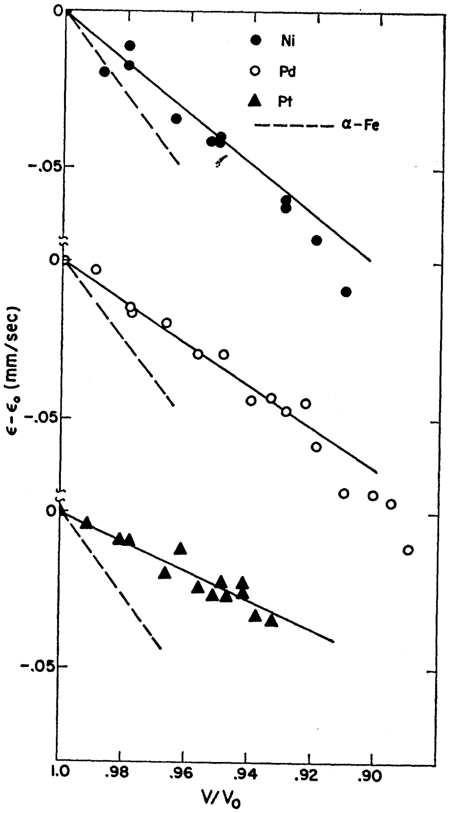

FIG 7. Isomer shift versus V/V_0 for Fe^{57} in Ni, Pd, and Pt.

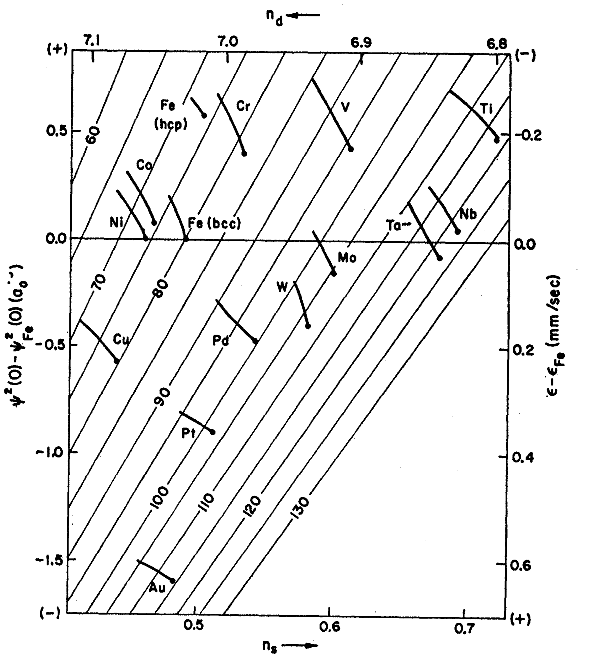

FIG. 8. Graph for correlating the Fe^{57} isomer shift with volume as well as amount of *s* and *d* character on the iron impurity (see text). Diagonal lines represent constant volume (a_0^3).

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[14] V. I. Gol'dauskii, in *Proceedings of the Dubna Conference on the Mössbauer Effect* (Consultants Bureau Enterprises, Inc., New York, New York, 1963), pp. 17–19.

[15] J. Danon, in *Applications of the Mössbauer Effect* (International Atomic Energy Agency, Vienna, Austria, 1966), Series No. 50, p. 89.

density-of-states curve which should be more Gaussian in character than in bcc iron. In a calculation, in I, for fcc iron with a Gaussian density of states, it was found that the shielding of the $3s$ electron by d-like electrons could lead to smaller values of $\Psi_{3s}^2(0)$ as the volume decreased. Such a behavior would counteract the expected increase in $\Psi_{4s}^2(0)$.

We feel the above treatment permits a reasonable qualitative understanding of the data. On the other hand, a more realistic treatment of the impurity problem and its relation to the volume should be attempted.

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Far-Infrared Optical Absorption of Fe^{2+} in ZnS

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The optical absorption of substitutional Fe^{2+} impurities in natural single crystals of cubic ZnS has been measured in the far infrared (10 to 100 cm^{-1}) at temperatures from 4 to 25°K. Several absorption peaks are identified with electric- and magnetic-dipole transitions between the five spin-orbit levels of the ^5E ground term of tetrahedral Fe^{2+}. The positions and absolute intensities of these peaks agree reasonably well with crystal field theory and with values obtained for the various parameters from previous measurements of the optical absorption in the near infrared. The separation K of the spin-orbit levels of the ^5E term is found to be 15.2 ± 0.4 cm^{-1}. Oscillator strengths for the transitions are in the range 5×10^{-9} to 5×10^{-8}. Lifetimes for spontaneous radiative decay of the excited levels are calculated to be of the order of $\frac{1}{2}$ to 30 h, and actual lifetimes are therefore determined by nonradiative processes. These observations support the conclusion that no pronounced Jahn-Teller effect occurs in the ^5E state of Fe^{2+} in ZnS.

I. INTRODUCTION

The present work is a study of the optical absorption of Fe^{2+} impurities in ZnS crystals at low temperatures in the far infrared. The measurements were made on natural crystals of cubic ZnS at temperatures between 4 and 25°K in the wavelength range from 100 to 1000 μ (wave number 10 to 100 cm^{-1}). Previous studies[1,2] of the low-temperature thermal conductivity of crystals of CdTe and $MgAl_2O_4$ containing Fe^{2+}, and studies[3] of the optical absorption in the near infrared of Fe^{2+} impurities in ZnS, CdTe, and $MgAl_2O_4$ have shown that there exist low-energy excited states of the Fe^{2+} ions lying in the range 10 to 100 cm^{-1} above the ground state. If light may induce transitions to these excited levels from the ground state, or among these excited levels when they are thermally populated, then absorption peaks should be observed in this region of the far infrared. In the work reported here, several such absorption peaks are found for Fe^{2+} in cubic ZnS, and their positions and intensities are compared with theory.

The Fe^{2+} impurity ions substitute for Zn^{2+} ions in natural crystals[3] of cubic ZnS and thus occupy lattice sites of tetrahedral symmetry. The ground term of $Fe^{2+}(3d^6)$ should then be ^5E, which is split in second order by spin-orbit interaction. The previous optical studies[3] of the fine structure of the $^5E\rightarrow{}^5T_2$ absorption band supported the predictions of crystal field theory for the ^5E term,[4] indicating that ^5E is split into five uniformly spaced spin-orbit levels with an interval of about 15 cm^{-1}. These results indicated that Fe^{2+} in ZnS does not undergo a static Jahn-Teller distortion in the ^5E state. While a dynamical Jahn-Teller effect was proposed[3] to account for the levels found for the $^5T_2$ state and may be present as well in ^5E, no evidence was obtained that indicated that such an effect was strong enough in ^5E to cause any marked change in the spin-orbit splitting of this state from that given by crystal field theory. These conclusions are given further support by the results of the present investigation.

Earlier studies[5–10] of optical reflectivity and absorption within the wavelength range examined in the present work have been reported for ZnS but have been concerned with ZnS itself and not with impurity ab-

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[2] G. A. Slack, Phys. Rev. **134**, A1268 (1964).

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[4] W. Low and M. Weger, Phys. Rev. **118**, 1119 (1960).

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[6] J. Strong, Phys. Rev. **38**, 1818 (1931).

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