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[15]We used 42 values of n for the 21-layer film. With five symmetrized combinations of planar wave vectors, we again had a 210×210 matrix to diagonalize.

[16]This sum of plane waves actually gives us the pseudo wave function; i.e., the very rapid oscillation of the wave function due to its orthogonality to the 1s core function is not included.

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Optical Detection of Paramagnetic Resonance in the Excited State of F Centers in CaO†

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A detailed analysis of this double-resonance experiment shows that the emission takes place from the ^3P excited level whose degeneracy is lifted by the Jahn-Teller coupling to E_g modes of vibration. An energy-level crossing effect is observed and its origin discussed.

From the structural point of view the F center in the alkali halides is one of the simplest point defects. As such it has served as a model for many theories and as a test for new experimental techniques. The F' center (two electrons in an anion vacancy), though nearly as simple, has received much less attention since its ground-state level is nonmagnetic and its first excited level is not bound. One of the interesting results in the recent development of the study of the point defects in the alkaline-earth oxides is that, because of the extra charge of the vacancy, the two electrons of the F center[1] are more tightly bound and the first excited level is a bound state. The energy-level scheme of these centers is analogous to the one for the helium atom. In CaO the $^1S \rightarrow {}^1P$ transitions give rise to a strong absorption band at 4000 Å. On the basis of calculations by Neeley and Bartram, Henderson, Stokowski, and Ensign[2] have attributed the fluorescence band observed around 6000 Å to the $^3P \rightarrow {}^1S$ transitions. Using an optical detection technique[3] we observed the paramagnetic resonance in this metastable level. Three equivalent tetragonal spectra were observed, showing that the orbital degeneracy is lifted either by Jahn-Teller coupling to E_g modes of vibration or by static deformations. The spectrum confirms that the emitting level is a spin triplet. Good agreement is found between the values of the spin-orbit coupling constant deduced from the lifetime and from the measured parameters of the spin Hamiltonian. We observed many effects similar to those taking place in excited triplet states of molecular crystals. For instance, the variation with magnetic field of the polarization of the fluorescence light clearly shows the effect of the crossing of Zeeman sublevels.

The measurements were carried out using apparatus described elsewhere.[4] Slight modifications allowed detection of the fluorescence light in directions perpendicular or parallel to the magnetic field which is produced by a 12-in. Varian magnet. The microwave cavity is immersed in the He bath of a metallic cryostat. It is rectangular or cylindrical for frequencies in the X or K bands, respectively. The analysis of the circular polarization of the emitted light is made through a piezo-optical modulator analogous to the one described by Jasperson and Schnatterly.[5] It can be transformed into a linear polarization analyzer by adding a quarter-wave plate. The photomultiplier signal is then detected in phase with the modulation. Two techniques may be used to detect the resonance in the excited level: (a)

One measures the polarization of the emitted light by the technique described above and looks at its variation in the presence of a microwave field when the magnetic field is swept through resonance. (b) One measures the level of the emitted light of a given polarization and looks at its variations when a resonance line is partially saturated; in this case the sensitivity is increased by modulating the microwave power and detecting in phase the variations of the light intensity.

A typical spectrum obtained with the second technique is shown in Fig. 1(b). The microwave frequency was 23 GHz and the power was square modulated at a frequency of ~500 Hz. The magnetic field was in the (100) plane and along the [001] direction. One notices the small linewidths (12 G). Lines corresponding to $\Delta M = 2$ transitions were also observed at low fields. Their small widths (1 to 3 G) allowed a precise determination of the g values. The angular variation of this spectrum was studied by rotating the magnetic

