the potential and electric dipole operators, respectively, have been suppressed in the above equations, but they are used in the text in the numerical evaluation of the oscillator strengths.

[1]K. H. Wickersheim and R. A. Lefever, J. Chem. Phys. 36, 844 (1962).

[2]D. L. Wood and J. P. Remeika, J. Appl. Phys. 38, 1038 (1967).

[3]A. J. Kurtzig, R. Wolfe, R. C. Lecraw, and J. W. Nielsen, Appl. Phys. Letters 14, 350 (1969).

[4]A. J. Kurtzig and H. J. Guggenheim, Appl. Phys. Letters 16, 43 (1970).

[5]F. J. Kahn, P. S. Pershan, and J. P. Remeika, Phys. Rev. 186, 891 (1969).

[6]N. T. Melamed, P. C. Viccaro, J. O. Artman, and F. De S. Barros, J. Luminescence 1/2, 348 (1970); and private communication.

[7]R. G. Wyckoff, *Crystal Structure* (Interscience, New York, 1948), Vol. II.

[8]D. S. McClure, J. Chem. Phys. 36, 2757 (1962). This reference summarizes many useful details concerning the optical absorption of transition-metal ions in Al_2O_3.

[9]J. J. Krebs, Phys. Rev. 135, A396 (1964).

[10]V. J. Folen, Phys. Rev. 125, 1581 (1962); J. W. Nielsen and E. F. Dearborn, J. Phys. Chem. Solids 5, 202 (1958).

[11]K. Moorjani and N. McAvoy, Phys. Rev. 132, 504 (1963).

[12]M. G. Townsend, Solid State Commun. 6, 81 (1968).

[13]G. Lehmann and H. Harder, Am. Mineralogist 55, 98 (1970).

[14]Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 753 (1954).

[15]R. Stevenson, *Multiplet Structure of Atoms and Molecules* (Saunders, Philadelphia, Pa., 1965).

[16]W. Low and G. Rosengarten, J. Mol. Spectry. 12, 319 (1964).

[17]K. A. Schroeder, J. Chem. Phys. 37, 1587 (1962).

[18]D. H. Goode, J. Chem. Phys. 43, 2830 (1965).

[19]Y. Shadmi, quoted in Ref. 16.

[20]S. Geschwind and J. P. Remeika, J. Appl. Phys. 33, 370 (1962).

[21]R. Englman, Mol. Phys. 3, 183 (1961).

[22]C. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circ. No. 467 (U. S. GPO, Washington, D. C., 1952), Vol. II.

[23]A. M. Clogston, J. Appl. Phys. 31, 198S (1960); H. H. Tippins, Phys. Rev. B 1, 126 (1970).

[24]A. L. Schawlow, D. L. Wood, and A. M. Clogston, Phys. Rev. Letters 3, 271 (1959).

[25]J. Ferguson, H. J. Guggenheim, and Y. Tanabe, J. Appl. Phys. 36, 1046 (1965).

[26]J. Ferguson, H. J. Guggenheim, and Y. Tanabe, Phys. Rev. Letters 14, 737 (1965).

[27]J. Ferguson, H. J. Guggenheim, and Y. Tanabe, J. Phys. Soc. Japan 21, 692 (1966).

[28]J. Ferguson, Solid State Commun. 5, 773 (1967); Australian J. Chem. 21, 307 (1968).

[29]W. Trifthäuser and D. Schroeer, Phys. Rev. 187, 491 (1969).

[30]Crystals supplied by C. S. Sahagian, Air Force Cambridge Research Laboratories, Bedford, Mass.

[31]D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1959), Vol. 9.

[32]J. O. Artman and J. C. Murphy, Phys. Rev. 135, A1622 (1964).

[33]S. Koide and M. H. L. Pryce, Phil. Mag. 3, 607 (1958).

[34]A. S. Barker, Jr., Phys. Rev. 132, 1474 (1963).

[35]S. P. S. Porto and R. S. Krishnan, J. Chem. Phys. 47, 1009 (1967).

[36]I. Adams, J. W. Nielsen, and M. S. Story, J. Appl. Phys. 37, 832 (1966).

[37]Y. Tanabe and H. Kamimura, J. Phys. Soc. Japan 13, 394 (1958).

[38]J. S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups* (Prentice-Hall, Englewood Cliffs, N. J., 1962).

