Theory of Electron-Nuclear Double Resonance in the Presence of External Stresses

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The spin Hamiltonian for piezo-hyperfine interaction (PHFI), i.e. the hyperfine interaction dependent on applied external stresses, is derived on the basis of symmetry considerations. The PHFI Hamiltonian is expressed in terms of the uniform deformation tensor components which are related to the external stresses by Hooke's law. The theory is extended to the case of an arbitrary (nonuniform) deformation. The shortcomings of the description of uniform deformation near a defect by local elastic constants are noted. A microscopic approach to the problem of describing the effect of external stresses on the hyperfine interaction (HFI) between the electron of a paramagnetic center and nuclei of the medium yields formulas which are valid for calculation of constants of the phenomenological Hamiltonian. The PHFI of F centers in alkali-halide crystals is studied in detail. The relation between the PHFI constants (in the approximation of a uniform deformation near a defect) and the probability for a direct relaxation transition induced by contact HFI is considered. It is shown that by comparing the theory in which nonuniformity of the deformation near defects is taken into account, with PHFI experiments, one can determine the static shifts of the ion in the immediate neighborhood of the paramagnetic center under various external stresses.

1. INTRODUCTION

EXTERNAL stresses lead to experimentally observed changes of the frequencies of electron-nuclear double resonance (ENDOR)[1,2]. Bailey et al.[1] cite experimental data on the change of the constants of the isotropic hyperfine interaction (HFI) of an F-center electron in KCl with the nuclei of the first coordination sphere under hydrostatic compression. Blum[3] investigated by an EPR method the change of the isotropic HFI constant under hydrostatic compression on F centers in LiF. The influence of external stresses on isotropic and anisotropic HFI of F centers in alkali-halide crystals (AHC) was investigated in greatest detail in[2]. A theoretical calculation of the coupling constants in the spin-Hamiltonian describing the piezo-hyperfine interaction (PHFI) makes it possible to determine the shifts and splittings of the ENDOR frequencies. A comparison of these results with the experimental quantities makes it possible, in principle, to determine the displacements of the nearest-neighbor ions. The information obtained from the shifts and splittings of the ENDOR frequencies under external static stresses is also of interest in connection with studies of the hyperfine spin-lattice relaxation and excited electronic states of a local paramagnetic center (PC).

We propose here a general method of constructing the HFI spin Hamiltonian in the presence of static displacements of the crystal-lattice ions. The obtained PHFI spin Hamiltonian makes it possible to interpret the ENDOR spectrum under arbitrary external stresses and at any orientation of the external magnetic field. We demonstrate the inadequacy of describing the ion displacements near PC by means of a uniform deformation tensor and of introducing local elastic constants to describe nonuniform deformation. The PHFI spin Hamiltonian, in which the ion displacements are expressed in terms of linear combinations of displacements, which transform in accordance with the corresponding representation of the point-symmetry group of the PC, is meaningful also in the case of nonuniform deformation near the PC. An experimental confirmation of the nonuniformity of the static deformation near a defect is the dependence of the PHFI constants on the orientation of the uniaxial compression axis in a plane perpendicular to the direction of the ion of the first coordination sphere of the F center in AHC (this will be arbitrarily called the azimuthal effect). For the case of uniaxial compression, we construct a phenomenological PHFI spin Hamiltonian that depends on the direction cosines of the compression axis and takes into account the nonuniformity of the deformation near the defect. A comparison of the theory with experiment has made it possible to determine the PHFI constants of the phenomenological Hamiltonian both in the rough approximation of uniform deformation, and when account is taken of the nonuniformity of the deformation near the PC. The probability W_x of the direct relaxation process, expressed in terms of the PHFI constants in the uniform-deformation approximation, agrees with the experimental value. General expressions are obtained, which make possible a microscopic calculation of the PHFI constants if one knows the dependence of the displacements near the defect on the external stresses.

2. SPIN HAMILTONIAN OF PIEZO-HYPERFINE INTERACTION

The piezo-hyperfine interaction will be defined as that part of the hyperfine interaction whose constants depend on the applied external stresses.

A. Let $u_\alpha^{(n)}$ be the α-component (α = x, y, z) of the displacement of the n-th nucleus from the equilibrium position as a result of the external stresses. In a regular crystal under uniform deformation, as is well known,

$$u_\alpha^{(n)} = \sum_\beta \varepsilon_{\alpha\beta} R_{0\beta}^{(n)}, \qquad (1)$$

where $R_0^{(n)}$ is the equilibrium position of the particles in the absence of deformation. The symmetrical strain tensor is connected with the symmetrical tensor of the external stresses $T_{\gamma\delta}$ by Hooke's law

$$\varepsilon_{\alpha\beta} = \sum_{\gamma\delta} s_{\alpha\beta\gamma\delta} T_{\gamma\delta}. \tag{2}$$

Here $s_{\alpha\beta\gamma\delta}$ is the elastic-constant tensor. In cubic crystals, this tensor has only three independent components:

$$s_{xxxx} = s_{11}, \quad s_{xxyy} = s_{12}, \quad s_{xyxy} = s_{44}/4 = 1/4c_{44}$$

($c_{\alpha\beta}$ is the elastic-modulus tensor in Voigt's notation).

Using the components of the strain tensor $\epsilon_{\alpha\beta}$, the electron spin vector **S**, and the nuclear spin $\mathbf{I}^{(n)}$ we can set up (in the approximation linear in $\epsilon_{\alpha\beta}$) the scalar quantity

$$\mathcal{H} = \sum_{n\alpha\beta\gamma\delta} \lambda^{(n)}_{\alpha\beta\gamma\delta} \varepsilon_{\alpha\beta} S_\gamma I^{(n)}_\delta, \tag{3}$$

Here $\lambda^{(n)}_{\alpha\beta\gamma\delta}$ is a fourth-rank tensor, $\lambda^{(n)}_{\alpha\beta\gamma\delta} = \lambda^{(n)}_{\beta\alpha\gamma\delta}$, and n is the number of the ion. The symmetry that simplifies the tensor $\lambda^{(n)}_{\alpha\beta\gamma\delta}$ is the local HFI symmetry. Thus, this is C_{4v} for the first and fourth coordination spheres of an F center in an AHC, C_{2v} for the second, and C_{3v} for the third. The nonzero components of $\lambda^{(n)}_{\alpha\beta\gamma\delta}$ are determined in exactly the same manner as for the elastic-modulus tensor[4], but their number is larger, because generally speaking $\lambda^{(n)}_{\alpha\beta\gamma\delta} \neq \lambda^{(n)}_{\gamma\delta\alpha\beta}$ and $\lambda^{(n)}_{\alpha\beta\gamma\delta} \neq \lambda^{(n)}_{\alpha\beta\delta\gamma}$. Within a single coordination sphere, the values of $\lambda^{(n)}_{\alpha\beta\gamma\delta}$ are the same for all ions.

