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Paramagnetic Resonance of the V_F Center in CaF_2[†]

JEROME SIERRO[*]
Argonne National Laboratory, Argonne, Illinois

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Natural CaF_2 crystals subjected to x rays at 77°K and then warmed to a temperature above 138°K contain V_F centers. The electronic structure of this electron-deficient center has been investigated by electron paramagnetic resonance. The parameters of the appropriate spin Hamiltonian have been determined. The center appears to consist of an F_2^- molecule ion associated with a Ca^{++} vacancy.

INTRODUCTION

An investigation by Hayes and Twidell[1] showed that the self-trapped hole center (V_K center[2]) can be found by x irradiation at low temperature in synthetic CaF_2 crystals. The molecule ion is aligned along [001] directions, where the F^--F^- distance is least, and has axial symmetry. The centers decay at 138°K and, in contrast to the alkali fluorides, no F_2^- molecule ions with a "bent" molecular bond due to a nearby vacancy (V_F centers[3]) are formed.

The work presented here describes the production and properties of the V_F center in x-irradiated *natural* crystals of fluorite.

EXPERIMENT

The single crystals of fluorite used in this experiment were natural samples of different origin. Most of them were colored and contained impurities such as Sr, Y, Mn, Gd and other rare earths. The crystals were first annealed for a few minutes at about 350°C to remove some paramagnetic centers already present. The samples were irradiated at different temperatures ranging from 77 to 300°K with x rays from a Machlett tube (50 kV, 50 mA, tungsten target) at a distance of $\frac{1}{2}$ in. from the tube window, or with a Co^{60} source of 4 kCi.

The resonance measurements were performed with a Varian EPR spectrometer model V-4500, with 100-kc/sec field modulation and a 6-in. electromagnet. Through the use of a variable temperature device (Varian V-4547 gas cryostat) measurements were made from liquid-nitrogen temperature up to 100°C. A copper-constantan thermocouple just outside the EPR cavity and directly below the sample was used to measure the temperature with an accuracy of ±5°C. The microwave frequency was measured with a calibrated cavity wavemeter (Hewlett Packard X532B) and the magnetic field with an NMR gaussmeter (Harvey-Wells 6501) in conjunction with a frequency counter (Syston-Donner 1037).

The fluorite crystals cleave along (111) planes and the samples used were of good enough quality to be oriented by cleavage. The crystal to be measured was mounted on the end of a Lucite rod, the axis of which could be tipped with respect to the magnetic field. The crystal could be further oriented by rotation about this axis.

The decay temperatures of the centers were determined in the following way. After the centers were produced, the intensity of the EPR spectrum was followed as a function of the temperature using a pulse-annealing technique. The sample was warmed to a given temperature, held there for 5 min, cooled to liquid-nitrogen temperature, and the EPR spectrum remeasured. This procedure was repeated at successively higher temperatures. The intensity of the EPR spectrum was plotted against annealing temperature and the point of maximum rate of change in the intensity was defined as the decay temperature.

RESULTS

Before irradiation, most of the samples showed an EPR spectrum due to Gd^{3+} in cubic symmetry. After x irradiation at 77°K the Gd^{3+} spectrum nearly disappeared and a strong spectrum of V_K centers appeared.

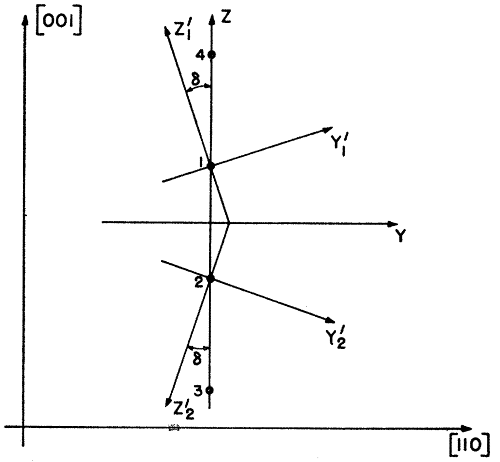

FIG. 1. The symmetry of the V_F center in CaF_2. The axes x,y,z are the orthorhombic axes corresponding to the over-all symmetry. The axes x_i', y_i', z_i' are the principal axes of the hyperfine tensor $T^{(i)}$.

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[*] Present address: University of Geneva, School of Physics, Geneva, Switzerland.

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[2] T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957); T. O. Woodruff and W. Känzig, *ibid.* **5**, 268 (1958); R. Gazzinelli and R. Mieher, Phys. Rev. Letters **12**, 644 (1964).

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TABLE I. Fitted parameters of the spin Hamiltonian and decay temperature for the V_K and V_F centers in LiF and CaF_2.