PHYSICAL REVIEW B VOLUME 4, NUMBER 3 1 AUGUST 1971

Theoretical Estimates of the Isotropic hfs Constants of Small Ions in the Neighborhood of a Massive Ion with an Unpaired Electron*

Supriya Ray

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 15 December 1970)

Estimates of the isotropic part of the hyperfine constants of several small ions in the presence of a massive ion with an unpaired electron, by the use of a simple method, are reported here. Calculated results are found to be quite essential in the understanding of isotropic hfs observed in similar systems in the crystal environment.

I. INTRODUCTION

Considerable attention has been focused in recent years on the use of paramagnetic-resonance spectra and optical spectra to detect impurity centers in x-irradiated α (low)-quartz.[1,2] As a substituent for silicon in the quartz lattice, germanium (as well as a few other elements, including aluminum,

iron, and titanium) is believed to enter as a Ge^{4+} ion, becoming Ge^{3+} after trapping an electron.[1,3-5] The electron is made available on x irradiation. There are also small alkali-metal ions (Li^+), protons (H^+), and H^- ions, which occupy various interstitial sites, creating stable charge-compensated paramagnetic centers. For germanium, numerous alkali-containing centers are known, but alkali-hydrogen-compensating centers ($GeHLi_2$) have been the most recent findings.[6]

Experimental observations of g values, and isotropic and anisotropic hfs of various types clearly identify these impurity centers in the lattice, but provide no definite evidence regarding their locations, relative positions, or geometry. Several phenomenological attempts have been made to obtain the geometry of the centers, but in no case has common agreement been reached.[3,5,6] The main difficulty is the complexity of the problem itself. An *ab initio* theoretical calculation at this time might prove to be very useful and stimulating to experimentalists, but it would be a very costly affair while the geometry of these centers is still in doubt. Therefore, in the present author's opinion, calculations of a simple nature would provide valuable clues to the whole problem.

Let us summarize the main features of the problem: First, each paramagnetic-impurity center is an effective-nuclear-charge center, which gives rise to a sizable attractive potential. The unpaired electron, which is liberated during x irradiation and trapped at the germanium center,[3,5,6] probably moves around and spends time at those interstitial-impurity centers where there are appreciable attractive potentials, provided there are no barriers to the electronic motion to the center. Second, the ligand orbitals centered at the four nearest-neighbor oxygens in the lattice (in quartz, silicon is surrounded by four oxygens at tetrahedral configurations) play several important roles. They produce an attractive polarization field at some centers and a Pauli repulsive force at others (where ligand orbitals act as barriers). Besides these two major features, there are several secondary effects arising from the interaction of the core electrons, at various impurity centers, with the unpaired electron and the ligand electrons. One of the most important of these effects is the core-polarization effect.[7] All these features simultaneously influence the system and, consequently, the size of the unpaired electronic spin density at the nucleus of each impurity center is appreciably altered. Thus, the observed isotropic hfs constant at each impurity center will be different from that of the corresponding free ion. Therefore, the determination of the isotropic hfs constant alone may provide sufficient information to visualize the geometry of the problem.

Again, not all the features will be equally effective at all the centers. At some centers the potential produced by the effective charge at the center is dominant. On the other hand, there are centers where the ligand orbital effects are equally important. The third feature, the core polarization, is of secondary importance here. The core-polarization contribution to the isotropic hfs becomes dominant only in cases where there are no unpaired electronic spin densities at the nucleus.[7] In the present calculation, we have decided to determine only the contribution arising from the potential at the center. In this way, we will be able to label some centers according to whether the contribution of ligand orbital effects is important or not. This may provide us with important clues as to the geometry of the impurity centers.

To make the problem tractable, we have simplified it still further. Instead of dealing with all the interstitial impurities surrounding the substitutional impurity Ge^{4+} ion in one picture, we treat each interstitial impurity ion individually in the presence of the substitutional Ge^{4+} ion, separated by a reasonable internuclear distance. Then the problem becomes a simple two-centered diatomic-type problem. An electron sees two different potentials at adjacent positions and is under the influence of both. Our problem is to determine these two potentials and their interaction with the electron. When the interaction Hamiltonian, comprising the kinetic-energy part and the potential-energy part, is found, a Schrödinger equation is solved get to the wave function for the electron. The rest is then the usual evaluation of the spin density at the nucleus of the interstitial impurity, and the corresponding isotropic hfs constant.