Let us construct in this manner, for example, the spin Hamiltonian for the local symmetry C_{4v}. Retaining only those components of the tensor $\lambda_{\alpha\beta\gamma\delta}$ which differ from zero for the ions on the symmetry axis z, we obtain

$$\begin{aligned}
\mathcal{H}^{(1)}(z) = {} & (\lambda_{xxxx}\varepsilon_{xx} + \lambda_{yyxx}\varepsilon_{yy} + \lambda_{zzxx}\varepsilon_{zz}) S_x I_x^{(1)} + (\lambda_{xxyy}\varepsilon_{xx} + \lambda_{yyyy}\varepsilon_{yy} \\
& + \lambda_{zzyy}\varepsilon_{zz}) S_y I_y^{(1)} + (\lambda_{xxzz}\varepsilon_{xx} + \lambda_{yyzz}\varepsilon_{yy} + \lambda_{zzzz}\varepsilon_{zz}) S_z I_z^{(1)} \\
& + \lambda_{xyxy}\varepsilon_{xy}(S_x I_y^{(1)} + S_y I_x^{(1)}) + \lambda_{xzxz}\varepsilon_{xz} S_x I_z^{(1)} + \lambda_{xzzx}\varepsilon_{xz} S_z I_x^{(1)} \\
& + \lambda_{yzyz}\varepsilon_{yz} S_y I_z^{(1)} + \lambda_{yzzy}\varepsilon_{yz} S_z I_y^{(1)} = [a_1^{(1)}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \\
& + a_3^{(1)}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})]\mathbf{S}\mathbf{I}^{(1)} - [B_1^{(1)}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \\
& + B_{3,1}^{(1)}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}) + B_{3,2}^{(1)}(\varepsilon_{xx} - \varepsilon_{yy})] S_x I_x^{(1)} - [B_1^{(1)}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \\
& + B_{3,1}^{(1)}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})] S_y I_y^{(1)} - B_{3,2}^{(1)}(\varepsilon_{xx} - \varepsilon_{yy})] S_y I_y^{(1)} \\
& + 2[B_1^{(1)}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) + B_{3,1}^{(1)}(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy})] S_z I_z^{(1)} \\
& + \text{terms with } S_\gamma I^{(1)}_{\delta,\gamma\neq\delta} = \Delta a^{(1)} \mathbf{S}\mathbf{I}^{(1)} + \sum_{\gamma\delta} \Delta B^{(1)}_{\gamma\delta} S_\gamma I^{(1)}_\delta.
\end{aligned} \tag{4}$$

The piezo-hyperfine constants $a^{(m)}_\mu$ and $B^{(m)}_{\mu,i}$ (μ is the number of the reducible representation Γ_μ of the group O_h, according to which the corresponding combinations of the tensor $\epsilon_{\alpha\beta}$ transform, i numbers the rows of the representation, and m is the number of the coordination sphere) are expressed in terms of $\lambda_{\alpha\beta\gamma\delta}$ and describe the changes of the constants of the HFI Hamiltonian[5] under arbitrary external stresses. $a^{(m)}_\mu$ and $B^{(m)}_{\mu,i}$ characterize respectively the isotropic and anisotropic PHFI (and we always have $\Delta B^{(m)}_{xx} + \Delta B^{(m)}_{yy} + \Delta B^{(m)}_{zz} = 0$).

For a regular cubic crystal we have

$$\begin{aligned}
\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \equiv \varepsilon(\Gamma_1^+) &= (s_{11} + 2s_{12})(T_{xx} + T_{yy} + T_{zz}) = (s_{11} + 2s_{12}) T(\Gamma_1^+), \\
2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy} \equiv \varepsilon_1(\Gamma_3^+) &= (s_{11} - s_{12}) T_1(\Gamma_3^+), \\
\varepsilon_{xx} - \varepsilon_{yy} \equiv \varepsilon_2(\Gamma_3^+) &= (s_{11} - s_{12}) T_2(\Gamma_3^+), \quad \varepsilon_{xy} \equiv \varepsilon_1(\Gamma_5^+) = {}^1/_2 s_{44} T_1(\Gamma_5^+), \\
\varepsilon_{xz} \equiv \varepsilon_2(\Gamma_5^+) &= {}^1/_2 s_{44} T_2(\Gamma_5^+), \quad \varepsilon_{yz} \equiv \varepsilon_3(\Gamma_5^+) = {}^1/_2 s_{44} T_3(\Gamma_5^+).
\end{aligned} \tag{5}$$

Under hydrostatic compression ($T_{\alpha\beta} = -P\delta_{\alpha\beta}$) we find from (4) and (5) that the changes of the HFI constants as a result of the compression are

$$\begin{aligned}
\Delta a^{(1)} &= -3P a_1^{(1)}(s_{11} + 2s_{12}); \\
\Delta B_{zz} \equiv 2\Delta b^{(1)} &= -6P B_1^{(1)}(s_{11} + 2s_{12}).
\end{aligned} \tag{6}$$

For uniaxial compression along the k axis ($T_{\alpha\beta} = -Pk_\alpha k_\beta$) we have

$$\begin{aligned}
\Delta a^{(1)} &= -P[a_1^{(1)}(s_{11} + 2s_{12}) + a_{3,1}^{(1)}(s_{11} - s_{12})(3k_z^2 - 1)], \\
\Delta B_{xx}^{(1)} &= P[B_1^{(1)}(s_{11} + 2s_{12}) + B_{3,1}^{(1)}(s_{11} - s_{12})(3k_z^2 - 1) \\
&\quad + B_{3,2}^{(1)}(s_{11} - s_{12})(k_x^2 - k_y^2)], \\
\Delta B_{yy}^{(1)} &= P[B_1^{(1)}(s_{11} + 2s_{12}) + B_{3,1}^{(1)}(s_{11} - s_{12})(3k_z^2 - 1) \\
&\quad - B_{3,2}^{(1)}(s_{11} - s_{12})(k_x^2 - k_y^2)],
\end{aligned} \tag{7}$$

$$\Delta B_{zz}^{(1)} = -\Delta B_{xx}^{(1)} - \Delta B_{yy}^{(1)}. \tag{8}$$

The formulas for ions on the x and y axes are obtained from (4)—(8) by cyclic permutation of the indices.

