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Paramagnetic Resonance Spectra of Fe^{3+} in $ZnWO_4$

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The paramagnetic resonance spectra of Fe^{3+} in $ZnWO_4$ have been examined at millimeter and centimeter wavelengths. The spectra fit a conventional spin Hamiltonian (in susceptibility coordinates)

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S}+B_2^0O_2^0+B_2^2O_2^2+B_4^0O_4^0+B_4^2O_4^2+B_4^4O_4^4\,,$$

with $S=\frac{5}{2}$, $g=2.0019$, $B_2^0=-6.987$ kMc/sec, $B_2^2=+4.935$ kMc/sec, $B_4^0=+0.00326$ kMc/sec, $B_4^2=-0.00178$ kMc/sec, and $B_4^4=-0.0173$ kMc/sec. The slight reduction in the g value from the free-ion value and the sign of B_4^4 (which is positive in the distorted cubic axis system) are in agreement with the theoretical predictions of Watanabe. The hyperfine structure due to Fe^{57} could be observed in low-concentration, natural-abundance samples at 1.5°K. The hyperfine constant $|A_z|$ was found to be 28.9 ± 1.4 Mc/sec. A point-charge calculation of the axial crystalline-field parameter A_2^0 yielded a positive value which suggests that the coefficient of the quadratic dependence of B_2^0 on A_2^0 is negative.

INTRODUCTION

THE paramagnetic resonance spectra of Fe^{3+} in $ZnWO_4$ is of interest for several reasons. First, the large zero-field splittings found in Fe^{3+}:$ZnWO_4$ make it possible to test the accuracy of the conventional spin Hamiltonian[1,2] as opposed to the spin Hamiltonian of Koster and Statz[3,4] over a large range of frequencies and magnetic fields. Indeed, Aisenberg, Statz, and Koster[5] have pointed out that deviations from the conventional spin Hamiltonian are more likely to be found at high magnetic fields in substances with large zero-field splittings. The large zero-field splittings are also convenient for testing the theories of Watanabe[6] and Pryce,[7] which predict, for S-state ions, the dependence of D on the axial crystal-field strength. Nicholson and Burns[8] have recently made a study of this dependence for Fe^{3+} substituted in several crystals but in no case was D large and negative as in $ZnWO_4$. The small linewidths found for Fe^{3+} in $ZnWO_4$ at low concentrations made it possible to observe and study the hyperfine structure of the Fe^{57} isotope in its natural abundance in iron (see Fig. 1).

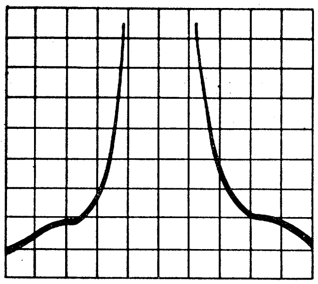

FIG. 1. Hyperfine structure of $(Fe^{57})^{3+}$ in naturally abundant Fe^{3+}: $ZnWO_4$.

The zinc tungstate crystals used in this work were pulled from a melt containing small amounts of Fe^{3+} [added as $Fe(NO_3)_3$] using the Czochralski technique as described by Van Uitert and Preziosi.[9] Li^+ ion was used to compensate for the difference in ionic charge of Zn^{2+} and Fe^{3+}. Crystals were aligned by cleaving them in the (010) plane as described in our previous publication[10] on Cr^{3+} in $ZnWO_4$. The y susceptibility axis was taken to be along the b crystallographic axis [perpendicular to the (010) cleavage plane] in agreement with Peter.[11] The position of the x and z susceptibility axes of Fe^{3+} were obtained from $ZnWO_4$ crystals containing both Cr^{3+} and Fe^{3+} using our earlier[10] crystallographic data for Cr^{3+} in $ZnWO_4$. The magnetic z axis was found to be rotated from the crystalline $+a$ axis toward the crystalline $+c$ axis by 45.2 ± 0.5 deg. The experimental apparatus has been described previously.[10] Measurements were carried out at room temperature except for the measurement of the hyperfine structure and the determination of the sign of B_2^0.