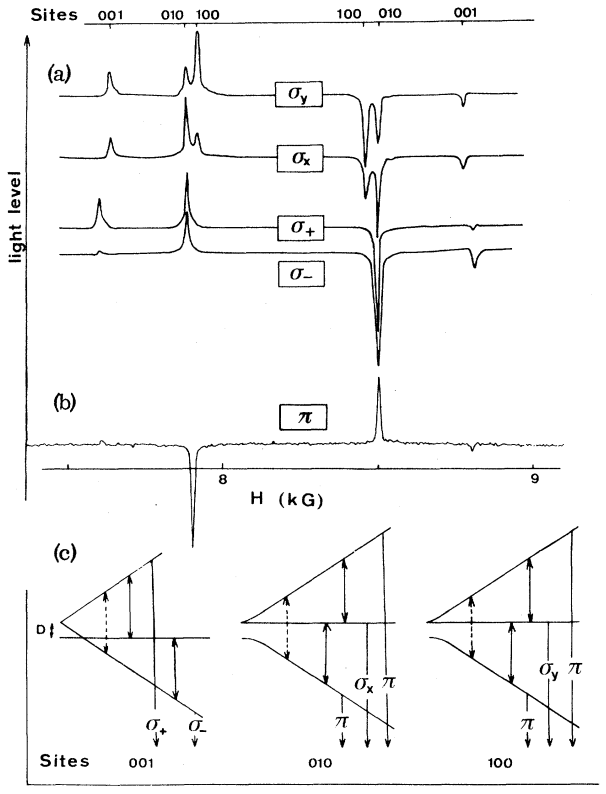

FIG. 1. Observation of the magnetic resonance using the variation in the intensities of the emitted light of various polarizations (a) σ_y, σ_x, σ_+, and σ_- (schematic); and (b) π (facsimile). (c) Predicted selection rules for the emission of polarized light. The magnetic field is along the [001] axis of the crystal, except for the σ_x and σ_y spectra where it is slightly misaligned.

field in the (100) plane. It showed the existence of three equivalent tetragonal sites. For any one of these the spin Hamiltonian is of the usual form for an $S = 1$ level[6] and is defined by the three parameters

$$g_{\parallel} = 2.002\,25 \pm 0.000\,15, \quad g_{\perp} = 2.0013 \pm 0.0003,$$

$$D = 598 \pm 1 \text{ G}.$$

These results are easily explained if, as suggested by Henderson, Stokowski, and Ensign,[2] the fluorescence is due to the $^3P \rightarrow {}^1S$ transitions and if the orbital degeneracy of the excited level is lifted either by a strong Jahn-Teller coupling to E_g modes of vibration, or by a static tetragonal field due, for instance, to the presence of an impurity on the first shell neighbors (F_A centers). As shown by Ham[7] the resonance spectra would be qualitatively the same in the two cases. The second hypothesis is rather improbable since both the absorption and the emission spectra do not depend on the origin of the crystal or on the way the centers are created. Moreover, as shown by Stark-effect measurements, the centers are centrosymmetric.[8] Other models such as those including a divacancy may be disregarded on the basis of the possible interconversion between F and F^+ centers.[2] Various effects such as the level crossing observed at low field (see below) would be difficult to explain in a purely static model, so that the orbital splitting of the ^3P level will be attributed to a Jahn-Teller effect and its magnitude will be designated $3E_{JT}$.

The spin-orbit interaction, Zeeman effect, and dipole-dipole interaction for this two-electron system are taken into account by the following Hamiltonian:

$$\mathcal{H} = \lambda(l_1 s_1 + l_2 s_2) + g_L \beta \vec{H} \cdot (\vec{l}_1 + \vec{l}_2) + g_0 \beta \vec{H} \cdot (\vec{s}_1 + \vec{s}_2) + \mathcal{H}_d,$$

where g_L and g_0 are, respectively, the orbital and the free-spin spectroscopic splitting factors, λ is the spin-orbit coupling constant, and $\mathcal{H}_d$ represents the spin-spin coupling. The parameters of the spin Hamiltonian are then calculated within the strong-coupling approximation. For the [001] site they are found to be

$$g_{\parallel} = g_0, \quad g_{\perp} = g_0 - \lambda g_L / 3E_{JT},$$

$$D = D_d - \lambda^2/12E_{JT} + \lambda^2/4\Delta,$$

where Δ is the energy separation between the ^1P_x, ^1P_y, and the ^3P_z levels and is the sum of the exchange energy and of the Jahn-Teller splitting

(and possibly a third term taking into account the coupling of the ^3P and ^1P electronic states to totally symmetrical modes of vibration). The axial term D is the sum of three terms. The first one is due to the spin-spin interaction and appears in the first order of perturbation. The second and the third appear when the spin-orbit interaction is calculated in the second order of perturbation; they are due, respectively, to mixing of the ^3P_z states with the $^3P_{x,y}$ and $^1P_{x,y}$ states. According to this model the $^3P \rightarrow {}^1S$ transitions are made partially allowed by the mixing through spin-orbit interaction of the ^1P and ^3P states, so that the oscillator strength is $(\lambda/2\Delta)^2$ and the selection rules are those indicated in Fig. 1(c).