The change of the ENDOR frequencies as a result of external stresses can be easily obtained by adding to the constants a and $B_{\gamma\delta}$ in the general formula for the ENDOR frequencies (cf., e.g.,[5,6]) their changes Δa and $\Delta B_{\gamma\delta}$ due to pressure from (6)—(8) and expanding the obtained expression in terms of the small terms proportional to P.

It is seen from (6)—(8) that within the framework of the homogeneous-deformation approximation the hydrostatic compression changes in the same manner the constants a and B of all the ions, and a change in the direction of k does not change Δa if $\mathbf{k} \perp \mathbf{R}_0^{(1)}$ ($\mathbf{R}_0^{(1)}$ is the radius vector of the ion of the first sphere). If we denote by $\Delta a^{(1)}_{\parallel(\perp)}$ the change of $a^{(1)}$ following compression along $\mathbf{k} \parallel (\perp) \mathbf{R}_0^{(1)}$, then it follows from (6) and (7) that

$$\Delta a_\parallel^{(1)} + 2\Delta a_\perp^{(1)} = \Delta a^{(1)}_{\text{hydro.}} \tag{9}$$

The constants for the ions on the axes x, y, and z vary differently under uniaxial compression, depending on the values of the factors $3k_\alpha^2 - 1$). This leads to a splitting of the ENDOR frequencies in certain cases. For example, if the magnetic field is $\mathbf{H} \parallel [110]$ and $\mathbf{k} \parallel [010]$, then at P = 0 the ENDOR frequencies of the first sphere are the same on the x and y axes, but at $P \neq 0$ they will be different, since $3k^2 - 1$ is equal to -1 and 2 respectively for α = x and y. This splitting can be observed if it is larger than the second-order structure due to the indirect interaction of the equivalent nuclei[5] (in the absence of quadrupole interactions, the splitting due to the indirect interaction is proportional to $a^2/4\nu_0$, where ν_0 is the electron Zeeman frequency). On the other hand if $a^2/4\nu_0$ is of the order of $a_1\epsilon_{\alpha\alpha}$, then the operator H from (3) should be taken into account together with the indirect-interaction operator, and external stresses will change the structure of the second-order ENDOR line. The changes $\Delta B_{\gamma\gamma}$ lead to a change of the angular dependences of the ENDOR frequencies. We note that in an experimental reduction of the ENDOR

spectra at $P \neq 0$ it is necessary to take into account the appearance of terms $S_\gamma I_\delta^{(1)}$ with $\gamma \neq \delta$ in $\mathcal{H}$ of (4); these terms may not be present when P = 0.

The PHFI spin Hamiltonian for the symmetry C_{2v} (for example, for the second coordination sphere of an F center in an AHC), obtained by the method given above, takes with allowance for (5) the form (for the ions $[\pm 1, \pm 1, 0]$)

$$\begin{aligned}\mathcal{H}^{(2)} &= [a_1^{(2)}(s_{11}+2s_{12})T(\Gamma_1^+)+a_3^{(2)}(s_{11}-s_{12})T_1(\Gamma_3^+)\\ &+{}^1/_2 a_5^{(2)} s_{44} T_1(\Gamma_5^+)]\mathbf{SI}^{(2)} - [B_{xx1}^{(2)}(s_{11}+2s_{12})T(\Gamma_1^+)\\ &+B_{xx3}^{(2)}(s_{11}-s_{12})T_1(\Gamma_3^+)+{}^1/_2 B_{xx5}^{(2)} s_{44} T_1(\Gamma_5^+)]S_x I_x^{(2)}\\ &-[B_{yy1}^{(2)}(s_{11}+2s_{12})T(\Gamma_1^+)+B_{yy3}^{(2)}(s_{11}-s_{12})T_1(\Gamma_3^+)\\ &+{}^1/_2 B_{yy5}^{(2)} s_{44} T_1(\Gamma_5^+)]S_y I_y^{(2)} + [(B_{xx1}^{(2)}+B_{yy1}^{(2)})(s_{11}+2s_{12})T(\Gamma_1^+)\\ &+(B_{xx3}^{(2)}+B_{yy3}^{(2)})(s_{11}-s_{12})T_1(\Gamma_3^+)+{}^1/_2(B_{xx5}^{(2)}+B_{yy5}^{(2)})s_{44}T_1(\Gamma_5^+)]S_z I_z^{(2)}\\ &+\text{terms with c } S_\gamma I_\delta^{(2)},\quad \gamma \neq \delta. \end{aligned} \tag{10}$$

From this we get for uniaxial compression along **k**:

$$\begin{aligned}\Delta a^{(2)} &= -P[a_1^{(2)}(s_{11}+2s_{12})+a_3^{(2)}(s_{11}-s_{12})(3k_z^2-1)+{}^1/_2 a_5^{(2)} s_{44} k_x k_y],\\ \Delta B_{xx}^{(2)} &= P[B_{xx1}^{(2)}(s_{11}+2s_{12})+B_{xx3}^{(2)}(s_{11}-s_{12})(3k_z^2-1)+{}^1/_2 B_{xx5}^{(2)} s_{44} k_x k_y],\\ \Delta B_{yy}^{(2)} &= P[B_{yy1}^{(2)}(s_{11}+2s_{12})+B_{yy3}^{(2)}(s_{11}-s_{12})(3k_z^2-1)+{}^1/_2 B_{yy5}^{(2)} s_{44} k_x k_y].\end{aligned} \tag{11}$$

For the ions $[\pm 1, \pm 1, 0]$ it is necessary to reverse the signs of the terms of symmetry Γ_5 in (10) and (11). Unlike in (4), the PHFI Hamiltonian (10) contains shear components proportional to s_{44}. For the remaining ions of the second sphere, the formulas are obtained from (1) and (11) by suitable cyclic permutation.

B. It is seen from (7) that in the uniform-deformation approximation the isotropic HFI constant a should not depend on the azimuth of the compression axis if the latter lies in a plane perpendicular to the z axis ($k_z = 0$). The same approximation leads to another symmetry relation (9). If relations (7) and (9) are not satisfied in the experiment, this means that the spin Hamiltonian is not linear in $T_{\gamma\delta}$. The tables of the experimental data[2] show that (7) and (9) is not satisfied. Since the changes of the HFI constants in[2] are directly proportional to the value of the pressure P, the failure to satisfy (9) and the azimuthal effect can be attributed only to the inadequacy of the uniform-deformation approximation. The nonuniformity of the deformation can be taken into account phenomenologically by choosing as the variables for the PHFI spin Hamiltonian not the ion displacements, but the external stresses directly.

