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TEMPERATURE DEPENDENCE OF THE HYPERFINE INTERACTION CONSTANTS IN F CENTERS

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The temperature dependence of the hyperfine interaction constants of F centers in KCl and LiF was investigated in the temperature interval 4.2–570°K. Unlike KCl, in LiF a qualitative difference was observed between the temperature dependences of the constants in different coordination spheres. The performed theoretical calculation is in agreement with experiment. The possibility of different behaviors of the hyperfine-interaction constants with variation of temperature for different spheres is demonstrated.

INTRODUCTION

AN investigation of the temperature dependence of the hyperfine interaction constants has made it possible to assess the character of the spin–phonon interaction. The most accurate data on the hyperfine interaction constants can be obtained by the electron nuclear double resonance (ENDOR) method.[1-6] It is significant that when this procedure is used it is possible to obtain the values of the constants for several coordination spheres surrounding the local electronic center (LEC).

In the present paper, the ENDOR method is used to study the temperature dependence of the hyperfine interaction constants of F centers in KCl and LiF crystals. A theoretical interpretation of the obtained results is presented.

EXPERIMENT

For the measurements we used single crystals of KCl and LiF grown by the Kyropoulos method in an air atmosphere. The F centers in KCl were obtained by electrolytic coloring, and in LiF by γ irradiation. In both cases, the F-center concentration was $\sim 10^{18}$ cm^{-3}.

The investigations were performed with an ENDOR superheterodyne spectrometer operating in the 3-cm band.[7] The low temperature measurements were made using a cryostat described in [5]. For the high-temperature measurements we used the device shown in Fig. 1. In this device, a stable temperature was maintained as a result of good thermal insulation (mica, teflon, quartz, ceramic) and stabilization of the power supply, (UIP-1). The resonator was not cooled specially during the operation, and its temperature did not exceed 50–60°C.

To study the temperature dependence, we plotted the ENDOR spectra at angles zero and 45° between the magnetic field and the [100] crystallographic axis. In KCl the temperature dependence of the hyperfine interaction constants was investigated in coordination spheres I–IV. Figure 2 shows the results for the isotropic constant a of coordination spheres I and II. Coordination spheres III and IV were investigated on the temperature interval 4.2–77°K. We were unable to observe a change in the

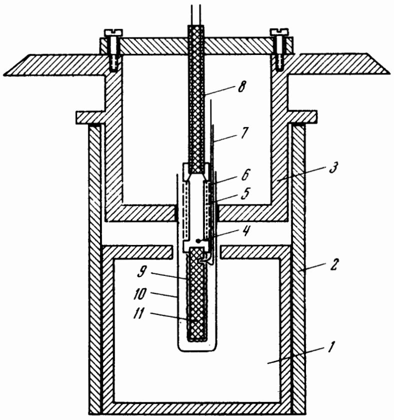

FIG. 1. Setup for high-temperature measurements: 1 – resonator at TE_{011} mode; 2 – cup, 3 – holder with dial for reading the angles, 4 – copper base of heater, 5 – heater, 6 – heat insulator (mica), 7 – thermocouple (copper-constantan), 8 – ceramic rod, 9 – teflon ribbon, 10 – quartz finger, 11 – sample.

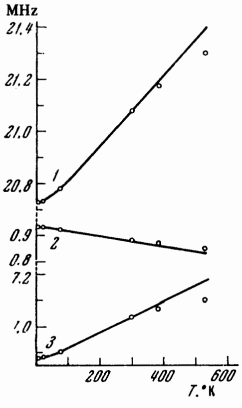

FIG. 2

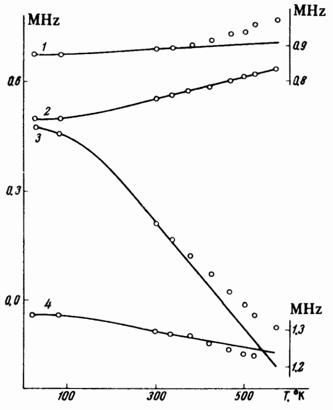

FIG. 3

FIG. 2. Temperature dependence of the hyperfine interaction constants (in MHz) of the F centers in KCl: 1 – $a_I(T)$, 2 – $b_I(T)$, 3 – $a_{II}(T)$. Solid lines – theory, points – experiment.