Crystal	Center	$g_{\parallel}$	$g_{\perp}$	$T_1=T_2$ $T_{x'x'}=T_{y'y'}$ (G)	$T_1=T_2$ $T_{z'z'}$ (G)	$T_3=T_4$ $T_{xx}=T_{yy}$ (G)	$T_3=T_4$ T_{zz} (G)	δ (deg)	Decay temp. (°K)
LiF	V_K[a]	2.003 ± 0.001	2.023 ± 0.001	59 ± 1	887 ± 1				120
	V_F[b]	2.001 ± 0.002	2.023 ± 0.002	56 ± 10[c]	915 ± 1			4.2 ± 0.5[c]	230
CaF_2	V_K[d]	2.001 ± 0.001	2.020 ± 0.001	48.5 ± 2	899.9 ± 1.0	≤4	15.1 ± 0.3		138
	V_F	2.002 ± 0.002	2.019 ± 0.002	45 ± 10	916 ± 1	≤4	13.2 ± 0.5	1.7 ± 0.5	330

[a] Reference 2. [b] Reference 3. [c] Calculated from the experimental values of Känzig (Ref. 3). [d] Reference 1.

A detailed analysis of this spectrum showed it to be identical with the spectrum of V_K centers that Hayes and Twiddell[1] observed in synthetic crystals of fluorite.

After thermal bleaching of the V_K centers at 138°K a new spectrum, closely related to the V_K spectrum, is formed. A careful study of the angular variation of the lines for rotation of the crystal about a [001] or a [110] axis indicated a close relation between this center and the V_F center in LiF.[3] Thus we identify the new center in CaF_2 as an F_2^--molecule ion with two nonequivalent fluorine nuclei 1 and 2. From the orientations of the magnetic field **H** for which the two nuclei become geometrically equivalent, it can be concluded that the symmetry of the V_F center in CaF_2 is that of an isoceles triangle lying in a (110)-type plane with the base along a cube edge (Fig. 1). The over-all symmetry is orthorhombic and there are six equivalent and equally populated orientations for the center. The V_F center in CaF_2, similar to that of the V_K center, shows an additional hyperfine structure due to two neighboring fluorine nuclei 3 and 4. Within the limits of our experimental results, the two nuclei 3 and 4 can be considered as equivalent for any direction of the magnetic field.

The symmetry of the center requires that the two tensors $\mathbf{T}^{(i)}$ which describe the hyperfine interaction of the hole with the two fluorine nuclei $i=1,2$ are equal, but that their principal axes x_i', y_i', z_i' are rotated with respect to the orthorhombic axes x,y,z. As shown in Fig. 1 the angles of rotation are $+\delta$ and $-\delta$ and the axis of rotation is x. The principal axes of the tensor $\mathbf{T}^{(i)}$ for $i=3,4$ are along the x,y,z directions.

The hyperfine spectrum has been analyzed in terms of a spin Hamiltonian of the form:

$$\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+\mathcal{S}\cdot\sum_{i=1}^{4}\mathbf{T}^{(i)}\mathbf{I}^{(i)},$$

where β is the Bohr magneton, $g_{\parallel}$ and $g_{\perp}$ are the components of the g-tensor parallel and perpendicular to the z axis (axial symmetry approximation), $\mathcal{S}$ is the spin operator of the electron and $\mathbf{T}^{(i)}$ and $\mathbf{I}^{(i)}$ are, respectively, the hyperfine tensor and the nuclear spin operator of the ith fluorine nuclei.

The parameters in the spin Hamiltonian were calculated from the experimental data using perturbation theory up to second order. This approximation does not permit an accurate determination of $T_{x'x'}$ and $T_{y'y'}$, but the error can be estimated by applying the same calculation procedure to the V_K centers where the accurate value was obtained with a computer. The results of fitting the parameters of the spin Hamiltonian to the experimentally observed spectra are summarized in the table along with values appropriate to other related centers.

As in the case of the V_K center, the EPR lines of the V_F center in CaF_2 have a fluorine satellite structure when H is not parallel to the z direction. Such a structure arises from the simultaneous flipping of the electron spin and a nearest-neighbor fluorine nuclear spin due to a weak coupling between them.[4] The measured spacing of the satellite lines is 4.0 ± 0.5 G. The theoretical value is 4.2 G.