In the case of uniaxial compression along **k**, the uniform deformation is described by the spin Hamiltonian

$$\mathcal{H}^{(n)} = -P\sum_{\alpha\beta\gamma\delta}\mu_{\alpha\beta\gamma\delta}^{(n)} k_\alpha k_\beta S_\gamma I_\delta^{(n)},\quad \mu_{\alpha\beta\gamma\delta}^{(n)} = \sum_{\eta\xi}\lambda_{\eta\xi\gamma\delta}^{(n)} s_{\eta\xi\alpha\beta}. \tag{12}$$

To describe the nonuniformity of the deformation, we introduce invariants of higher order:

$$\mathcal{H}^{(n)} = -P\sum_{\gamma\delta} S_\gamma I_\delta^{(n)}\left[\sum_{\alpha\beta}\mu_{\alpha\beta\gamma\delta}^{(n)} k_\alpha k_\beta + \sum_{\alpha\beta\eta\xi}\nu_{\alpha\beta\eta\xi\gamma\delta}^{(n)} k_\alpha k_\beta k_\eta k_\xi\right]. \tag{13}$$

The tensors $\mu_{\alpha\beta\gamma\delta}^{(n)}$ and $\nu_{\alpha\beta\eta\xi\gamma\delta}^{(n)}$ are simplified, just as $\lambda_{\alpha\beta\gamma\delta}^{(n)}$ from (3), by the local point-symmetry group of the HFI. For the ions on the z axis of the first coordination sphere, (13) yields, with allowance for the connection between the k_α^2,

$$\begin{aligned}\Delta a^{(1)} &= -P[a_1 + a_2(3k_z^2-1)+a_3 k_z^4 + a_4 k_x^2 k_y^2 + a_5(k_x^4+k_y^4)]\\ &= -P[\delta a_1^{(1)} + \delta a_3^{(1)}(3k_z^2-1)+\delta a' k_z^4 + \delta a'' k_x^2 k_y^2],\\ \Delta B_{xx}^{(1)} &= P[\delta B_1^{(1)} + \delta B_{3,1}^{(1)}(3k_z^2-1)+\delta B_{3,2}^{(1)}(k_x^2-k_y^2)\\ &\quad +\delta B' k_z^4 + \delta B'' k_x^2 k_y^2 + \delta B'''(k_x^4-k_y^4)],\\ \Delta B_{yy}^{(1)} &= P[\delta B_1^{(1)} + \delta B_{3,1}^{(1)}(3k_z^2-1)-\delta B_{3,2}^{(1)}(k_x^2-k_y^2)\\ &\quad +\delta B' k_z^4 + \delta B'' k_x^2 k_y^2 - \delta B'''(k_x^4-k_y^4)].\end{aligned} \tag{14}$$

Allowance for the primed constants explains the azimuthal effect and the failure to satisfy (9).

It is of interest to note that the problem of the distribution of the stresses near a spherical cavity in a continuum that is uniformly deformed at infinity[4] leads to inhomogeneous stresses.

C. The PHFI spin Hamiltonian can also be obtained by another method. Let $Q_i(\Gamma_{\alpha\tau}, m)$ be the symmetrized displacements of the nuclei of the m-th sphere of the PC surroundings, transformed in accordance with i-th row of the irreducible representation Γ_α of the point symmetry group G of the PC; $I_j^{(n)}(\Gamma_{\beta t})$ are linear combinations of the spins of nuclei of the n-th coordination sphere, the interaction with which is under consideration; $S_k(\Gamma_\gamma)$ are linear combinations of the operators of the electron spin components S_x, S_y, and S_z, and τ and t number identical irreducible representations encountered more than once. Then the Hamiltonians of the PHFI with the nuclei of the n-th sphere is given by

$$\mathcal{H}^{(n)} = \sum_{\alpha\beta\gamma(\tau t)ijkm} d_{\alpha\beta\gamma(\tau t)}^{(n)}(m) S_k(\Gamma_\gamma)\langle\Gamma_\alpha\Gamma_\beta ij|\Gamma_\gamma k\rangle Q_i(\Gamma_{\alpha\tau}, m) I_j^{(n)}(\Gamma_{\beta t}). \tag{15}$$

Here $\langle\Gamma_\alpha\Gamma_\beta ij|\Gamma_\gamma k\rangle$ are the Clebsch-Gordan coefficients of the point-symmetry group[7]. If the representation Γ_γ is encountered $c_{\alpha\beta\gamma}$ times in the direct product $\Gamma_\alpha \times \Gamma_\beta$ ($c_{\alpha\beta\gamma} = 0$ or 1), then the index (τt) assumes $\sum_{\alpha\beta} c_\alpha c_\beta c_{\alpha\beta\gamma}$ values, where c_α and c_β are the number of values assumed by τ and t, respectively, and $d_{\alpha\beta\gamma(\tau t)}^{(n)}(m)$ are the constants of the spin Hamiltonian.

The Hamiltonian (15) is the most general and is valid for nonuniform deformation near a defect. In the case of uniform deformation, naturally, (15) goes over into (3).

Allowance for the nonuniformity of the deformation for several coordination spheres in (15) makes the method quite cumbersome. However, if the deviations from uniformity are significant only for the displacements of the ions of the nearest surrounding of the PC (the ions of the first sphere), then we can write

$$\begin{aligned}\mathcal{H}^{(n)} &= \sum_{\alpha\beta\gamma(\tau t)ijk} d_{\alpha\beta\gamma(\tau t)}^{(n)}(1) S_k(\Gamma_\gamma)\langle\Gamma_\alpha\Gamma_\beta ij|\Gamma_\gamma k\rangle Q_i(\Gamma_{\alpha\tau}, 1) I_j^{(n)}(\Gamma_{\beta t})\\ &\quad + \sum_{\alpha'\beta'\gamma'\delta'} \tilde{\lambda}_{\alpha'\beta'\gamma'\delta'}^{(n)} \varepsilon_{\alpha'\beta'} S_{\gamma'} I_{\delta'}^{(n)},\end{aligned} \tag{16}$$

where the second term takes into account the displacements of the ions of the second and succeeding coordination sphere. For an ion of the first sphere on the x axis, Eq. (16) yields[1)]