From the value of $g_\perp$ one deduces that $\lambda g_L/3E_{JT}$ is of the order of 10^{-3}. The value of the oscillator strength measured by Henderson, Stokowski, and Ensign[2] leads to $\lambda/\Delta \approx 1.5\times10^{-3}$. This shows that even if one assumes a small value of g_L (≈ 0.5) the exchange energy is not large with repect to the Jahn-Teller splitting. From the shape of the emission spectra one may estimate the order of magnitude of this splitting to be $3E_{JT} \approx 2500$ cm^{-1}, so that for $g_L = 0.5$ one gets $\lambda \approx 5$ cm^{-1}. One sees that the second-order effect of the spin-orbit coupling is too small by more than an order of magnitude to be able to explain the experimental value of D. One thus attributes the D parameter mainly to spin-spin coupling.

The sign of D may be obtained by the analysis of the spectrum shown in Fig. 1(a). Consider the two extreme lines which correspond to $\Delta M = 1$ transitions of the [001] center whose axis is nearly parallel to the magnetic field. If D is positive the low-field line corresponds to the $M = 0 \rightarrow +1$ transition so that one expects an increase of the intensity of the σ_+ light when this transition is partially saturated. Saturation of the high-field line would, on the other hand, decrease the population of the $M = -1$ level and the intensity of the σ_- light would decrease. For D negative the situation would be reversed: Saturation of the low-field and high-field lines would, respectively, induce a decrease and an increase of the emitted σ_+ light. Examination of Fig. 1 clearly shows that D is positive. It also shows that the selection rules indicated for σ_+ and σ_- light are well obeyed. For the [100] and [010] centers and $D > 0$ the low-field and high-field lines are due, respectively, to the $M = -1 \rightarrow 0$ and $M = +0 \rightarrow +1$ transitions, but now it is the $M = 0$ levels which emit σ light. From the observed variations of the intensities, one deduces again that D is positive. A further test of the model was given by monitoring the σ_x or the π light. We verify (for instance, see Fig. 1) that saturation of the low-field line of the [010] center induces an increase of the σ_x intensity and a decrease of the π intensity. Similarly saturation of the low-field line of the [100] center induced an increase of the σ_y intensity and a decrease of the π light.

It seems difficult to reconcile the existence of tetragonal sites and the observation of the above selection rules with the study of the stress effect on these centers made by Louat, Champagnon, and Duval.[9] These authors observed that for stresses applied along ⟨100⟩ and ⟨110⟩ directions the zero-phonon line splits into two and three components, respectively. For a ⟨110⟩ stress, tetragonal centers are expected to split into two components only. The splitting pattern is in fact very similar to the one observed for F^+ centers in CaO.[10] This means that the emitting centers are in very nearly cubic symmetry and that either the Jahn-Teller effect is small, or the couplings to E_g and T_{2g} modes are approximatively equal. Our results, on the other hand, imply predominant coupling to E_g modes.

A detailed study of the optical pumping cycle has not been done but preliminary results merit attention. At a given magnetic field and temperature the circular polarization was found to be the same at all wavelengths of the emission band, including the zero-phonon line. According to the above model the circular polarization should be given by $\tau = \tanh(\beta H/kT)$ for the [001] orientation of the magnetic field and for $2\beta H \gg D$. At very low temperature (1.6°K) the signal was found to saturate at high field (10 kG) as predicted by this expression. It was smaller than predicted by 40 to 60% according to the origin of the crystal. The polarization was larger for crystals containing V impurities. At higher temperatures (4.2°K) the agreement was better. These observations may be explained if the relaxation times are not very short with respect to the lifetime so that Boltzmann equilibrium is not reached.