The results of the pulse annealing experiments are shown in Fig. 2. The efficiency of the conversion of V_K centers into V_F centers depends upon the origin of the sample. The highest conversion efficiency observed was 60% in a yellow fluorite from Cave in Rock, Illinois. The observed decay temperature of the V_F center is given in the table. In contrast to LiF, x irradiation of

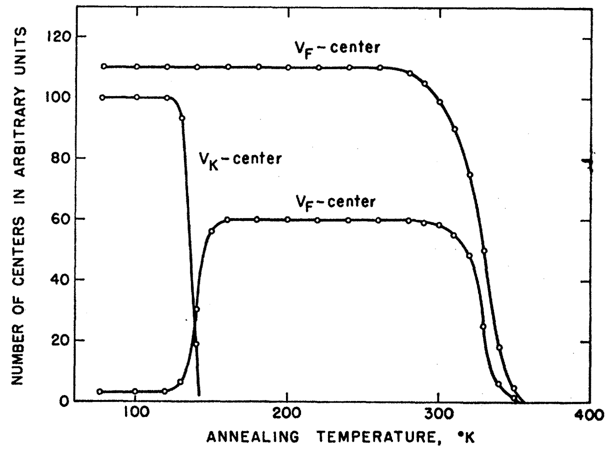

FIG. 2. Concentration of the two trapped-hole centers in CaF_2 measured after 5 min annealing pulse at the temperature given on the abscissa. The crystal was x irradiated at liquid nitrogen (lower curves) and dry ice (upper curve) temperature. The EPR spectrum was measured at liquid-nitrogen temperature.

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[4] J. M. Baker, W. Hayes, and M. C. M. O'Brien, Proc. Roy. Soc. (London) **A254**, 273 (1960).

natural fluorite at a higher temperature than the decay temperature of the V_K center does produce V_F centers.

DISCUSSION

The most important facts that an acceptable model of the V_F center in CaF_2 must explain are the following:

(1) The V_F center is essentially an F_2^- molecular ion. The unpaired electron spin interacts strongly with two nonequivalent fluorine nuclei 1 and 2 and more weakly with two other fluorine nuclei 3 and 4. All four nuclei lie in a (110) type plane.

(2) The thermal stability is higher for the V_F center than for the V_K center.

(3) The distance between nuclei 1 and 2 is smaller for the V_F center than for the V_K center as indicated by the change of $T_{z'z'}$.

(4) The V_F center cannot be formed in CaF_2 crystals grown by a fusion technique.

(5) The V_F center can be formed at temperatures higher than the decay temperature of the V_K center.

The simplest model that explains (1) is an F_2^- molecule ion closely associated with a lattice imperfection lying in a [110] type plane. The high thermal stability suggests that the imperfection has a negative change. The fluorite structure is cubic (space group O_h^5) and can be described as a cubic lattice of F^- ions with Ca^{++} ions at every other body center. Three simple imperfections can be considered in this structure:

(a) an interstitial F^- ion at the center of an empty cube of fluorines;

(b) a monovalent cation substiuted for Ca^{++}, the most probable impurity being Na^+;

(c) a Ca^{++} vacancy.

The first two imperfections (a) and (b) can be ruled out by the fact that they do not favor a reduced internuclear distance of the F_2^- molecule ion. Furthermore, both fluorine and sodium have a nuclear spin which would interact with the center and give a splitting or at least a broadening of the lines. In addition both defects can be introduced in synthetic crystals which show no V_F center after x irradiation.

The remaining imperfection, a Ca^{++} vacancy, explains the points (1) to (3). The high thermal stability is due to the double negative charge of the defect. This also accounts for the higher thermal stability of the V_F center in CaF_2 as compared to LiF where the associated imperfection, an Li^+ vacancy, bears a single negative charge.

The formation of V_F centers at temperatures where the holes migrate ($T > 138$°K) and the impossibility of producing these centers in synthetic crystals suggest that the Ca^{++} vacancies are already present in the natural crystals before irradiation. All artificial single crystals of CaF_2 are grown by direct fusion techniques and it has been shown[5–7] that trivalent ions substitute for the Ca^{++} ion when incorporated as impurities in CaF_2. Charge compensation then occurs by means of interstitial F^- ions residing at the nearest octahedral interstices of the fluorite lattice.[5–7] Charge compensation by Ca^{++} ion vacancies does not occur in these crystals. In nature, crystals of CaF_2 are deposited from solution and the temperature of formation does not exceed a few hundred degrees centigrade. A typical example is the fluorite of southern Illinois where the temperature of formation was obtained by studying fluid inclusions in the crystals and ranged from 83 to 115°C.[8] At these low temperatures the charge compensation of substituted trivalent impurities may be achieved as well by Ca^{++} vacancies as by interstial F^- ions. The charge compensation is not local since most of the natural fluorites exhibit the EPR of Gd^{3+} in a cubic environment. However, in samples where a large number of V_F centers can be formed, indicating a high concentration of Ca^{++} vacancies, the cubic spectrum of Gd^{3+} is associated with an unusual Gd^{3+} spectrum of lower symmetry. This spectrum could be due to charge compensation by a Ca^{++} vacancy among the next-nearest neighbors since the departure from cubic symmetry is small.

In conclusion, the model of an F_2^- molecule ion adjacent to a Ca^{++} vacancy for the V_F center in CaF_2 is in accord with all the experimental facts and has a good chance of being correct.

We have referred to the V_F center spectrum on a previous occasion[9] as being due to V_K centers. This assignment, as made evident by the present paper, was in error.

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