[1)]The odd representations $Q_i(\Gamma_a^-)I_j^{(n)}(\Gamma_\beta^-)$ vanish from (16), owing to the invariance of the Hamiltonian under translation of the crystal as a whole.

$$\mathcal{H}^{(1)} = [a^{(1)}_{1,1} Q_1(\Gamma_1^+, 1) + a^{(1)}_{1,3} Q_1(\Gamma_3^+, 1) + \tilde{a}^{(1)}_1 \varepsilon(\Gamma_1^+) + \tilde{a}^{(1)}_3 \varepsilon_1(\Gamma_3^+)]\mathbf{SI}^{(1)}$$
$$- [B^{(1)}_{1,1} Q_1(\Gamma_1^+, 1) + B^{(1)}_{1,3,1} Q_1(\Gamma_3^+, 1) + B^{(1)}_{1,3,2} Q_2(\Gamma_3^+, 1) + \tilde{B}^{(1)}_1 \varepsilon(\Gamma_1^+)$$
$$+ \tilde{B}^{(1)}_{3,1} \varepsilon_1(\Gamma_3^+) + \tilde{B}^{(1)}_{3,2} \varepsilon_2(\Gamma_3^+)] S_x I_x^{(1)} - [B^{(1)}_{1,1} Q_1(\Gamma_1^+, 1) + B^{(1)}_{1,3,1} Q_1(\Gamma_3^+, 1)$$
$$- B^{(1)}_{1,3,2} Q_2(\Gamma_3^+, 1) + \tilde{B}^{(1)}_1 \varepsilon(\Gamma_1^+) + \tilde{B}^{(1)}_{3,1} \varepsilon_1(\Gamma_3^+) - \tilde{B}^{(1)}_{3,2} \varepsilon_2(\Gamma_3^+)] S_y I_y^{(1)}$$
$$+ \Delta B^{(1)}_{zz} S_z I_z^{(1)} + \text{terms with } S_\gamma I_\delta^{(1)}, \quad \gamma \neq \delta. \qquad (17)$$

Here $a^{(n)}_{m,\alpha}$, $B^{(n)}_{m,\alpha,i}$, $\tilde{a}^{(n)}_\alpha$, $\tilde{B}^{(n)}_{\alpha,i}$ are independent linear combinations of $d^{(n)}_{\alpha\beta\gamma(\tau t)}(m)$ from (15). The expressions for $Q_i(\Gamma_{\alpha\tau}, 1)$ in terms of the displacements of the ions can be found, for example, in[8]. If the dependence of the displacements on the external stresses were known, the spin Hamiltonian (17) would contain 10 parameters describing the variation of a and $B_{\gamma\gamma}$ with pressure. Since the problem of the theory of microelasticity near the defect is quite complicated and we do not know its solution, we can use, in principle, Eq. (17) to determine $Q_i(\Gamma^+_\alpha, 1)$, meaning also the displacements of the ions of the first sphere of a point-like PC under the influence of external stresses. This nontrivial possibility of finding the shifts of the nearest surroundings of the PC under the influence of external stresses from the PHFI calls for experimental data with accuracy better than in[2].

D. To explain the influence of the pressure on the optical characteristics of the PC and on the EPR and ENDOR frequencies, the deformation near the PC is usually assumed to be uniform for each coordination sphere, and the parameters characterizing the deformation are assumed to vary from sphere to sphere. Since the number of these parameters for each sphere is equal to the number of elastic constants of the crystal, they are called the local elastic constants $s^{loc}_{\alpha\beta\gamma\delta}$ and are used in (2) in place of $s_{\alpha\beta\gamma\delta}$ of the regular crystal. By calculating in one way or another the constants in (4) or in expressions similar to it for EPR or optics[9,10], one can find by comparison with experiment the values of $s^{loc}_{\alpha\beta\gamma\delta}$, which usually differ from $s_{\alpha\beta\gamma\delta}$ by 2–6 times. When comparing $s^{loc}_{\alpha\beta\gamma\delta}$ determined from the constants Δa, $\Delta B_{\gamma\gamma}$, the optical data, etc., it must be borne in mind that, as seen from (15) and (17), the PHFI constants and other characteristics of the PC are determined by different combinations of the displacement of both the first and the succeeding spheres, and if the separation of the contributions from different spheres is difficult, this can lead to discrepancies between the values of $s^{loc}_{\alpha\beta\gamma\delta}$ determined from different experiments.

We wish to call attention to the fact that such a method of describing the nonuniformity of the deformation near the defect is only a partial solution, since the introduction of $s^{loc}_{\alpha\beta\gamma\delta}$ cannot explain the observed azimuthal effect in PHFI and the violation of symmetry relations of the type of (9). For uniaxial compression, a more general connection between $u^{(n)}$ and the pressure has the following form:

$$u^{(n)}_\alpha = -P\left[\sum_{\beta\gamma} M^{(n)}_{\alpha\beta\gamma} k_\beta k_\gamma + \sum_{\beta\gamma\delta\varepsilon} N^{(n)}_{\alpha\beta\gamma\delta\varepsilon} k_\beta k_\gamma k_\delta k_\varepsilon + \ldots\right].$$

The second term and those discarded describe the nonuniformity of the deformation within the limits of one sphere. Allowance for these terms makes it possible to explain the azimuthal effect in the PHFI and failure to satisfy (9). The local elastic constants can be introduced by putting $N_{\alpha\beta\gamma\delta\epsilon} = 0$ and

$$M^{(n)}_{\alpha\beta\gamma} = \sum_\delta s^{loc}_{\alpha\beta\gamma\delta} R^{(n)}_{0\delta}$$

(homogeneous deformations within the limits of a sphere). If the terms with $N^{(n)}_{\alpha\beta\gamma\delta}$ are not too small (and their values should apparently decrease with increasing rank of the coupling tensor), then neglect of these terms also leads to discrepancies between the values of $s^{loc}_{\alpha\beta\gamma\delta}$ determined from different experiments.

3. MICROSCOPIC THEORY OF THE CONSTANTS OF THE PHFI HAMILTONIAN

The microscopic approach to the problem of describing the action of external stresses on the HFI of a PC electron with the surrounding nuclei leads to a number of formulas that are suitable for the calculation of the constants of the phenomenological PHFI Hamiltonian.

