

Optical detection of the EPR of F centers in isotope-enriched $^{85}\text{RbCl}$ and $^{87}\text{RbCl}$ crystals

P. G. Baranov, Yu. P. Veshchunov, and N. G. Romanov

A. F. Ioffe Physico-Technical Institute, USSR Academy of Sciences

(Submitted 4 March 1980)

Pis'ma Zh. Eksp. Teor. Fiz. 32, No. 1, 3-6 (5 July 1980)

Direct experiments, which make it possible to establish the nature of the EPR line widths of F centers in the relaxed, excited state (RES) and to conclude that the wave function of the RES is localized, were performed. The g -factor shifts for the RES of F centers in alkali-halide crystals are explained.

PACS numbers: 61.70.Dx, 76.30.Mi,

The F centers are the simplest localized electron centers in alkali-halide crystals (AHC); however, the spatial distribution of the wave function of these centers in the relaxed, excited state (RES) and the broadening of the EPR lines in the RES has not been determined unambiguously. The RES of the F centers in AHC was investigated¹⁻⁵ by using the method of optical detection of the EPR. In this investigation we have obtained for the first time the EPR spectra in the ground state (GS) and in the RES of the F centers in RbCl crystals with the separated ^{85}Rb and ^{87}Rb isotopes.

An apparatus,³ which made it possible to record the luminescence intensity variation of the F centers during resonance, was used for optical detection of the EPR. Figure 1 shows the optically recorded EPR spectra of the F centers in the $^{87}\text{RbCl}$ (a) and $^{85}\text{RbCl}$ (b) crystals (98% enrichment) and in the RbCl crystal with a natural isotope content (72% ^{85}Rb with a nuclear spin $I = 5/2$ and nuclear magnetic moment

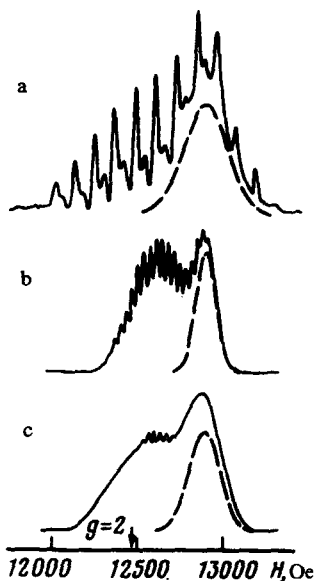


FIG. 1. Optically recorded EPR spectra (absorption lines) of the F centers in the $^{87}\text{RbCl}$ (a), $^{85}\text{RbCl}$ (b), and RbCl (c) crystals. $T = 1.8$ K, $\nu = 43.9$ GHz; $H \parallel [111]$.

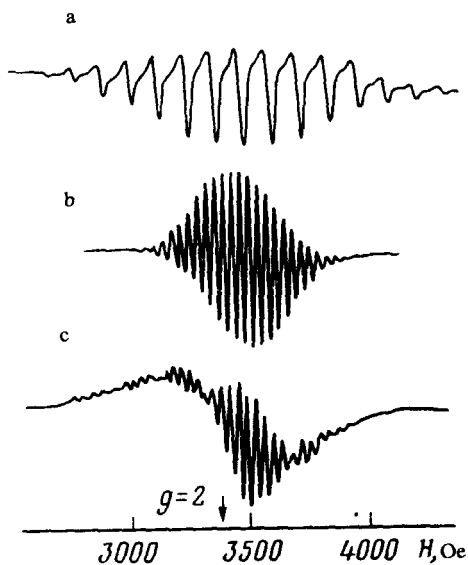


FIG. 2. EPR spectra (derivatives of the absorption lines) for the ground state of the F centers in the $^{87}\text{RbCl}$ (a), $^{85}\text{RbCl}$ (b), and RbCl (c) crystals. $T = 300$ K, $\nu = 9.2$ GHz, $H \parallel [111]$.

$\mu_N = 1.35$ and 28% ^{87}Rb with $I = 3/2$ and, $\mu_N = 2.74$). The spectra are a superposition of the GS and RES signals of the F centers (the latter are represented by dashed lines in Fig. 1). A large difference in the spectra for crystals with different rubidium isotope content indicates that the superhyperfine interaction (SHFI) of the F -center electron with the magnetic moments of rubidium nuclei influences the EPR line widths for the ground state and the RES. The superhyperfine structure (SHFS) in the optically recorded spectra (Fig. 1) is identical to that observed in the ground state of the F centers when the ordinary EPR method is used (Fig. 2). So far as we know, the SHFS in ionic crystals has been recorded for the first time by using the method of optical detection of the EPR.

The wave function is highly localized near an anion vacancy for the ground state of the F centers in AHC, and the SHFI with the nuclei of the six nearest Rb^+ ions is considerably greater than the interaction with the nuclei of the ions of the other coordination spheres.⁶ The ratio of the widths for the envelopes of the EPR lines of the ground state of the F centers in $^{87}\text{RbCl}$ and $^{85}\text{RbCl}$ is equal to the theoretical value of 2.2, which was obtained by assuming that these widths are determined only by the SHFI with the Rb^+ ions.