SPIN HAMILTONIAN PARAMETERS

As a preliminary step in analyzing the paramagnetic spectra of Fe^{3+} in $ZnWO_4$, the two zero-field splittings were determined. This was done by measuring, along the z magnetic axis, the resonant frequency versus magnetic field characteristics of the appropriate transitions down to zero magnetic field. The zero-field splittings were found to be 60.950 and 76.926 kMc/sec. These values were used to derive an approximate spin Hamiltonian (using only the B_2^0 and B_2^2 crystal-field terms and taking $g=2$).[11] Approximate eigenvalues obtained from this Hamiltonian were used to identify transitions at medium and high magnetic field intensities. The approximate values of $|B_2^0|$ and $|B_2^2|$ found from these zero-field splittings were 6.950 and 5.058 kMc/sec, respectively. These values are in reasonable

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[7] M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).
[8] W. J. Nicholson and G. Burns, Phys. Rev. **129**, 2490 (1963).
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[11] M. Peter, Phys. Rev. **113**, 801 (1959).

agreement with 7.02 and 5.15 kMc/sec found in the same way by Peter *et al.*[12] at liquid-helium temperatures.

In order to obtain more accurate spin Hamiltonian parameters, additional data were taken along the three susceptibility axes at magnetic fields up to about 21 kOe. These data were fitted to a spin Hamiltonian in susceptibility coordinates:

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+B_2^0O_2^0+B_2^2O_2^2+B_4^0O_4^0+B_4^2O_4^2+B_4^4O_4^4, \quad (1)$$

where the first term gives the interaction with the applied magnetic field and the remaining terms describe the effect of the crystalline electric field on the ground-state Zeeman levels. The g value was assumed isotropic. The coefficients B_n^m are parameters determined experimentally and each O_n^m is an operator function having the same transformation properties as the corresponding spherical harmonic. The operator forms of O_2^0, O_4^0 and O_4^4 are given explicitly by Baker *et al.*,[13] and the other two operators are[3]

$$O_2^2=\tfrac{1}{2}(S_+^2+S_-^2),$$

$$O_4^2=\tfrac{1}{2}[S_+^2(7S_z^2+14S_z-S(S+1)+9)+S_-^2(7S_z^2-14S_z-S(S+1)+9)].$$

The secular equation was solved numerically on a 7090 computer. An iterative process was used in which the Hamiltonian parameters were varied until the mean-square deviation between experimental and calculated data was reduced to a minimum. The spin Hamiltonian parameters are given in Table I and a comparison between experimental and calculated data in Table II.

The negative sign for B_2^0 was deduced from the relative intensities of the Kramer's doublets at 4.2 and 1.8°K. The parameter B_2^2 was chosen positive so that the y axis would lie along the monoclinic b axis.[10] Figure 1 shows the hyperfine structure of Fe^{57} in a $ZnWO_4$ crystal containing a low concentration of iron with isotopes in their natural abundance. Measurements were made at 1.5°K along the z axis at a frequency of 8896 Mc/sec. The separation between hyperfine components was 10.3±0.5 G, indicating $|A_z|=28.9\pm1.4$ Mc/sec. This value is close to the coupling constant found for Fe^{57} in[14] ZnO and[15] MgO.

The data listed in Table II indicate that the conventional spin Hamiltonian[1,2] given in Eq. (1) accounts for the observed transition frequencies to within our experimental accuracy which is limited largely by errors in magnetic-field measurements and in aligning the sample along the magnetic axes. Indeed, all the possible crystal-field terms consistant with the crystal symmetry (C_{2h}^4) of zinc tungstate are included in our spin Hamiltonian and only terms linear in magnetic field and third or fifth order in spin operators can be added (e.g., HO_3^0, HO_5^0, etc.[3]). Furthermore, there is no apparent increase in the deviations between calculated and observed transitions with magnetic field in Table II which would indicate the need for such terms. The same con-

TABLE I. Spin Hamiltonian parameters[a] for Fe^{3+} ion in $ZnWO_4$ at room temperature.