A. The Hamiltonian of an electron of a PC in a deformed crystal can be written in the adiabatic approximation in the form

$$\mathcal{H}_{ad} = T_e + V(\mathbf{r}, \mathbf{R}) + \sum_n f^{(n)}(\mathbf{S}, \mathbf{I}^{(n)}) X^{(n)}(\mathbf{r} - \mathbf{R}^{(n)}) + \mathcal{H}', \qquad (18)$$

where T_e and $V(\mathbf{r}, \mathbf{R})$ are respectively the kinetic and potential energy of the electron, $\mathbf{R}$ is the aggregate of the coordinates of the nuclei, $f^{(n)}(\mathbf{S}, \mathbf{I}^{(n)})$ are the spin operators, $X^{(n)}$ is the coordinate part of the HFI, and $\mathcal{H}'$ is the spin-orbit interaction and the Zeeman energy of the electron in an external field. Expanding $\mathcal{H}_{ad}$ in a series in the small static displacement and retaining only the linear terms, we obtain

$$\mathcal{H}_{ad} = \mathcal{H}_0 + \mathcal{H}' + W, \qquad (19)$$

$$\mathcal{H}_0 = T_e + V(\mathbf{r}, \mathbf{R}_0), \qquad (20)$$

$$W = \sum_i \mathbf{u}^{(i)} \frac{d}{d\mathbf{R}^{(i)}_0} V(\mathbf{r}, \mathbf{R}_0) + \sum_n f^{(n)}(\mathbf{S}, \mathbf{I}^{(n)}) \left[X^{(n)}(\mathbf{r} - \mathbf{R}^{(n)}_0) + \frac{dX^{(n)}_0}{d\mathbf{R}^{(n)}_0} \mathbf{u}^{(n)}\right].$$

We are interested in a spin Hamiltonian that is linear in the ion displacements and in the spin operators $f^{(n)}(\mathbf{S}, \mathbf{I}^{(n)})$, such that its eigenvalues give the corrections, due to the HFI, to the energy of the ground state. Accurate to terms of second order of perturbation theory, we have

$$\mathcal{H}_{SI} = \left\langle 0 \left| \sum_n f^{(n)} \left[X^{(n)}_0 + \frac{dX^{(n)}_0}{d\mathbf{R}^{(n)}_0} \mathbf{u}^{(n)}\right] \right| 0 \right\rangle + 2 \sum_{j \neq 0} \frac{1}{E_{0j}} \times \left\langle 0 \left| \sum_n f^{(n)} X^{(n)}_0 \right| j \right\rangle \langle j | LV | 0 \rangle,$$

$$L = \sum_i \mathbf{u}^{(i)} \frac{d}{d\mathbf{R}^{(i)}_0}, \qquad (21)$$

$|0\rangle$ and $|j\rangle$ are respectively the coordinate functions of the ground and excited states of the PC.

Using the identical transformations[11]

$$\langle j | LV | 0 \rangle = \langle j | [L, \mathcal{H}_0] | 0 \rangle = E_{0j} \langle j | L | 0 \rangle,$$

$$\left\langle 0 \left| \frac{dX^{(n)}_0}{d\mathbf{R}^{(n)}_j} \right| 0 \right\rangle = \left\langle 0 \left| -\frac{dX^{(n)}_0}{d\mathbf{r}} \right| 0 \right\rangle = 2 \left\langle 0 \left| X^{(n)}_0 \frac{d}{d\mathbf{r}} \right| 0 \right\rangle,$$

$$\sum_i \frac{d}{d\mathbf{R}^{(i)}_j} V(\mathbf{r}, \mathbf{R}_0) = -\frac{d}{dr} V(\mathbf{r}, \mathbf{R}_0), \qquad (22)$$

we can transform (21) into

$$\mathcal{H}_{SI}=\sum_n f^{(n)}(\mathrm{S},\mathrm{I}^{(n)})\left[\langle 0|X_0^{(n)}|0\rangle+2\left(\left\langle 0\left|X_0^{(n)}\sum_i(\mathbf{u}^{(i)}-\mathbf{u}^{(n)})\frac{d}{d\mathbf{R}_0^{(i)}}\right|0\right\rangle-\langle 0|X_0^{(n)}|0\rangle\left\langle 0\left|\sum_i(\mathbf{u}^{(i)}-\mathbf{u}^{(n)})\frac{d}{d\mathbf{R}_0^{(i)}}\right|0\right\rangle\right)\right]. \quad (23)$$

For the isotropic HFI we have

$$f^{(n)}(\mathrm{S},\mathrm{I}^{(n)})X_0^{(n)}=\tau^{(n)}\mathbf{SI}^{(n)}\delta(\mathbf{r}-\mathbf{R}_0^{(n)}),\quad \tau^{(n)}={}^8/_3\pi g^{(n)}_\beta g^{(n)}_n\beta^{(n)}_n \quad (24)$$

and we obtain from (23)

$$a^{(n)}=a_0^{(n)}+\sum_i(\mathbf{u}^{(i)}-\mathbf{u}^{(n)})\frac{da_0^{(n)}}{d\mathbf{R}_j^{(i)}}\Big|_{R_0^{(n)}}-2a_j^{(n)}\left\langle 0\left|\sum_i(\mathbf{u}^{(i)}-\mathbf{u}^{(n)})\frac{d}{d\mathbf{R}_0^{(i)}}\right|0\right\rangle. \quad (25)$$

This formula is a correct expansion of $a^{(n)}$ in terms of the differences between the ion displacements. The usually employed expansion of $a^{(n)}$ in terms of the displacements of the other ions.

Assuming that the excited states that contribute to the PHFI lie in a narrow energy interval, we can take out the energy denominator in (21) with a mean value $-\Delta E$. Then

$$a^{(n)}=a_0^{(n)}\left\{1-\frac{2}{\Delta E}\sum_i(\mathbf{u}^{(i)}-\mathbf{u}^{(n)})\left[\frac{dV}{d\mathbf{R}_j^{(i)}}\Big|_{R_0^{(n)}}-\left\langle 0\left|\frac{dV}{d\mathbf{R}_0^{(i)}}\right|0\right\rangle\right]\right\}. \quad (26)$$

The change of the constant of the HFI with the nuclei of the n-th sphere turns out to be proportional to the HFI constant for this sphere.

