Anisotropic spin-spin interaction of Dy^{3+} ion pairs associated with a color center in crystal CaF_2

S. A. Kazanskiĭ
State Optical Institute

(Submitted 17 February 1979)

Pis'ma Zh. Eksp. Teor. Fiz. **29**, No. 9, 525–528 (5 May 1979)

While studying the EPR of complex color centers in a CaF_2 :Dy crystal by means of an optical detection method we observed an EPR signal with an anomalously high value of $g_{\parallel} = 36.4 \pm$ ($g_{\perp} < 10$) which is attributed to pairs of Dy^{3+} ions that are coupled by anisotropic ferromagnetic exchange interaction.

PACS numbers: 61.70.Dx, 76.30.Mi

Antiresonance (AR) in CaF_2 :Dy crystals with color centers (CC) was observed as sharp emission lines in a broad (400–550 nm) CC absorption band.[1] Based on a study of the effect of an external field on CC absorption bands with AR, it was shown that AR occurs as a result of interaction between a complex CC and an associated rare-earth (RE) impurity.[2] According to existing notions, a CC in undoped CaF_2 crystals is modeled as an F_2 ⟨100⟩-center—two adjacent interacting anion vacancies filled by two electrons–and its ground state consists of the $^1S_0$ singlet, such that the CC exhibits no natural paramagnetism. However, exchange interaction with a RE impurity—Dy^{3+} ions–leads to the existence in an external magnetic field $\mathbf{H}_0$ of a small induced magnetic moment in the CC ground state which, in turn, determines the existence of magnetic circular dichroism (MCD) $\Delta\kappa$ in the CC absorption band. The magnitude of $\Delta\kappa(H)$ may be used to judge the extent of the spin projection of an RE impurity ground state in the $\mathbf{H}_0$ direction; $\Delta\kappa = 0$ at $H_0 = 0$ and it saturates at $H_0 > 10$ kgauss. Estimates of the averaged value of the $\bar{g}$-factor of an RE impurity from the field dependence $\Delta\kappa(H) = \Delta\kappa_{\max} \operatorname{th}(\bar{g}\beta H/2kT)$ at $T \approx 8.6$ °K in disordered crystals are in a range $16 < \bar{g} < 30$. At $T = 1.8$ and 4.2 °K $\Delta\kappa(H)$ exhibits hysteresis which attests to the large spin-lattice relaxation time of the RE impurity in the 0.1–5 kgauss fields (~ 10 min at $H_0 = 5$ kgauss). As the magnetic field decreases below 10 kgauss, $\Delta\kappa$ remains the same down to 0.1 kgauss and only at a lower value of H_0 does it rapidly decrease to zero which corresponds to the establishment of a thermal equilibrium in a system of spin sublevels of the RE impurity due evidently, to cross-relaxation.

In this paper we report on an investigation of the EPR of the ground state of an RE impurity that is associated with CC in the case of MCD optical detection in a CC absorption band at $T = 1.8$ °K. Ordered CaF_2:Dy specimen with CCs($n_{Dy} \sim 10^{19}$, $n_{cc} \sim 10^{16}$–10^{17} cm^{-3}) measuring $2 \times 2 \times 2$ mm^3 were placed in a cylindrical microwave resonator (TE_{01}, $\lambda = 8$ mm, $Q = 5000$) with apertures that allow passage of probing light. One of the experimental setups was as follows: a specimen was kept in a field $H_0 = 10$ kgauss; subsequently, microwave power was turned on ($P_e = 1$–400 mW) and the magnetic field 10 kgauss→0 was scanned at a rate $v = 0.1$–0.2 kgauss/min. Moreover, $\Delta\kappa(H)$ at the resonant value of H_0 was shown to contain special features (EPR signals) in the form of steps (Fig. 1) that correspond to the disorientation of a portion

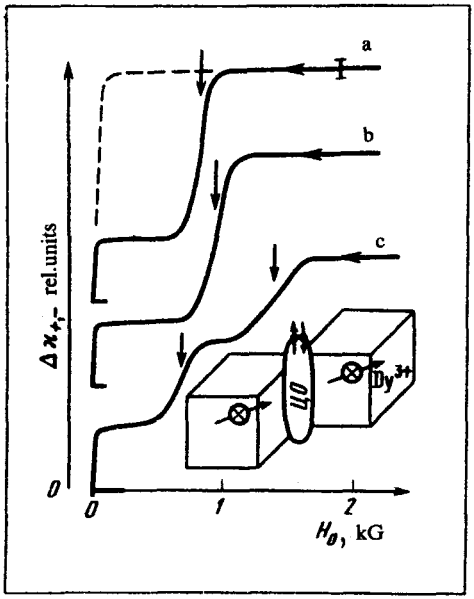

FIG. 1. EPR spectrum: $P_e = 300$ mW, $\nu_e = 35.6$ Hz. Orientation: a—$\mathbf{H}_0 \| \mathbf{C}_2$; b—$\mathbf{H}_0 \| \mathbf{C}_4$; c—$\mathbf{H}_0 \| \mathbf{C}_3$. Resonant field H_0 and scanning direction, $v = 0.1$ kgauss/min. Dotted line shows the function $\Delta\kappa(H)$ at $P_e = 0$.

of spins of an RE impurity associated with a CC. The step height was linearly dependent on scanning time and microwave power (at small powers), and was saturated up to $\sim 80\%$ at $P_e = 400$ mW. Analysis of the well-defined orientation dependence of the EPR spectrum shows that the principal axis of the g-tensor of an RE impurity ground state is directed along the C_2-axis of a crystal, moreover $g_{\|} = 36.4 \pm 1$. The remaining g-tensor components are valued at $|g_{\perp}| < 10$.