Optical detection of level crossing confirms this hypothesis. The variation with field of the circular and linear polarizations, $(I_\pi - I_\sigma)/(I_\pi + I_\sigma)$, is shown in Fig. 2. One notices a well-marked "line" at 600 G. This field corresponds to the crossing of the $M = -1$ and 0 levels of the [001] centers. These "lines" broaden very rapidly as soon as the field is slightly misoriented with respect to the crystal axis. The effect observed in circular polarization is easy to understand if, as

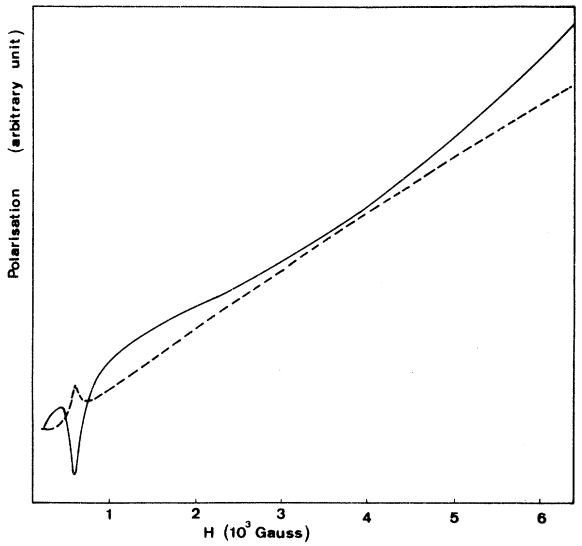

FIG. 2. Variation of circular (dashed curve) and linear (solid curve) polarization with magnetic field.

suggested above, Boltzmann equilibrium is not reached at low temperature. Then the population of the $M=0$ level should be large since its radiative lifetime is infinite. At the level crossing point, large mixing of the $M=0$ and -1 levels occurs and direct emission of σ_- light is more efficient in depopulating the $M=0$ level than relaxation to the $M=+1$ level. One thus sees that the circular polarization increases. According to this model the intensity of the light emitted by the [001] center, $I_\sigma = I_{\sigma_+} + I_{\sigma_-}$, is constant so that in order to explain the observation of the level crossing in σ, π polarization one has to assume that some transfer of excitation from one set of tetragonal centers to the other sets takes place. This confirms that the presence of tetragonal sites is due to the Jahn-Teller coupling and not to a static crystal field effect. In the former case it is known[11] that a given center may tunnel from one Jahn-Teller well to the other in a time short with respect to the relaxation time T_1.

The existence of these tunneling effects is confirmed by double-resonance experiments. It is seen in Fig. 1(a) that saturation of an EPR line belonging the [100] tetragonal spectrum has an effect on the intensity of the light polarized in the x direction. Since the [100] centers emit light polarized only along the y and z directions, one again has to assume the possibility for a given center to tunnel from one well to the others. Similar effects were observed in circular polarization: Saturation of transitions of the [100] or [010] centers, neither of which emit pure σ_+ or σ_- light, induces changes in the quantity $I_{\sigma_+} - I_{\sigma_-}$ comparable to that observed with saturating transitions belonging to the [001] centers. These effects are particularly strong when transient phenomena are observed after the application of a microwave pulse. They are under more detailed study at present in this laboratory.

The EPR spectra as well as the selection rules observed for the emission of polarized light in this double-resonance experiment show that the emission takes place from a ^3P ($^3\Gamma_4$) level strongly coupled to E_g modes of vibration. The level crossing and the other observed dynamical effects are well explained if one assumes that radiative emission and tunneling between different Jahn-Teller wells compete with paramagnetic relaxation in establishing population equilibrium in the magnetic sublevels of the excited state. This technique should be very useful for the study of diverse excited triplet-level systems such as those of the Tl^+-like ions and the self-trapped excitons in alkali halides.

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[1]According to the new nomenclature, the one- and two-electron centers in the divalent compounds are called F^+ and F, respectively.

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