B. Using the δ-like nature of the isotropic HFI, we obtain from (21)

$$a^{(n)}=a_0^{(n)}+2\tau^{(n)}\sum_{j\neq 0}\frac{1}{E_{0j}}\psi_0(\mathbf{R}_j^{(n)})\psi_j(\mathbf{R}_0^{(n)})\left\langle j\left|\sum_i(\mathbf{u}^{(i)}-\mathbf{u}^{(n)})\frac{dV}{d\mathbf{R}_j^{(i)}}\right|0\right\rangle,$$

$$\left\langle j\left|\sum_i(\mathbf{u}^{(i)}-\mathbf{u}^{(n)})\frac{dV}{d\mathbf{R}_j^{(i)}}\right|0\right\rangle=\mathbf{u}^{(n)}\left\langle j\left|\frac{dV}{d\mathbf{r}}\right|0\right\rangle+\langle j|LV|0\rangle. \quad (27)$$

Assume that (1) is correct. Then

$$L=\sum_{\alpha\beta\delta}\varepsilon_{\alpha\beta}R_{0\alpha}^{(i)}\frac{d}{dR_{0\beta}^{(i)}}.$$

If the wave function ψ_0 of the PC ground state transforms in accordance with a fully-symmetrical representation (for an F center, in accordance with the representation Γ_1^+ of the O_h group), then the first matrix element in (27) differs from zero only for excited states that transform in accordance with the same representation as dV/dr (the vector representation Γ_4^- for the O_h group). The operator L in the O_h group can be represented in the form of a sum of operators that transform in accordance with the representations Γ_2^+, Γ_3^+, and Γ_5^+. Using the usual selection rules and taking into account only the nearest excited states, we can write the isotropic HFI constant in the form

$$a^{(n)}=a_0^{(n)}+2\tau^{(n)}\psi_0(\mathbf{R}_0^{(n)})\left\{C_{2p\Gamma_4^-}\sum_{\alpha\beta}\varepsilon_{\alpha\beta}R_{0\alpha}^{(n)}\psi_{2p\Gamma_4^-,\beta}(\mathbf{R}_0^{(n)})+C_{2s\Gamma_1^+}\psi_{2s\Gamma_1^+}(\mathbf{R}_0^{(n)})\sum_\alpha\varepsilon_{\alpha\alpha}+\ldots\right\}, \quad (28)$$

where C_j is the corresponding matrix element from (27), divided by the energy difference. We note that although the deformation of the symmetry Γ_5^+ scrambles the functions $\psi_{3d\Gamma_5^+}(\mathbf{R}_0^{(n)})$ in (28), the values of these functions at the locations of the ions of the first coordination sphere of an F center are equal to zero (the functions $\psi_{3d\Gamma_5^+}(\mathbf{r})$ vanish on the axes x, y, and z), and therefore the functions $\psi_{3d\Gamma_5^+}(\mathbf{r})$, in contradiction to[2], make no contribution to $\Delta a^{(1)}$ of the nuclei of the first sphere.

Just as in the case of ENDOR in the presence of electric fields[12,13], the comparison of the experimental data for different variants of crystal compression with (28) yields information on the values of the wave functions of the excited states of the PC at the lattice sites. However, in our case it is more difficult to obtain information on the excited states, since the deformations, unlike the electric field, mix up functions of different irreducible representations. In addition, the uniform-deformation approximation is not too good for the first sphere.

4. COMPARISON OF THEORY WITH EXPERIMENT

Bailey et al.[1] give the changes, per unit pressure, of the constants of isotropic and anisotropic HFI between an F-center electron and the nuclei of the first coordination sphere in KCl, KBr, and LiF, with the nuclei of the second sphere of KCl, and the fourth sphere of KBr. The changes of the constants are directly proportional to the applied pressure. To describe the experimental data, phenomenological formulas were constructed in[2], namely, the constant of the isotropic HFI was expanded in terms of the displacements, and relation (1) was used. The quantities δa_1 and δa_3 (see[2] for the notation) turned out to be related to each other:

$$\delta a_1=-\frac{PR}{3}\frac{\partial a}{\partial z}(s_{11}+2s_{12})=\frac{s_{11}+2s_{12}}{s_{11}-s_{12}}\delta a_3. \quad (29)$$

To explain the experiment, Bailey[2] had to introduce into the formulas additional terms having the same symmetry properties as the main terms (thereby actually violating the relation (29)). In addition, there were introduced in the formula for the PHFI of the first sphere additional terms with symmetry Γ_5^+, which, as shown in Sec. 3, should not introduce a contribution to the isotropic PHFI of the first sphere. (We note that a more correct expansion of the hyperfine constant a is (25), the expansion in terms of the differences between the ion displacements, from which (29) does not follow.) The phenomenological formulas (6)—(8), (11), and (14) were obtained by a more general method than Bailey's formulas[2]. The piezo-hyperfine constants in these formulas are parameters of the theory and are obtained by comparison with experiment.

A. We consider first the uniform-deformation approximation. Assume that (1) is valid. Table I lists the changes of the HFI constant a for different variants of the compression of the crystal, obtained from (7)—(14) with a suitable choice (see Tables II and III) of the parameters of the theory, and the experimental[2] values of these changes. For the constants B, the errors in the experimental data are so large, that comparison of theory with experiment is meaningless. We see that the experimental data on the PHFI of the first coordination sphere are described with accuracy 30—40%. In addition, the azimuthal effect is not described, and relation (13) is not satisfied, the deviation exceeding the experimental errors. In the second sphere, the agreement between the theory and experiment is good. The difference between the data predicted by the phenomenological theory and the experimental data is due to the inhomo-

Table I. Experimental[2] and theoretical values of $\Delta a/P$ [kHz/(kg/mm^2)]

Crystal	Sphere	Compression	100			110			111		
		Quantity	Experiment	Theory (7)*	Theory (14)	Experiment	Theory (7)	Theory (14)	Experiment	Theory (7)	Theory (14)
KCl	I	$\Delta a_{\parallel}/P$	30.9±2.1	28.5	30.6	—	—	—	—	—	—
		$\Delta a_{\perp}/P$	−4.1±2.1	−7.5	−4.4	−8.7±1.1	−7.5	−7.9	—	—	—
		$\Delta a_{45°}/P$	—	—	—	7.3±1.1	10.5	8.7	—	—	—
		$\Delta a_{55°}/P$	—	—	—	—	—	—	3.4±0.9	4.5	1.8
	II	$\Delta a_{\parallel}/P$	—	—	—	11.7±0.8	11.6	—	—	—	—
		$\Delta a_{60°}/P$	—	—	—	−1.5±0.6	−1.8	—	—	—	—
		$\Delta a_{\perp}/P$	−3.5±0.8	−2.25	—	−16.8±0.8	−14.3	—	−8.1±0.6	−10.3	—
		$\Delta a_{35°}/P$	—	—	—	—	—	—	6.8±0.8	7.0	—
		$\Delta a_{45°}/P$	−1.3±1.3	−1.35	—	—	—	—	—	—	—
KBr	I	$\Delta a_{\parallel}/P$	37.5±3.1	34.5	37.5	—	—	—	—	—	—
		$\Delta a_{\perp}/P$	−3.2±3.5	−5.5	−3.2	−1.1±1.9	−5.5	−1.4	—	—	—
		$\Delta a_{45°}/P$	—	—	—	—	—	—	7.0±3.0	14.0	7.0
LiF	I	$\Delta a_{\parallel}/P$	27.4±1.6	27.1	—	—	—	—	—	—	—
		$\Delta a_{\perp}/P$	−5.2±3.0	−5.2	—	—	—	—	—	—	—

*The numbers in the columns "theory (7), (14)" are obtained by using the phenomenological parameters from Tables II and III, respectively.