Nevertheless, the problem to be solved is really a many-electron problem. Since we neglect the interaction of core electrons of Ge^{4+} with the unpaired electron, we can adopt some sort of pseudopotential approach[8] for determining the potential at the germanium ion. We confined our calculations to the cases of $(Ge^{4+}\text{-}H^+)e^-$, $(Ge^{4+}\text{-}H^-)e^-$, and $(Ge^{4+}\text{-}Li^+)e^-$ ion pairs. The same internuclear separation is used for each case, because our calculation is by no means an attempt to attain an accurate quantitative agreement.

Section II outlines the essential features of the present method. Section III contains the calculation and results for each pair and in Sec. IV, we discuss our results with reference to the actual problem.

II. METHOD OF CALCULATION

As already mentioned, our method is simple, designed mainly to illuminate some vital aspects, so that they may provide clues to stimulate further experimental and theoretical investigations on the actual problem. Therefore, our method, quan-

titatively speaking, is an approximate attempt not on the actual problem, but rather on the skeleton, and may suffer from oversimplification.

The potential that the unpaired electron sees at the germanium ion is chosen, for the sake of computational simplicity, to be the average effective potential that can be obtained by using some sort of pseudopotential approach. Thus, the main crudeness lies in our method of determining this potential. But the potential that the electron experiences at the interstitial ionic center is calculated in the spirit of the Hartree-Fock calculation.

The Hamiltonian for the unpaired electron interacting with two potentials, centered, respectively, at the germanium ion and the interstitial ion, is given by

$$H = -\tfrac{1}{2}\nabla_1^2 + V_{\mathrm{Ge}} - \frac{Z_s}{r_{s1}} + \sum_{i=1}^{n} \frac{1}{r_{1i}} , \tag{1}$$

where V_{Ge} refers to the effective potential that the unpaired electron experiences at the germanium center.

The third and fourth terms of Eq. (1) represent the interaction of the unpaired electron with the nucleus and n electrons, respectively, of the Sth interstitial ion considered.

A determinantal wave function

$$\Psi = \det[\phi_1\alpha, \ldots, \phi_{n/2}(\alpha \text{ or } \beta), \quad \varphi(\alpha \text{ or } \beta)] \tag{2}$$

is built from orbitals $\phi_1\alpha, \ldots, \phi_{n/2}(\alpha \text{ or } \beta)$ representing n electrons of the Sth interstitial ion and $\varphi(\alpha \text{ or } \beta)$, representing the unpaired electron. Ψ corresponds to the eigenfunction of the Hamiltonian operator H given in Eq. (1), and the energy eigenvalue for the said electron is given by

$$E = \langle\varphi|\,(-\tfrac{1}{2}\nabla_1^2)\,|\varphi\rangle + \langle\varphi|\,V_{\mathrm{Ge}}\,|\varphi\rangle - Z_s\langle\varphi|\,r_{s1}^{-1}\,|\varphi\rangle + \sum_{i=1}^{n/2} [2\langle\varphi(1)\phi_i(2)|\,r_{12}^{-1}\,|\varphi(1)\phi_i(2)\rangle - \langle\varphi(1)\phi_i(2)|\,r_{12}^{-1}\,|\varphi(2)\phi_i(1)\rangle] . \tag{3}$$

However, φ is not known in this case. Applying[8] a variational principle, φ can be determined easily, provided that V_{Ge} is known. First, we must choose an appropriate variational function for φ. In doing so, we take into account the following: When the unpaired electron comes entirely under the influence of the field of the germanium ion, the Ge^{4+} ion temporarily becomes a Ge^{3+} ion, hence the unpaired electron would primarily occupy the state of a 4s orbital[9] of a Ge^{3+} ion. Similarly, in the other extreme, the electron comes entirely under the influence of the Sth interstitial ion which, after accommodating the electron in its appropriate orbital, becomes an ion with a higher electron content or temporarily a neutral atom. Thus, the most logical choice for φ would be a linear combination of those orbitals that the electron would occupy in the two extreme cases. Thus, the chosen φ is