$g=2.0019$

$B_2^0=\frac{1}{3}D=-6.987$ kMc/sec

$B_2^2=E=+4.935$ kMc/sec

$B_4^0=+0.00326$ kMc/sec

$B_4^2=-0.00178$ kMc/sec

$B_4^4=-0.0173$ kMc/sec

[a] y axis along monoclinic b axis: z axis in the (010) plane rotated 45.2 ±0.5° from $+a$ toward $+c$ axis.

TABLE II. Observed and calculated transition frequencies for Fe^{3+} in $ZnWO_4$.

θ (deg)	φ (deg)	Magnetic Field (kOe)	Transition Freq. obs	(kMc/sec) calc	Deviation (kMc/sec)
0	0	0	60.950	60.991	+0.041
0	0	0	76.926	77.012	+0.086
0	0	12.332	70.823	70.837	+0.014
0	0	19.479	70.823	70.932	+0.109
90	0	5.929	70.783	70.755	−0.028
90	0	14.397	70.783	70.808	+0.025
0	0	12.967	73.2796	73.278	−0.002
90	90	18.423	70.104	70.146	+0.042
90	90	19.192	70.1009	70.069	−0.032
90	90	9.460	70.104	69.997	−0.107
0	0	1.289	8.767	8.771	+0.004
10	0	1.296	8.767	8.767	0.000
20	0	1.320	8.767	8.765	−0.002
30	0	1.360	8.767	8.762	−0.005
40	0	1.415	8.767	8.758	−0.009
45	0	1.449	8.767	8.761	−0.006
50	0	1.485	8.767	8.757	−0.010
60	0	1.564	8.767	8.757	−0.010
70	0	1.641	8.767	8.757	−0.010
80	0	1.701	8.767	8.761	−0.006
90	0	1.725	8.767	8.766	−0.001
0	0	5.433	56.018	56.020	+0.002
0	0	4.067	56.018	56.012	−0.006
0	0	2.038	56.018	56.012	−0.006
0	0	5.096	57.410	57.439	+0.029
0	0	4.169	57.410	57.406	−0.004
0	0	1.416	57.410	57.420	+0.010
0	0	0.477	59.728	59.732	+0.004
0	0	4.338	59.728	59.715	−0.013
0	0	4.547	59.728	59.740	+0.012
0	0	0.725	63.021	63.012	−0.009
0	0	3.740	63.021	63.046	+0.025
0	0	4.579	63.021	63.000	−0.021
0	0	3.267	64.922	64.931	+0.009
0	0	4.717	64.922	64.885	−0.037
0	0	1.371	64.922	64.919	−0.003
0	0	0.827	74.093	74.089	−0.004

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[14] W. M. Walsh, Jr., Bull. Am. Phys. Soc. **6**, 117 (1961); W. M. Walsh and L. W. Rupp, Jr., Phys. Rev. **126**, 952 (1962).

[15] E. S. Rosenvasser and G. Feher, Bull. Am. Phys. Soc. **6**, 117 (1961).

clusion regarding the adequacy of the conventional spin Hamiltonian has been reached by Symmons and Bogle[16] in the case of Fe^{3+} in Al_2O_3.