Table II. Phenomenological parameters used in the calculations with the aid of formulas (7)*

Parameter, kHz/kg/mm^2	KCl		KBr	LiF
	Sphere I	Sphere II	Sphere I	Sphere I
a_1 $(s_{11}+2s_{12})$	4.5	−1.65	7.5	5.66
a_3 $(s_{11}-s_{12})$	12	−0.3	13.0	10.86
$^1/_2 a_5 s_{44}$	—	−26	—	—

*In those cases when the number of parameters was less than the number of experimental data, the parameters were determined by least squares.

Table III. Phenomenological parameters used in the calculations with the aid of formula (14)

Parameter, kHz/kg/mm^2	KCl	KBr	Parameter, kHz/kg/mm^2	KCl	KBr
	Sphere I	Sphere I		Sphere I	Sphere I
δa_1	1.4	−3.2	$\delta a'$	17.6	40.7
δa_3	5.8	0	$\delta a''$	−14.1	−4.8

geneity of the deformation near the defect. This is confirmed by the better agreement between theory and experiment for the second sphere, on which the nonuniformity of the deformation should exert apparently a smaller influence than on the first. We call attention to the high sensitivity of the PHFI to shear deformations. The fact that in[2] there are no data on PHFI for the third, fifth, etc. spheres is apparently due to the smallness of the variation of the HFI constants with pressure, since the HFI constants themselves are small in these spheres, and according to (26) the changes are proportional to the constant itself.

B. The results of the use of formulas (14), which take into account the nonuniformity of the deformation, are given in the third column of Table I. Within the limits of experimental error, formula (14) describes practically accurately the data of[2] for the constant a, and the number of the parameters of the theory is smaller than the number of the experimental data. The azimuthal effect and the failure to satisfy (9) are explained. It can therefore be stated that the invariants taken into account in (13) are sufficient for the description of the experiment. Allowance for the nonuniformity of the deformation in the second sphere can also be made on the basis of (13), but at the present accuracy of the experiment this has no practical value.

5. SPIN-LATTICE RELAXATION AND PHFI

The constants of the PHFI Hamiltonian in the homogeneous deformation approximation (4) should determine the probabilities of the spin-lattice transitions due to modulation of the HFI by the thermal vibrations of the lattice. In particular, if the constant $a^{(1)}$ predominates, then only $a_1^{(1)}$ and $a_3^{(1)}$ will determine the transition probability in the direct relaxation process (W_x transition).

In the long-wave approximation,

$$\varepsilon_{\alpha\beta} = i\sqrt{\frac{\hbar}{2MN}}\sum_{\varkappa j} e_{\varkappa j,\,\alpha}\varkappa_\beta \omega_{\varkappa j}^{-1/2}(a_{\varkappa j} - a_{\varkappa j}^{+}),$$

where $\mathbf{e}_{\kappa j} = -\mathbf{e}_{-\kappa j}$ is the polarization vector, κ is the wave vector of the phonon, $\omega_{\kappa j}$ is the phonon frequency, $a_{\kappa j}^{+}$ and $a_{\kappa j}$ are the phonon creation and annihilation operators, j is the branch of the oscillations, M is the reduced mass of the unit cell, and N is the number of cells in the crystal. By the usual methods, we obtain the probability of the reorientation of the spins of the electron and one nucleus:

$$W_x = \frac{4\pi^4\hbar}{\rho}\nu_0^3(\bar{n}_0+1)\frac{2}{3}I(I+1)(S_-)^2_{M-1,\,M} \times\left[\frac{(a_1^{(1)})^2+{}^4/_5(a_3^{(1)})^2}{v_l^5}+\frac{6}{5}\frac{(a_3^{(1)})^2}{v_t^5}\right]. \quad (30)$$

Here $\nu_0 = g\beta H/\hbar$, $\bar{n}_0$ is the Planck factor at the frequency ν_0, ρ is the density of the crystal, v_l and v_t are the sound velocities, and $a_1^{(1)}$ and $a_3^{(1)}$ are given in frequency units. Substituting $a_1^{(1)}$ = 27.1 MHz and $a_3^{(1)}$ = 52.6 MHz, values obtained by comparing the phenomenology and experiment (the elastic constants were taken from[14]) we obtain for the spin-lattice relaxation time $\tau = (2N_S W_X)^{-1}$ (N_S is the number of neighbors of the PC)

of an F centers in KCL the value $\tau = 72$ min for $v = 4.09 \times 10^5$ cm/sec and $v_t = 2.312 \times 10^5$ cm/sec,[14], which is in fair agreement with the experimentally measured value[15] 83 min. Thus, the uniform-deformation model describes spin-lattice relaxation sufficiently well.

6. CONCLUSION

The microscopic calculation of piezo-hyperfine constants breaks up into two independent problems. One is the influence of the electronic structure of the center on the PHFI. This problem is solved by standard methods of quantum mechanics and expresses the PHFI constants in terms of the ion displacements under the influence of the external stresses. The second problem is that of the microscopic theory of elasticity, which should yield the dependence of the ion displacements near the defect on the external stresses. It is not trivial. The usual uniform-deformation approximation (1) does not describe all the experimental facts. The introduction of phenomenological local elastic constants is also a rather crude approximation, since it cannot describe, for example, the azimuthal effect in the PHFI. Finally, we note that the PHFI constants should depend on the temperature, and the pertinent experiments are of interest. This dependence can be taken into account theoretically by making use of the spin-phonon interaction and the anharmonicity (the expansion of the lattice).

We have shown in this paper that the experimental data on PHFI can be explained completely only by taking into account the nonuniformity of the deformation near the defects. We have also obtained fundamental formulas for a microscopic calculation of the PHFI constants.

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