$$\varphi = A\,\phi_{4s}^{\mathrm{Ge}} + B\,\phi_{(n/2+1)s}^{S} , \tag{4}$$

where the coefficients A and B are to be determined as variational parameters. The next thing to resolve is the problem of not knowing V_{Ge}. The approximate method that we have chosen is as follows: If we substitute the expression of φ given in Eq. (4) into the first three terms of Eq. (3), we obtain some terms involving V_{Ge}:

$$\langle\phi_{4s}^{\mathrm{Ge}}|\,(-\tfrac{1}{2}\nabla^2 + V_{\mathrm{Ge}})\,|\phi_{4s}^{\mathrm{Ge}}\rangle = \epsilon_{4s}^{\mathrm{Ge}} , \tag{5}$$

$$\langle\phi_{(n/2+1)s}^{S}|\,(-\tfrac{1}{2}\nabla^2 + V_{\mathrm{Ge}})\,|\phi_{4s}^{\mathrm{Ge}}\rangle = \epsilon_{4s}^{\mathrm{Ge}}\langle\phi_{(n/2+1)s}^{S}|\,\phi_{4s}^{\mathrm{Ge}}\rangle , \tag{6}$$

and

$$\langle\phi_{(n/2+1)s}^{S}(1)|\,V_{\mathrm{Ge}}\,|\phi_{(n/2+1)s}^{S}(1)\rangle = ? . \tag{7}$$

$\epsilon_{4s}^{\mathrm{Ge}}$ is the eigenvalue of the 4s orbital[9] of the Ge^{3+} ion, and $\langle\phi_{(n/2+1)s}^{S}|\,\phi_{4s}^{\mathrm{Ge}}\rangle$ is the overlap integral. They can both be easily found. Thus, the terms given in Eqs. (5) and (6) involving V_{Ge} can be determined without even knowing V_{Ge}. But the term expressed by Eq. (7) cannot be determined without knowing V_{Ge}. The function $\phi_{(n/2+1)s}^{S}$ must be localized around the Sth interstitial ion, and in that region V_{Ge} would have its asymptotic form, $Z_{\mathrm{eff}}^{\mathrm{Ge}}/r_{\mathrm{Ge}\,1}$, where $Z_{\mathrm{eff}}^{\mathrm{Ge}}$ is the effective nuclear charge of Ge^{3+}. After taking into account the screening effect of the electron, $Z_{\mathrm{eff}}^{\mathrm{Ge}}$ is taken to be 3.15 in this case. Thus, for Eq. (7) we take the approximate form

$$\langle\phi_{(n/2+1)s}^{S}(1)|\,V_{\mathrm{Ge}}\,|\phi_{(n/2+1)s}^{S}(1)\rangle \cong -Z_{\mathrm{eff}}^{\mathrm{Ge}}\langle\phi_{(n/2+1)s}^{S}(1)|\,\frac{1}{r_{\mathrm{Ge}\,1}}\,|\phi_{(n/2+1)s}^{S}(1)\rangle . \tag{8}$$

The isotropic hfs constant at the nucleus of the Sth interstitial ion, arising from the unpaired electronic spin density $\varphi^2(r_{S1}=0)$, via the Fermi contact term,[10] is given by

$$A_{\mathrm{hfs}}^{S} = \tfrac{16}{3}\pi\mu_S\mu_e a_0^{-3} m_s/I_S J h x\varphi^2 \qquad (r_{S1}=0) , \tag{9}$$

where μ_S is the nuclear magnetic moment of the Sth interstitial ion, μ_e the magnetic moment of the electron, m_s the magnetic component of the electronic spin, and I_S the corresponding nuclear spin of the S interstitial ion. J refers to the total angular momentum, a_0 is the Bohr radius, and h is Planck's constant.