FIG. 3. Temperature dependence of hyperfine interaction constants of F centers in LiF: 1 – $a_{VI}(T)$ (right-hand scale), 2 – $a_{III}(T)$ (left-hand scale), 3 – $a_{IV}(T)$ (left-hand scale), 4 – $a_{VIII}(T)$ (right-hand scale).

constants for these spheres.

In LiF [8] in coordination spheres III and IV, when the temperature increased from 4.2 to 570°K, the anisotropy of the hyperfine interaction constant increased while in IV and VIII it decreased. Plots of the variation of the constants are shown in Fig. 3. In coordination spheres V and IX, in the indicated interval of temperature variation, no change was observed in the constants.

In both crystals, the temperature variation of the anisotropic constant of the hyperfine interaction, b, is weaker than that of the isotropic constant. The constant b always decreases with increasing temperature.

To describe the experimental results, we used for the ENDOR frequencies an expression corresponding to a spin Hamiltonian of axial symmetry.[5] The deviation, characteristic of spheres VI and VIII, of the symmetry of the spin Hamiltonian from axial symmetry, was not taken into account in order to simplify the reduction of the results. Allowance for this deviation improves the hyperfine constant of the interactions by not more than 1%, which is insignificant in the study of the general course of the temperature dependence.

THEORY. DISCUSSION OF RESULTS

With sufficient accuracy (for our purpose), the ENDOR frequencies can be obtained from the spin Hamiltonian

$$\mathcal{H} = \sum_n \Big(g_{\text{nuc}} \beta_{\text{nuc}} \mathbf{H}_0 \hat{\mathbf{I}}_n + a_n \hat{\mathbf{S}} \hat{\mathbf{I}}_n + \sum_{p,q} D_{npq} \hat{S}_q \hat{I}_{np} \Big). \tag{1}$$

The first term in the brackets is the Zeeman energy of the n-th nucleus, and the second and third terms are the energies of the isotropic and anisotropic hyperfine interactions.

Let us expand the hyperfine constants (HFC) in a series in the independent differences of the displacements $\mathbf{u}_{nl} = \mathbf{u}_n - \mathbf{u}_l$:

$$a_n = a_n^{(0)} + \sum_l \left(\frac{\partial a_n}{\partial \mathbf{u}_{nl}} \right)_0 \mathbf{u}_{nl} + \frac{1}{2} \sum_{l,l'} \left(\frac{\partial^2 a_n}{\partial \mathbf{u}_{nl} \partial \mathbf{u}_{nl'}} \right)_0 \mathbf{u}_{nl} \mathbf{u}_{nl'} + \ldots,$$

$$D_{npq} = D_{npq}^{(0)} + \sum_l \left(\frac{\partial D_{npq}}{\partial \mathbf{u}_{nl}} \right)_0 \mathbf{u}_{nl} + \frac{1}{2} \sum_{l,l'} \left(\frac{\partial^2 D_{npq}}{\partial \mathbf{u}_{nl} \partial \mathbf{u}_{nl'}} \right)_0 \mathbf{u}_{nl} \mathbf{u}_{nl'} + \ldots \tag{2}$$

In order to obtain the experimentally observed quantities, it is necessary to average (2) over all the phonons. It is easy to show (see, for example, [9]) that in this case

$$\langle \mathbf{u}_{nl} \rangle = 0,$$

$$\langle \mathbf{u}_{nl} \mathbf{u}_{nl'} \rangle = \delta_{ll'} \frac{4\hbar}{NM} \sum_{\mathbf{k},s} \left[\left(\exp\left\{ \frac{\hbar \omega_s(\mathbf{k})}{k_{\mathrm{B}} T} \right\} - 1 \right)^{-1} + \frac{1}{2} \right] \frac{\sin^2(\mathbf{k}\mathbf{R}_l^{(0)}/2)}{\omega_s(\mathbf{k})}. \tag{3}$$

Here **k** is the wave vector, s = 1, 2, 3 is the number of the oscillation branch, $\omega_s(\mathbf{k})$ is the frequency of the phonon with given **k**, $\mathbf{R}_l^{(0)}$ is the distance between the undisplaced nuclei n and l, $M = (M_+ + M_-)/2$, M_+ and M_- are the masses of the positive and negative ions, N is the total number of atoms in the crystal, and k_{B} is Boltzmann's constant.