DISCUSSION

Trivalent iron has a $3d^5$ electron configuration for which the Hund ground term is $^6S_{5/2}$. The crystal field cannot lift this sixfold spin degeneracy. Starting with Van Vleck and Penney,[17] several workers[6,7,18–20] have shown that there are higher order interactions arising from combined crystal-field, spin-orbit, and spin-spin interactions which can lift the degeneracy and give rise to a zero-field splitting. Watanabe[6] has calculated the ground-state splitting for the Fe^{3+} ion in a nearly cubic field with a small axially-symmetric field superposed on it. For $D=3B_2^0$, Watanabe derives the expression,

$$D=-\frac{6S^2\Delta^2}{35P^2D'}+\frac{24\Delta'M'}{25E'}, \qquad (2)$$

where

$$\Delta=\tfrac{1}{4}(5/\pi)^{1/2}eA_2^0\langle 3d|r^2|3d\rangle$$

and

$$\Delta'=(5/\pi)^{1/2}eA_2^0\langle 3d|r^2|4s\rangle .$$

M' is an integral of the spin-spin interaction and P, D', and E' are the energies of the ^4P, ^4D, and $4s\ ^6D$ excited states. The first term on the right-hand side of Eq. (2) arises from a spin-orbit crystal-field perturbation of the form

$$\langle ^6S|W_{LS}|^4P\rangle\langle ^4P|V_{AX}|^4D\rangle\langle ^4D|V_{AX}|^4P\rangle\langle ^4P|W_{LS}|^6S\rangle ,$$

and the second term which was originally proposed by Pryce[7] is the result of a spin-spin: axial crystal-field perturbation,

$$\langle 3d^5\ ^6S|W_{SS}|3d^44s\,^6D\rangle\langle 3d^44s\,^6D|V_{AX}|3d^5\ ^6S\rangle .$$

More recently, Germanier *et al.*[21] have repeated this calculation of D using the above terms plus two additional terms linear in the axial field,

$$\langle ^6S|W_{LS}|^4P\rangle\langle ^4P|V_{AX}|^4D\rangle\langle ^4D|W_{LS}|^4P\rangle\langle ^4P|W_{LS}|^6S\rangle .$$

and

$$\langle ^6S|W_{SS}|^4D\rangle\langle ^4D|V_{AX}|^4P\rangle\langle ^4P|W_{LS}|^6S\rangle .$$

They obtain from their calculation the approximate value

$$D\approx -3.3\times10^{-23}A_2^0+6.9\times10^{-44}(A_2^0)^2, \qquad (3)$$

where conversion factors have been included in the numerical parameters so that D is in cm^{-1} and A_2^0 in V/m^2. An important point is that the positive sign of the quadratic term in Eq. (3) is opposite to that obtained by Watanabe from Eq. (2). In addition to the analytical expression in Eq. (3), Germanier *et al.* have derived a semiempirical relation analogous to Eq. (3) from pressure induced axial distortions of the electric field acting on Fe^{3+} in MgO, and point-charge calculations of A_2^0 for several other host lattices. The relation between D and A_2^0 determined in this fashion is

$$D=+3.5\times10^{-21}A_2^0-8.0\times10^{-42}(A_2^0)^2, \qquad (4)$$

where the units are identical to those in Eq. (3). The signs in Eq. (4) are opposite to those in Eq. (3) and the constants are two orders of magnitude larger indicating that a rather large discrepancy between theory and experiment still exists.

A direct experimental measurement of A_2^0 has never been made. Recently, however, Nicholson and Burns[8] have used the Mössbauer effect to measure the quadrupole splitting of Fe^{57} in several host lattices. Since the quadrupole coupling constant is related to the axial field parameter as

$$eqQ/h=(eQ/h)(1-\gamma_\infty)(5/\pi)^{1/2}A_2^0, \qquad (5)$$

A_2^0 can be measured if the antishielding factor γ_∞ and the quadrupole moment Q are known. In addition, if one assumes that Q and γ_∞ are constant for Fe^{3+} substituted in different host lattices, then a plot of D versus eqQ/h gives the dependence of D on A_2^0. The results of Nicholson and Burns had considerable scatter but tended to show that the sign of the quadratic term in A_2^0 was positive in opposition to the theoretical predictions of Watanabe [Eq. (2)]. This tentative conclusion of Nicholson and Burns regarding the sign of the (A_2^0) term depended mostly on the large positive value of $D(+0.678\ cm^{-1})$ found for Fe^{3+} in rutile. In contrast to rutile, Fe^{3+} in $ZnWO_4$ has a large negative value of $D(-0.699\ cm^{-1})$. It is, therefore, of interest to determine the sign and approximate magnitude of A_2^0 at the Fe^{3+} site in $ZnWO_4$ to help clarify the relation between A_2^0 and D.