III. CALCULATION AND RESULTS FOR ION PAIRS

In this section we give the essential steps of the calculation and the results of specific cases follow-

TABLE I. ϕ_{4s}^{Ge} wave function[a]: linear combination of ten basis functions X_{nlm}.

n	l	m	ζ	Coefficients
1	0	0	30.754	−0.03268
1	0	0	36.3802	−0.00090
2	0	0	26.6899	−0.02049
2	0	0	13.9652	0.11818
3	0	0	12.73	0.08110
3	0	0	7.80673	−0.18003
3	0	0	5.21033	−0.21692
4	0	0	2.9869	0.40064
4	0	0	1.93414	0.63445
4	0	0	1.28343	0.08065

[a]*Tables of Atomic Functions*, edited by E. Clementi (IBM Corp., San Jose, California, 1965).

ing the method described in Sec. III. The $(Ge^{4+}\text{-}H^{+})e^{-}$ ion pair is taken first, followed by $(Ge^{4+}\text{-}H^{-})e^{-}$ and $(Ge^{4+}\text{-}Li^{+})e^{-}$. We have chosen the internuclear separation of 5 bohr in each case. All the two-centered one-electron and two-electron integrals are computed accurately by using the diatomic-molecular-program package, called BISON.[11]

A. $(Ge^{4+}\text{-}H^{+})e^{-}$ Ion Pair

There is no interstitial core electron in this case, because a proton (H^{+}) is the 5th interstitial ion. Therefore, only the first three terms are retained in Eq. (3), i.e.,

$$E=\langle\varphi|\,(-\tfrac{1}{2}\nabla_1^{2}-r_{H^{+}1}^{-1}+V_{Ge})|\,\varphi\rangle\ . \tag{10}$$

When the electron comes under the influence of the H^{+} ion, which temporarily becomes an H atom, the electron occupies the 1s orbital of the H atom. Thus, the choice for the variational function φ in this case is given by

$$\varphi=A\phi_{4s}^{Ge}+B\phi_{1s}^{H^{+}}\ . \tag{11}$$

After carrying out the variational calculation with the computed values of

$$\begin{aligned}
&\langle\phi_{1s}^{H^{+}}|\,(-\tfrac{1}{2}\nabla^{2}-r_{H1}^{-1})|\,\phi_{1s}^{H^{+}}\rangle=\epsilon_{1s}^{H}=-0.5\ \text{a.u.},\\
&\langle\phi_{4s}^{Ge}|\,(-\tfrac{1}{2}\nabla^{2}+V_{Ge})|\,\phi_{4s}^{Ge}\rangle=\epsilon_{4s}^{Ge}=-0.8442\ \text{a.u.},\\
&\langle\phi_{1s}^{H^{+}}|\,\phi_{4s}^{Ge}\rangle=0.12303\ ,\\
&\langle\phi_{1s}^{H^{+}}|\,r_{Ge1}^{-1}|\,\phi_{1s}^{H^{+}}\rangle=0.1999\ ,
\end{aligned} \tag{12}$$

we find the variational coefficients $A=-0.9981$, and $B=0.2575$. Then the calculated φ is

$$\varphi=0.2575\phi_{1s}^{H^{+}}-0.9981\phi_{4s}^{Ge}\ . \tag{13}$$

ϕ_{4s}^{Ge} is a linear combination of ten basis functions of the form

$$X_{nlm}=[(2\zeta)^{n+1/2}/(2n!)^{1/2}]r^{n-1}e^{-\zeta r}Y_{lm}\ . \tag{14}$$

In Table I, the exponents, coefficients, etc., are given. The calculated energy E is −1.02999 a.u. From Eq. (13) we evaluate

$$\varphi^{2}(r_{H1}=0,\ r_{Ge1}=5\ \text{bohr})=0.01974\ ,$$

which is substituted in Eq. (9) to obtain

$$\begin{aligned}
A_{hfs}^{H^{+}}&=4.4644\times0.01974\times10^{9}\ \text{Hz}\\
&=88.14\ \text{MHz}\ .
\end{aligned}$$

B. $(Ge^{4+}\text{-}H^{-})e^{-}$ Ion Pairs

The H^{-} is a stable ion, containing two electrons which occupy the spin-up and spin-down states of the core orbital. When the unpaired electron enters into the sphere of the H^{-} ion, it temporarily becomes a H^{2-} ion (unstable). The determinantal wave function Ψ is given by

$$\Psi=\det(\phi_1\alpha,\ \phi_1\beta,\ \varphi\alpha)\ , \tag{15}$$

and the energy functional is

$$\begin{aligned}
E=&\langle\varphi|\,(-\tfrac{1}{2}\nabla_1^{2}-r_{H^{-}1}^{-1}+V_{Ge})|\,\varphi\rangle\\
&+2\langle\phi_1(1)\varphi(2)|\,r_{12}^{-1}|\,\phi_1(1)\varphi(2)\rangle\\
&-\langle\phi_1(1)\varphi(2)|\,r_{12}^{-1}|\,\phi_1(2)\varphi(1)\rangle\ ,
\end{aligned} \tag{16}$$