The long-wave approximation used in [10] to calculate the sum over k is suitable only at low temperatures. To obtain the temperature dependence of the HFC in a wider range, we shall use the Debye approximation. Then, replacing $\sin^2(\mathbf{k}\cdot\mathbf{R}_l^{(0)}/2)$ by its mean value ½, we obtain

$$\langle \mathbf{u}_{nl}^2 \rangle = \frac{18\hbar}{M\omega_D^3} \int_0^{\omega_D} \left[\left(\exp\left\{ \frac{\hbar\omega}{k_{\mathrm{B}} T} \right\} - 1 \right)^{-1} + \frac{1}{2} \right] \omega \, d\omega$$

$$= \frac{18\hbar^2}{M k_{\mathrm{B}} \Theta} \int_0^1 \left(\frac{1}{e^{\Theta t/T} - 1} + \frac{1}{2} \right) t \, dt. \tag{4}$$

Here ω_{D} is the Debye frequency and Θ is the Debye temperature of the crystal. If we put

$$\frac{1}{2} \sum_l \left(\frac{\partial^2 a_n}{\partial \mathbf{u}_{nl}^2} \right)_0 \equiv a_n^{(2)}, \quad \frac{1}{2} \sum_l \left(\frac{\partial^2 D_{npq}}{\partial \mathbf{u}_{nl}^2} \right)_0 \equiv D_{npq}^{(2)}, \tag{5}$$

then the measured HFC are given by

$$a_n(T) = a_n^{(0)} + a_n^{(2)} \langle \mathbf{u}_{nl}^2 \rangle,$$

$$D_{npq}(T) = D_{npq}^{(0)} + D_{npq}^{(2)} \langle \mathbf{u}_{nl}^2 \rangle. \tag{6}$$

Since on the average the symmetry of the crystal is not changed by the oscillations, the ENDOR frequencies can be obtained in accordance with the usual rules.[11] For spheres having axial symmetry, the frequencies of the ENDOR transitions are given by

$$h\nu(T) = g_{\text{nuc}} \beta_{\text{nuc}} H_0 \pm {}^1\!/_2 [a(T) + b(T)(3\cos^2\alpha - 1)], \tag{7}$$

where $b(T) = {}^1\!/_2 D_{33}(T)$ and α is the angle between the symmetry axis and the external magnetic field $\mathbf{H}_0$ (we shall henceforth omit the index n for simplicity).

Comparing the experimentally obtained a(T) and b(T) with (6), we can determine $a^{(0)}$ and $b^{(0)}$—the HFC in the rigid lattice—and $a^{(2)}$ and $b^{(2)}$—the sums of the second derivatives of the HFC with respect to the difference of the displacements (owing to the existence of zero-point oscillations, the HFC in a rigid lattice does not coincide with the HFC at 0°K). To determine these parameters in KCl and LiF, we used the data of the present work and of [8] at 20 and 300°K. The obtained parameters for different coordination spheres are listed in the table. The theoretical curves a(T) at these values of the parameters and the experimentally measured HFC are given in Figs. 2 and 3.

To plot the theoretical b(T) curve for the first coordination sphere of KCl we used $b^{(0)} = 0.92$ and $b^{(2)} = 0.46$. For other spheres, the temperature dependence of b(T) is less sharply pronounced, and one can only state that b decreases in all spheres with increasing temperature. The fact that b always decreases with increasing temperature, while a can either increase or decrease, depending on the number of the coordination sphere, does not agree with the results of [10], where a and b have a similar temperature dependence in any sphere. This conclusion is connected apparently with

Values of parameters $a^{(0)}$ and $a^{(2)}$.

	KCl		LiF			
	I	II	III	IV	VI	VIII
$a^{(0)}$, MHz	20,645	6,844	0,436	0,77	0,86	1,387
$a^{(2)}$, MHz/Å^2	3,21	1,37	2,62	—12,72	0,693	—1,98

the assumption made that all the forces are short-range, an assumption which is hardly valid for the anisotropic hyperfine interaction.