The EPR lines of the F centers in the relaxed excited state, which were recorded for the $^{87}\text{RbCl}$ and $^{85}\text{RbCl}$ crystals, have a Gaussian shape. The ratio of the RES line widths for these crystals, equal to 2.15 ± 0.1 , is almost the same as that for the ground state. Thus, the width and shape of the EPR lines for the RES of the F centers in RbCl is determined by the SHFI with the Rb^+ ions. If the RES of the F centers is considered to be a diffuse state,⁵ then SHFI with the Cl^- ions should occur in the EPR line width, which decreases the ratio of the line widths to 1.93 for the RES of the F centers in $^{87}\text{RbCl}$ and $^{85}\text{RbCl}$. These considerations allow us to conclude that the wave function of the RES of the F centers is apparently not diffuse, and the EPR line width

is determined by the SHFI with the six nearest rubidium ions. This is also confirmed by the results of an optical detection of the EPR in the RES of the F centers in ^{41}KCl crystals for which a narrowing of the RES line compared with the natural KCl was observed. Such a narrowing should not occur in a diffuse wave function of the RES of the F centers.

A decrease of the linewidths of the RES of the F centers in RbCl compared with the linewidths for the ground state indicates that a delocalization of the electron in the second and third coordination spheres increases. The constants of the isotropic SHFI with the nuclei of the Rb^+ ions of the first coordination sphere for the RES of the F centers in RbCl, which were obtained from the EPR line widths, are equal to 130 MHz (^{87}Rb) and 39 MHz (^{85}Rb).

Additional lines, which require further study, were observed in the optically recorded EPR spectra of the F centers in KCl and RbCl.

Large negative shifts of the g factors relative to the g factor of a free electron were observed in the RES of the F centers in alkali-halide crystals. These shifts are drastically different in different crystals and in many cases exceed the shifts in the ground state by an order of magnitude. The g -factor shifts in the RES of the F centers can be accounted for if we assume that the RES is a localized $2s$ state. Let us represent the wave function of the F centers in the RES as a determinant comprised of a hydrogen-like $2s$ function and wave functions of the ligands. This multielectron wave function can be replaced by a single wave function which can be obtained by orthogonalizing the $2s$ function to the wave functions of the ligands. The F -center wave function $|F^{\text{RES}}\rangle$ obtained in this manner contains an impurity of the s and p shells of the ligands, where the p shells are the main contribution to Δg . The Δg_i shift caused by the

TABLE 1.

Crystal	teor	exp
NaCl	-0 057	-0 032
KF	-0 012	-0 008
KCl	-0 024	-0 032
KBr	-0 246	-0 129
KI	-0 390	-0 372
RbCl	-0 114	-0 067
RbBr	-0 186	-0 162
RbI	-0 474	-0 368
CsI	-0 83	-0 60

ith ion can be calculated in the second-order perturbation theory with allowance for the spin-orbit interaction in the ligands⁷

$$\Delta g_i = \frac{4 \beta^2 Z_i}{\Delta E} \langle F^{\text{RES}} | \frac{L_z^2}{r^3} | F^{\text{RES}} \rangle, \quad (1)$$

where β is the Bohr magneton and Z_i is the effective nuclear charge.⁸

We used the average of the first excited RES level⁹ E_1 and of the lower RES level under the conduction band⁶ E_2 as the average excitation energy ΔE . We assumed that $\Delta E \approx E_2$ for the rubidium and cesium halides since E_1 for these crystals is not known. In the calculations we used the anisotropic SHFI constants A_p of the F centers in the RES, since the same integrals as those in Eq. (1) are used in the expression for A_p . We can see from the function $|F^{\text{RES}}\rangle$ that the values of A_p for the RES amount to about 3% of the isotropic SHFI constants A_s . Estimates of the A_s constants for the RES of the F centers were given in Ref. 3. The results of the calculations show that this analysis allowed us to correctly predict the order of magnitude and the relative variation of Δg for different alkali-halide crystals (see Table I).

¹Y. Ruedin, P. A. Schnegg, C. Jaccard, and M. A. Aegerter, Phys. Status Solidi B **54**, 565 (1972).

²L. F. Mollenauer and S. Pan, Phys. Rev. B **6**, 772 (1972)

³P. G. Baranov, Yu. Veshchunov, and N. G. Romanov, Fiz. Tverd. Tela **20**, 2622 (1978) [Sov. Phys. Solid State **20**, 1516 (1978)].

⁴P. G. Baranov, Yu. P. Veshchunov, and N. G. Romanov, Fiz. Tverd. Tela **20**, 3627 (1978) [Sov. Phys. Solid State **20**, 2096 (1978)].

⁵H. J. Reyher, K. Hahn, Th. Vetter, and A. Winnaker, Z. Phys. B **33**, 357 (1979).

⁶Physics of Color Centers, edited by W. B. Fowler, Academic, New York-London, 1968.

⁷F. Adrian, Phys. Rev. **107**, 488 (1957).

⁸R. G. Bannes and W. H. Smith, Phys. Rev. **93**, 95 (1954).

⁹I. Schneider, Abstr. Int. Conf. on Defects in Insulating Crystals, Gatlinburg, 1977, p. 385.