where

$$\begin{aligned}
\phi_1=&\,0.51076X_{100}(1.0)+0.17025X_{100}(0.5)\\
&+0.0454X_{200}(0.5)
\end{aligned} \tag{17}$$

is a linear combination of three basis functions and is predetermined for H^{-}. The values of the ζ's are placed in parentheses. The choice for the φ is here given by

$$\varphi=A_1X_{100}(1.0)+A_2X_{100}(0.5)+A_3X_{200}(0.5)+B\phi_{4s}^{Ge}\ . \tag{18}$$

In order to vary the energy functional E, given in Eq. (16), with respect to A_1, A_2, A_3, and B, we first evaluate the one-electron and two-electron molecular integrals involving $X_{100}(1.0)$, $X_{100}(0.5)$, $X_{200}(0.5)$, and ϕ_{4s}^{Ge}. In particular, the one-electron integrals involving V_{Ge} are evaluated according to the approximate prescription described in Eqs. (5)–(8). The coefficients A_1, A_2, A_3, and B, determined as variational parameters, are −0.5727, 0.6945, −0.5387, and 1.0171, respectively. The calculated total energy $\langle\Psi|H|\Psi\rangle$ is found to be −0.12398 a.u. We finally calculate $\varphi^{2}(r_{H^{-}1}=0,\ r_{Ge}=5\ \text{bohr})$ by substituting the calculated values in Eq. (18):

$$\varphi^{2}(r_{H^{-}1}=0,\ r_{Ge}=5\ \text{bohr})=0.03333\ , \tag{19}$$

which is substituted in Eq. (9) along with other constant quantities, to yield a hfs constant $A_{hfs}^{H^{-}}$ of 148.77 MHz.

C. $(Ge^{4+}\text{-}Li^{+})e^{-}$ Ion Pair

Accepting an additional electron, the Li^{+} ion becomes a neutral Li atom. This is a three-electron system, exactly like the previous one. In the determinantal wave function

$$\Psi = \det(\phi_1\alpha,\ \phi_1\beta,\ \varphi)\ , \tag{20}$$

ϕ_1 is taken as the core orbital of the Li atom and is expressed as a linear combination of four basis functions:

$$\phi_1 = 0.11192X_{100}(4.69) + 0.8820X_{100}(2.483) + 0.02147X_{100}(1.68) + 0.00051X_{200}(0.672)\ , \tag{21}$$

where the values of ζ are given in parentheses. The variational function φ is again chosen to be a linear combination of the four basis functions in ϕ_1 and ϕ_{4s}^{Ge}. Thus, we have

$$\varphi = A_1X_{100}(4.69) + A_2X_{100}(2.483) + A_3X_{100}(1.648) + A_4X_{200}(0.672) + B\phi_{4s}^{Ge}\ . \tag{22}$$

The expression of the energy functional E is the same as expressed by Eq. (16). A similar variational procedure is repeated to determine A_1, A_2, A_3, A_4, and B, which are found to be -0.01321, -0.05257, -0.07954, 0.64173, and 0.61238, respectively. $\langle\Psi|H|\Psi\rangle$, the total energy, is -6.7779 a.u. Next we evaluate $\varphi^2(r_{Li^{+}1}=0,\ r_{Ge}=5\ \text{bohr})$, obtaining