Calculation using the "detailed" wave function of the effective-mass method in the approximation of a simple band structure, but without assuming short-range forces, shows that $a^{(2)}$ and $b^{(2)}$ have opposite signs at certain distances from the defect. The HFC can be obtained from the following expressions:

$$a = \frac{8\pi}{3}\frac{\mu\mu_{\text{nuc}}}{SI}|\psi(\mathbf{R})|^2,$$

$$b = \frac{\mu\mu_{\text{nuc}}}{SI}\int|\psi(\mathbf{r})|^2\frac{3(\mathbf{r}-\mathbf{R})_z^2-|\mathbf{r}-\mathbf{R}|^2}{|\mathbf{r}-\mathbf{R}|^5}\,d\tau \tag{8}$$

(**R**—distance from the considered nucleus to the center of the vacancy). The detailed wave function is chosen in the form

$$\psi(\mathbf{r}) = U_0(\mathbf{r})\sqrt{\alpha^3/\pi}\,e^{-\alpha r}, \tag{9}$$

where $U_0(\mathbf{r})$ is the Bloch periodic factor.

If in (8) the rapidly-oscillating function $U_0(\mathbf{r})$ is taken outside at the average value, then only the integral over the smooth wave function remains. It was calculated in [12], and as a result we have

$$a = \frac{8}{3}\frac{\mu\mu_{\text{nuc}}}{SI}U_0^2(\mathbf{R})\,\alpha^3 e^{-2\alpha R},$$

$$b = \frac{\mu\mu_{\text{nuc}}}{SI}\frac{\overline{U_0^2}}{R^3}\left[1-e^{-2\alpha R}\left(1+2\alpha R+\frac{(2\alpha R)^2}{2}+\frac{(2\alpha R)^3}{6}\right)\right]. \tag{10}$$

In the adiabatic approximation it can be shown that the temperature dependence of the HFC is determined entirely by the dependence of the parameters of the smooth function on T. Differentiating (10) with respect to temperature, we obtain

$$\frac{da}{dT} = \frac{8}{3}\frac{\mu\mu_{\text{nuc}}}{SI}U_0^2(\mathbf{R})\,\alpha^2 e^{-2\alpha R}(3-2\alpha R)\frac{d\alpha}{dT},$$

$$\frac{db}{dT} = -\frac{8}{3}\frac{\mu\mu_{\text{nuc}}}{SI}\overline{U_0^2}R\alpha^3 e^{-2\alpha R}\frac{d\alpha}{dT}. \tag{11}$$

It follows from (11) that b varies monotonically with temperature. Yet da/dT reverses sign at $2\alpha R = 3$. Estimating the value of α by comparing $|\psi|^2$ in the coordination spheres I and III of KCl and LiF, we find that the derivatives da/dT and dB/dT have opposite signs already in coordination sphere I. This result agrees with experiment for close coordination spheres.

In remote coordination spheres of LiF, as seen from experiment, da/dT sometimes reverses sign. This is apparently connected with the complicated structure of the conduction band. Let the minima of the conduction band in **k**-space be in the equivalent points $\mathbf{k}_{0j}$. Then

$$\psi(\mathbf{r}) = \sum_j U_{\mathbf{k}_{0j}}(\mathbf{r})\exp(i\mathbf{k}_{0j}\mathbf{r})\varphi_j(\mathbf{r}), \tag{12}$$

where $\varphi_j(\mathbf{r})$ is the smoothed wave function of the single-valley problem. If such a case is realized in the crystal, then both the wave function and its derivative with respect to the parameters can reverse sign, depending on **r**. This leads to different behaviors of a(T), depending on the number of the coordination sphere.

A study of the temperature dependences of the HFC makes it possible to assess the magnitude of the thin-phonon interaction in crystals. Knowing $a^{(2)}$ and $b^{(2)}$ we can estimate, for example, the time of the spin-lattice relaxation of the F centers for two-phonon processes. If we use the calculation of [13], then we obtain for the relaxation times of the F centers in KCl a value which is larger by two orders of magnitude than that observed in experiment[14].

In conclusion we note that the deviation of the theoretical curves from experiment at high temperatures exceeds experimental error and is probably connected with the fact that at high temperatures it is necessary to take into account the next higher terms in the expansions (2).

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