In an effort to accomplish this, we have carried out a point charge calculation of A_2^0 on a 7090 computer. It is well known that the point-charge model must be used with some care.[22] It has, however, been used rather widely to obtain qualitative information about the crystal fields[23,24] and in some cases such as Ni^{2+} in[25] MgO has given satisfactory quantitative information. In order to determine the degree of convergence and the sensitivity to errors in atomic coordinates, a computer program was devised that made calculations over neutral

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[19] M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Letters 5, 145 (1960).

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[25] A. M. Germanier and R. Lacroix, Helv. Phys. Acta 34, 401 (1961).

TABLE III. X-ray data used in point-charge calculation.

2 Zinc	$\frac{1}{2}, Y_{\mathrm{Zn}}, \frac{1}{4}$ $\frac{1}{2}, 1-Y_{\mathrm{Zn}}, \frac{3}{4}$	(f) (f)
2 Tungsten	$0, Y_{\mathrm{W}}, \frac{1}{4}$ $0, 1-Y_{\mathrm{W}}, \frac{3}{4}$	(e) (e)
8 Oxygen $i=1,2$	X_i, Y_i, Z_i $-X_i, -Y_i, -Z_i$ $-X_i, Y_i, \frac{1}{2}-Z_i$ $X_i, Y_i, \frac{1}{2}+Z_i$	(g) (g) (g) (g)
$ZnWO_4$[a]	$a=4.68$ Å $b=5.73$ Å $c=4.95$ Å $\beta=90°30'$	
$NiWO_4$[b]	$a=4.60$ Å $b=5.73$ Å $c=4.95$ Å $\beta=90°5'$	
	$Y_{\mathrm{Ni}}=0.653$ $Y_{\mathrm{W}}=0.180$ $X_1=0.220$ $Y_1=0.110$ $Z_1=0.960$ $X_2=0.260$ $Y_2=0.380$ $Z_2=0.390$	

[a] E. K. Brock, Z. Physik Chem. **1B**, 409 (1928). E. K. Brock, Skrifter Norske Videnshaps-Akad Oslo. I. Mat Naturv. Kl, No. 8 (1929).
[b] R. O. Keeling, Acta. Cryst. **10**, 209 (1957).

shells of atoms out to a radius of 20 Å or about 3000 neighbors. The unit cell positions of the atoms used in the calculations are listed in Table III. The atomic positions were not available for $ZnWO_4$ so those for the isostructural compound $NiWO_4$ were used. This does not seem unreasonable since the major structural difference between $ZnWO_4$ and $NiWO_4$ is in the primitive translation "a" which differs by 0.08 Å. The unit cell dimensions for $NiWO_4$ and $ZnWO_4$ are also shown in Table III. A plot of A_2^0 and A_4^0 as a function of the logarithm of n, the total number of atoms in each successive neutral shell is shown in Figs. 2 and 3. It is clear from Fig. 2 that a nearest-neighbor or next-nearest-neighbor approximation is of questionable value for A_2^0 even assuming the applicability of the point charge model. For A_4^0 (Fig. 3) the convergence is much more rapid because of the r^{-5} dependence.