$$\varphi^2(r_{Li^{+}1}=0,\ r_{Ge}=5\ \text{bohr}) = 0.08148\ .$$

The calculated hfs constant at Li^{+} is found to be

$$A_{hfs}^{Li^{+}} = 141.38\ \text{MHz}\ .$$

IV. DISCUSSION OF RESULTS

As already mentioned, the hyperfine constants, calculated in Sec. III for the three ion pairs, do not, in the quantitative sense, correspond to the actual hyperfine constants observed at similar interstitial impurity centers in an x-irradiated, germanium-doped, quartz crystal (germanium is the substitutional impurity). But the physical picture and concepts, under which these skeletal calculations have been carried out, bear some resemblance to the actual problem. Comparing our calculated values with the actual experimental observations, we somewhat surprisingly find that, by using a rough estimate for V_{Ge} and a reasonable choice of the internuclear separation, our results in the case of the H^{+} ion and the H^{-} ion show very good relative agreement.[6] These indicate that the H^{+} or H^{-} interstitial ions are situated in unique positions in the lattice where the ligand orbitals have practically no interfering influence. On the other hand, the calculated result for the Li^{+} ion is quite large compared to the experimental value, which seems to indicate that the oxygen ligand orbitals have strong interfering effects on the Li^{+} impurity center so as to reduce greatly the unpaired electron spin density at the Li^{+} nucleus. This means that the interstitial Li^{+} ion occupies a unique position in the lattice where the admixture of ligand orbitals with that of the excess electron leads to a small electronic spin density at the Li nucleus. This information, combined with the lattice configuration, and the charge-density mapping of ligand electrons, would be sufficient to suggest a geometry of the impurity centers. Further theoretical and experimental investigations would be necessary to establish any conclusion. At this point, in the light of our calculations, we would only hope to stimulate such investigations.

It is worth noting that the spin density at the H^{-} ion is almost double that at the H^{+} ion, although one would anticipate the reverse. Therefore, some physical explanation is needed. Considering the relative electron affinity, one would agree that, of the three ions, Ge^{+4} has the strongest and H^{-} the weakest electron affinity. Naturally, the unpaired electron spends a relatively longer time in Ge^{+4} than in the H^{+} ion. But in the case of the H^{-} ion, the physical picture is different. The two electrons, which are initially bound to the H^{-} ion, become quite diffused over higher states in the presence of a massive positive ion and a third electron, eventually leading to a larger value for the unpaired spin density.

The calculations need to be repeated for several internuclear separations in order to reveal the temperature dependence of the results.

ACKNOWLEDGMENTS

The author would like to express his sincere thanks to Dr. G. Das for valuable discussions. He also expresses his gratitude to Dr. J. A. Weil for suggesting this calculation and for communicating the experimental results prior to their publication.

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] J. H. E. Griffith, J. Owen, and I. M. Ward, Nature 173, 439 (1954).

[2] J. H. E. Griffith, J. Owen, and I. M. Ward, in Proceedings of the Bristol Conference on Defects in Crystalline Solids, London Physical Society, 1954 (unpublished); M. C. M. O'Brian and M. H. L. Pryce, *ibid.*; M. C. M. O'Brien, Proc. Phys. Soc. (London) A231, 404 (1955); E. H. Jacobsen, N. S. Shiren, and E. B. Tucker, Phys. Rev. Letters 3, 81 (1959); R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. 119, 1204 (1960); F. Laves, P. Schindler, and H. E. Weaver, Nature 48, 714 (1961); J. Mackey, J. Chem. Phys. 39, 74 (1963); Bull. Am.

Phys. Soc. 7, 187 (1962); P. H. Carr and M. W. P. Strandberg, J. Phys. Chem. Solids 23, 923 (1962); A. L. Taylor and G. W. Farrell, Can. J. Phys. 42, 595 (1964); H. E. Weaver and P. Schindler, Nature 51, 82 (1964); S. T. Wang and G. W. Farrell, Can. J. Phys. 43, 1919 (1965); Kh. I. Zil'bershtein, V. A. Ioffe, and Yu. F. Fedorov, Kristallografiya 10, 727 (1965) [Sov. Phys. Crist. 10, 607 (1966)]; M. F. Lewis, H. M. Rosenberg, and J. K. Wigmore, Phys. Status Solidi 15, 317 (1966); R. A. Weeks, J. Am. Chem. Soc. 53, 176 (1970); R. Schandt and J. Schneider, Physik Kondensierten Materie 11, 19 (1970); J. H. Mackey, J. W. Boss, and D. E. Wood, J. Magnetic Res. 3, 44 (1970).

[3]J. H. Anderson and J. A. Weil, J. Chem. Phys. 31, 427 (1959); Bull. Am. Phys. Soc. 3, 135 (1958); 4, 284 (1959); 4, 416 (1959); Y. Haven, A. Katz, and J. S. Van Wieringen, Philips Res. Rept. 21, 446 (1966); in *Proceedings of the Eleventh Colloque Ampère* (North-Holland, Amsterdam, 1963), p. 403; Verres Refractaires 12, 191 (1958), F. J. Fiegl and J. H. Anderson, J. Phys. Chem. Solids 31, 575 (1970); Bull. Am. Phys. Soc. 9, 654 (1964); J. A. Weil and J. H. Anderson, J. Chem. Phys. 35, 1410 (1961).