Since the critical value of the g-factor for a doubly degenerate ground state of a single Dy^{3+} ion in a local crystal field is $g \sim 20$[3] (the $^6H_{15/2}$ term of configuration $4f^9$), it may be concluded that the spectrum of optically-detected EPR contains a pair of Dy^{3+} ions associated with a CC which replaces two adjacent Ca^{2+} ions (along the C_2 axis) in the cation sublattice (see the center model in Fig. 1). As is well known,[4] the spin-spin interaction of two Kramers ions with effective spin $S = 1/2$ leads to the occurrence of triplet and singlet states of the pair. If, as in our case, the interaction is

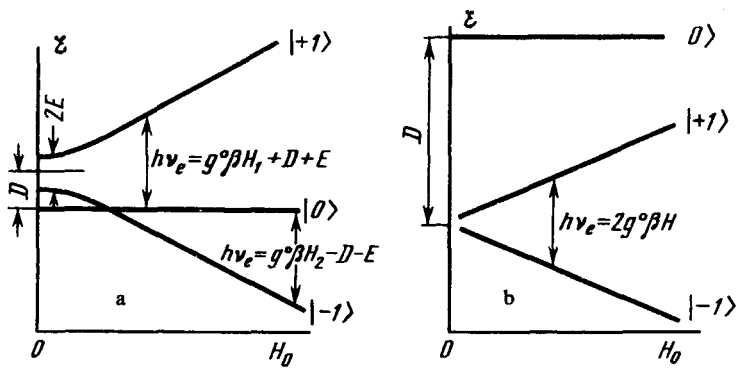

FIG. 2.

ferromagnetic, the triplet state $S = 1$ is situated at a lower energy. Interaction anisotropy characterized by parameters D and E leads to splitting of the triplet state in a zero magnetic field (Fig. 2a) and is normally small, thus the EPR spectrum of ion pairs contains allowed transitions $|-1\rangle \leftrightarrow |0\rangle$ and $|0\rangle \leftrightarrow |+1\rangle$ for a somewhat larger and smaller— than for isolated ions—values of the resonant field H_0. The optical EPR spectrum of a Dy^{3+}—Dy^{3+} pair contains only the forbidden transition $|-1\rangle \rightarrow |+1\rangle$ with a doubled g-factor with respect to an isolated ion (Fig. 2b). Allowed transitions were not observed, whence $D > 4$ cm^{-1}.[1)] Preservation of the magnitude of the spin moment of a Dy^{3+}—Dy^{3+} pair as the magnetic field decreases from 10 to 0.1 kgauss in experiments without microwave input enables one to determine a value of the level splitting $|-1\rangle, |+1\rangle$ in a zero magnetic field: $2E < 0.15$ cm^{-1}. The unusually high value of D (and the small value of E) for a Dy^{3+}–Dy^{3+} pair is associated with a large magnitude and strong anisotropy of the g-factor of single Dy^{3+} ions,[4] which in certain cases may be very large[4]: $g_{\parallel}^0 \sim (16-20) \gg g_{\perp}^0 \; 0$.

Our analysis of the large spin-lattice relaxation time and the low intensity of EPR lines detected optically shows that $g_{\perp}^0 \sim 0$ for each Dy^{3+} ion in a pair. This means that the doubled—in comparison with a single ion—magnetic moment of the ground state of a Dy^{3+}—Dy^{3+} pair associated with a CC may be oriented only along the axis which connects these RE ions (C_2 axis, see the center model in Fig. 1) independently of magnetic field orientations.

The author thanks Corresponding-Member of the USSR Academy of Sciences P. P. Feofilov for attention to this work.

[1)]To evaluate "D", experiments were carried out with a magnetic field scan from 0 to ~ 5 kgauss (motion along the lower half of the hysteresis loop of $\Delta\kappa(H)$[2] when the $|+1\rangle$ level is populated). We should note that in the approximation of dipole-dipole interaction among the Dy^{3+} ions the value of D is approximately 2.5 cm^{-1}. Experimental estimates indicate the exchange nature of the interaction.

[1]V.A. Arkhangel'skaya and P.P. Feofilov, Opt. Spektrosk. **28**, 1219 (1970).
[2]S.A. Kazanskiĭ, ibid. **43**, 466 (1977) [**43**, 275 (1977)].
[3]M.V. Eremin, R.K. Luks and A.L. Stolov, Fiz. Tverd. Tela **12**, 3473 (1970) [Sov. Phys. Solid State **12**, 2820 (1970)].
[4]A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970 (Russian translation, M., Mir, 1972, vol. 1, pp. 175, 554, 561).