The six oxygens surrounding a zinc site come close to forming a regular octahedron. The field at the Zn site is thus predominantly cubic with a significant but smaller axial component. In order to determine the effect on A_2^0 of slight differences in the atomic coordinates between $NiWO_4$ and $ZnWO_4$, calculations were made varying the atomic coordinates by several percent. The results are shown in Table IV. While the variations tried are only a minute fraction of all the possible ones, they do indicate a considerable sensitivity of A_2^0 to small changes in oxygen coordinates. In no case was A_2^0 negative. A further point which suggests the qualitative validity of the point charge calculation is that it correctly predicts[10] for Cr^{3+} in $ZnWO_4$ the relative sign and magnitude of D/E.

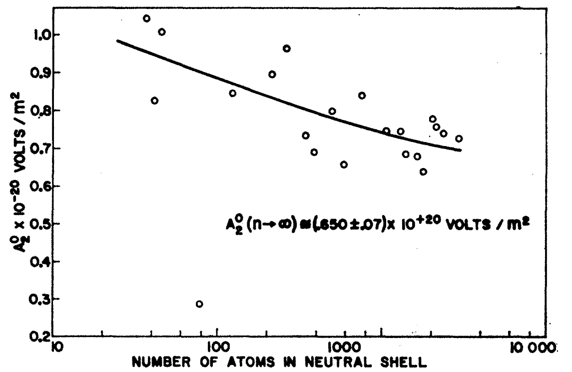

FIG. 2. Point-charge calculation of A_2^0 as a function of the number of atoms included in the calculation.

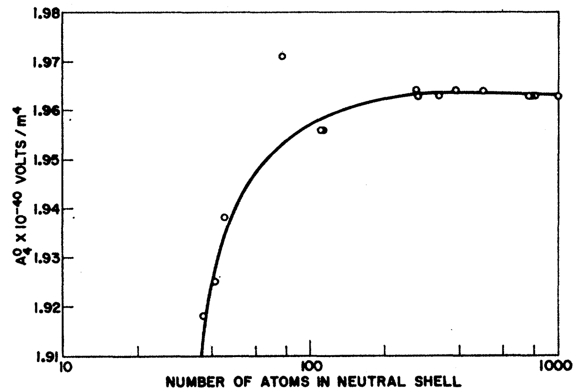

FIG. 3. Point charge calculation of A_4^0 as a function of the number of atoms included in the calculation.

The positive sign for the linear term in Eq. (4) seems reasonably well established since it is based on rather direct pressure experiments. If A_2^0 is positive in Fe^{3+}:$ZnWO_4$ as indicated by the point-charge calculation, then the quadratic term must be negative in order to account for the negative value of D. Attempts to use Eq. (4) to derive a value of A_2^0 for Fe^{3+} in $ZnWO_4$ lead to either $+5.9\times10^{20}$ or -1.5×10^{20} V/m². This lack of agreement between A_2^0 calculated by Eq. (4) and the point-charge model may be due to an inaccuracy of the quadratic coefficient in Eq. (4) which is itself based

TABLE IV. Sensitivity of point-charge calculation of A_2^0 to changes in atomic coordinates.

Changes in atomic coordinates[a]		A_2^0 in V/m²×10⁻²⁰
$\delta Y_{\mathrm{W}}=$	-0.02	$A_2^0=+0.52$
	-0.01	$+0.60$
	$+0.01$	$+0.85$
	$+0.02$	$+0.98$
$\delta Y_{\mathrm{Zn}}=$	-0.02	$+0.85$
	-0.01	$+0.75$
	$+0.01$	$+0.79$
	$+0.02$	$+0.91$
$\delta X_1=\delta Y_1=\delta Z_1=$	-0.02	$+0.03$
	-0.01	$+0.37$
	$+0.01$	$+1.07$
	$+0.02$	$+1.51$
$\delta X_2=\delta Y_2=\delta Z_2=$	-0.02	$+1.27$
	-0.01	$+1.01$
	$+0.01$	$+0.48$
	$+0.02$	$+0.56$

[a] Normalized to the unit cell dimensions.

on point-charge calculations of A_2^0 in several of host lattices were D for Fe^{3+} is known. Also, the recent work of Lyubimov *et al.*[26] has shown that higher multipole terms which have been neglected in the point-charge calculation can make sizable contributions to the electric field gradients in ionic crystals.