[4]D. R. Hutton, Phys. Letters 12, 310 (1964); T. I. Barry and W. J. Moore, Science 144, 289 (1964); T. I. Barry, P. McNamara, and W. J. Moore, J. Chem. Phys. 42, 2599 (1965); G. Lehmann and W. J. Moore, *ibid.* 44, 1741 (1966); L. M. Matarrese, J. S. Wells, and R. L. Peterson, *ibid.* 50, 2350 (1969); Bull. Am. Phys. Soc. 9, 502 (1964); Natl. Bur. Std. (U. S.) Tech. Note 372, 1969 (unpublished); A. R. Cook and L. M. Matarrese, J. Chem. Phys. 50, 2361 (1969).

[5]P. M. Wright, J. A. Weil, T. Buch, and J. H. Anderson, Nature 197, 246 (1963); H. Rinneberg and J. A. Weil (unpublished).

[6]J. A. Weil, J. Chem. Phys. (to be published).

[7]M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) 73, 811 (1957); V. Heine, Czech. J. Phys. B13, 619 (1963); Phys. Rev. 107, 1002 (1957); D. A. Goodings, *ibid.* 123, 1706 (1961); T. P. Das and A. Mukhenji, J. Chem. Phys. 33, 1808 (1960).

[8]J. D. Weeks, A. Hazi, and S. A. Rice, Advan. Chem. Phys. XVI, 283 (1969).

[9]The 4*s* orbital of the Ge^{1+} ion is used in our calculation, since our calculation is approximate.

[10]E. Fermi, Z. Physik 60, 320 (1930).

[11]Arnold C. Wahl, P. J. Bertoncini, K. Kaiser, and Robert H. Land, AEC Research and Development Report No. ANL-7271 (unpublished).

PHYSICAL REVIEW B VOLUME 4, NUMBER 3 1 AUGUST 1971

Hyperfine Interactions of ^{57}Fe in Fe_3C†

M. Ron
Department of Materials Engineering, Technion—Israel Institute of Technology, Haifa, Israel

and

Z. Mathalone*
Department of Physics, Technion—Israel Institute of Technology, Haifa, Israel

(Received 4 March 1971)

The absence of the quadrupole interaction from the room-temperature spectrum of Fe_3C is shown to be only apparent. The spectrum was unfolded into two components in accordance with the two known structural sites, *G* (general) and *S* (special). The electric field gradient is found to be axially symmetric at each site. The quadrupole interaction is found to be 0.32 mm/sec for the *G* site and −0.58 mm/sec for the less-symmetric *S* site. The angles θ between the magnetic field $\vec{H}$ and the electric field gradient V_{zz} were found to be 50° and −50° for *G* and *S*, respectively. The hyperfine fields are found to be $H_G = 205$ kOe and $H_S = 207$ kOe. No difference in the isomer shift could be observed. The only indications of two sites in the room-temperature spectrum are the broadening (and therefore shortening) of the $+\frac{3}{2} \rightarrow +\frac{1}{2}$ transition line (sixth line), and a smaller broadening of the $-\frac{1}{2} \rightarrow -\frac{1}{2}$ transition line (second line).

INTRODUCTION

The χ-iron carbide Fe_5C_2 has been widely studied.[1,2] It is monoclinic and has the space group $C_{2/2}$. The iron atoms occupy two sets of eightfold general positions (type I and II) and one fourfold set (type III).

In accordance with the structure determination by Fasiska and Jeffrey,[3] the θ-iron carbide Fe_3C (cementite) is orthorhombic and has the space group P_{nma}. The iron atoms are located in two types of sites. An iron atom Fe_G at the general *G* site has 3 C and 11 Fe nearest neighbors in a less-asymmetric arrangement than an iron atom, Fe_S, at the special *S* site with 2 C and 12 Fe nearest neighbors.

The two carbides have been widely studied by the Mössbauer effect. The Mössbauer spectrum of the χ carbide has been shown to have a fine structure due to the different sites of the iron atoms.[4]