The g value of 2.0019 is slightly less than the free-ion value and is in excellent agreement with the value 2.0020 calculated by Wantanabe.[6] The positive sign of the cubic crystal-field splitting parameter $a=24B_4^4$ is also in agreement with the theoretical predictions of Watanabe[6] (remembering that O_4^4 changes sign on rotating 45° from the susceptibility axis system to the distorted cubic axis system).

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Theory of Absorption of Electromagnetic Radiation by Hopping in *n*-Type Silicon and Germanium

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The absorption of electromagnetic radiation at 0°K in the wavelength region from 100 to 800 μ and from 500 μ to 2.5 cm in n-type silicon and germanium, respectively, has been investigated. Concentrations of donors up to 2×10^{18} cm^{-3} in Si and 6×10^{16} cm^{-3} in Ge, and compensation ratios up to 0.2, were considered. The model used was that of photon-induced hopping of an electron between the ground states of the donors. The formula for the absorption coefficient is derived and numerical results are presented. The range of validity of our results is also discussed. Absorption coefficients of the order of 10^2 cm^{-1} in Si and 10^1 cm^{-1} in Ge were obtained.

INTRODUCTION

THE ac impurity hopping conduction has been studied, both experimentally and theoretically, up to the frequencies of the order of 10^9 cps.[1–4] The model used was that of phonon-induced hopping of a carrier from the neutral majority impurity center to the ionized one. Both Coulomb potential of the nearest ionized minority center and the external field were taken into account to obtain the energy differences for these transitions.

The purpose of the present work is to study another mechanism of hopping, namely, the photon-induced transitions and their effect on the absorption of electromagnetic radiation in n-type Si and Ge at 0°K. We are interested in the wavelength region from 100 to 800 μ and from 500 μ to 2.5 cm in Si and Ge, respectively. In these wavelength regions at 0°K other absorption mechanisms (lattice vibrations, excitations of neutral impurity centers, free carriers) are, in principle, absent. The occurrence of absorption induced by carriers generated by impact ionization of neutral impurities can be also avoided for low intensities of radiation.

Tanaka and Fan in their paper[4] proposed the photon-induced hopping for explanation of a part of their experimental results concerning the ac impurity conduction in p-type Si at wavelengths larger than 3 cm. Apart from the fact that we are interested in n-type materials, our approach is unapplicable to their case because we consider the electron-phonon interaction to be weak. This is not true, however, if the relaxation energy of the lattice deformed by interaction with the localized carrier is larger than the energy difference $\hbar\omega$ for transition, which is the case in p-type Si at wavelengths larger than about 2 mm.[5,5a]

In the following we shall obtain first the electron states in the two-center Hamiltonian in a nondeformed crystal lattice with an additional electrostatic field. Then we obtain the transition rate for photon-induced

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[1] M. Pollak and T. H. Geballe, Phys. Rev. **122**, 1742 (1961).

[2] M. Pollak, Phys. Rev. **133**, A564 (1964).

[3] S. Golin, Phys. Rev. **132**, 178 (1963).

[4] S. Tanaka and H. Y. Fan, Phys. Rev. **132**, 1516 (1963).

[5] J. Mycielski, Phys. Rev. **125**, 1975 (1962).

[5a] *Note added in proof.* Recently the idea of Tanaka and Fan was developed by S. Tanaka, M. Kobayashi, E. Hanamura, and K. Uchinokura [Phys. Rev. **134**, A256 (1964)] in a way similar to ours. They do not investigate, however, our case $kT\ll\hbar\omega$ and they use several approximations absent in our treatment. They compare their results with the experimental data for Si at 9 Gc/sec and that seems to be unjustified (see above).