OPTICAL SPIN POLARIZATION IN M-LIKE CENTERS IN CaO†

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In some well-known cases, electron spin inversion by optical pumping has been effected through use of circularly polarized light, or by laser excitation.[1] We report here a striking, simple example of spin polarization by broad-band, unpolarized light in certain color centers, resulting in emissive spin-resonance (ESR) transitions. The system to be described might have use as a light-pumped microwave or millimeter-wave maser material. The polarization process here is especially intriguing because it is indirect, and seems to depend only on relaxation from higher excited states with sharply defined selection rules.

Our experiment concerns a defect center in neutron-irradiated CaO crystals, which we call F_t. In the ESR spectrum at 300°K this center is seen as a set of six narrow (<1 G) lines, almost centered about the strong line at $g = 2.000$ due to the simple F center[2,3] [Fig. 1(a)]. From anisotropy and intensity studies at room, liquid-air, and helium temperatures, we assign the six lines to a triplet state of a two-electron system, rather like the alkali-halide M center,[4] the latter having (110) symmetry while the F_t sextet shows (100) axes. The likely[5] structure is two electrons in, respectively, the opposing O^{2-} sites of a linear trivacancy $O^{2-}-Ca^{2+}-O^{2-}$ in the NaCl-like CaO lattice. Approximately, this is an exchange-coupled F-center pair, apart from the intervening Ca vacancy. (The latter is proposed partly on electrostatic stability grounds.) The ESR spectrum is consistent with a two-electron spin Hamiltonian:

$$\mathcal{H} = B\vec{S}_1\cdot\vec{S}_2 + g\mu_B\mu_0\vec{H}_0\cdot\vec{S} + [\mu_0(g\mu_B)^2/r^3][\vec{S}_1\cdot\vec{S}_2 - 3(\vec{S}_1\cdot\vec{r}_1)(\vec{S}_1\cdot\vec{r}_1)], \quad (1)$$

where $\vec{r}_1$ is a unit vector along (100), (010), or (001); mks units are used. We write exchange, Zeeman, and dipole-dipole couplings. As written, g is isotropic, and has measured value 2.002 ± 0.001. (Though the model mentioned should give an axial g tensor, the anisotropy is apparently small.) Equation (1) has familiar $S = 0$ and $S = 1$ states, the latter having the two ESR transitions M_S: $(-1 \rightarrow 0)$ and $(0 \rightarrow 1)$, meaning, in fact, six lines are generally seen. From the measured maximum splitting of 328 G of a line pair, the mean interelectron distance is to first order (weak dipolar coupling) $r \cong 38/(\Delta H_{max})^{1/3} \cong 5.5$ Å, which we feel not inconsistent with the O-O distance 4.8 Å in CaO. As in the M center,[4] the singlet is lowest. The triplet, virtually empty at 4°K, is fully populated at 300°K, and we estimate $B/k = (50 \pm 20)$°K.

Light illumination at 4.2 and 1.6°K was found to populate the triplet in the striking way shown in Fig. 1(b). As seen, the three low-field ESR lines are all inverted, the intensities varying in an odd-symmetry pattern about the center of the spectrum. An Osram HBO-500 Hg lamp was used, with unpolarized light incident normal to H_0 via quartz Dewar windows. The sample was fixed with silver paint on a copper cav-

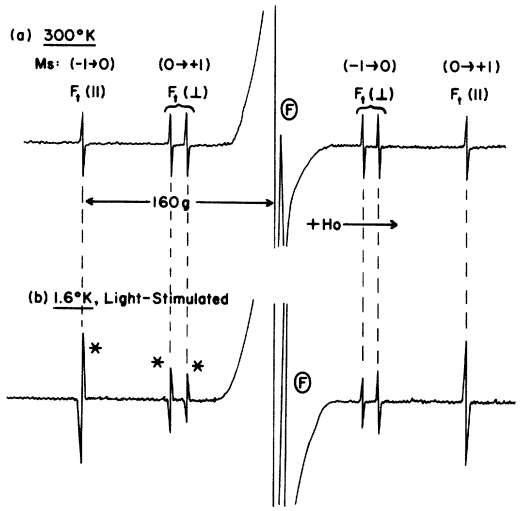

FIG. 1. Derivative ESR spectra at 9.5 kMc/sec of CaO color centers, with F_t-center triplet lines centered about F-center line ($g = 2.000$). At $T \cong 1.6$°K, (b), the F_t lines are shown as stimulated by light in the region $3000 \lesssim \lambda \lesssim 4000$ Å (HBO-500 lamp plus 7-54 filter)—they are below noise level with light off. The low-field lines are inverted (emissive). H_0 is oriented slightly off a (100) crystal axis, in order to resolve the two inner pairs of lines. Intensity scales in (a) and (b) are unrelated. At 300°K one F_t line has intensity ≃1/50 relative to the F center, with F-center density $\simeq 3\times 10^{18}$/cc.

ity wall, immersed in helium. It had size $3\times 3\times 0.5$ mm, with about 2×10^{16} F centers and 1/7 this many F_t centers. Pains were taken to keep the sample temperature rise down to a couple of degrees under illumination, as judged partly by the F-center spin temperature. (No obvious bleaching of either the F or F_t centers was seen, with repeated illuminations.) It was made clear that at least 90% of the F_t signal strengths were from optical pumping.

Light peaked near 3.6 eV (7-54 Corning filter) was found most effective; light of energy less than 2.7 eV (4500 Å) via cutoff filters gave no F_t signals. Within chart-recorder response times (~0.5 sec), the F_t lines vanished and recovered immediately upon shuttering the light off and on. ESR saturation suggested an (effective) T_1 of order 10^{-2} sec for the light-induced lines, while, for comparison, $T_1 > 0.1$ sec for the F center.

The spin polarization is of the tensor type and is an aspect of the axial symmetry of the F_t center. Though it does not depend on all details of the model, it can be described with the level diagram of Fig. 2, using nomenclature for the above-suggested F_t-center model. We use ground and first-excited Heitler-London configurations of two electrons in opposite sites of an O–Ca–O trivacancy[6]; s_1 and s_2 mean $1s$-like states at sites 1 and 2, respectively, p_1 and p_2 mean $2p$-like states. In D_{4h} symmetry one has the representations noted. Shown is a "one-electron," Franck-Condon (direct) excitation, followed by cascade to the $(s_1 s_2)\,^3A_{2u}$ triplet. The plus-and-minus intensities of Fig. 1(b) mean the process prefers to populate the $M_S = 0$ sublevels for F_t with axis along H_0, but the $M_S = \pm 1$ levels for $F_t \perp H_0$. (It is needed also that the direct spin-lattice relaxation time in the low triplet be long compared to the triplet lifetime τ; then the "effective" T_1 estimated above must be just τ.)

The downward transition to the low triplet is no doubt at least partly radiationless, with a more or less complex lattice relaxation. But if we suppose for brevity that tetragonal symmetry about the F_t-center axis z is not disturbed during this relaxation, and that spin-orbit coupling is weak compared to the axial splittings, the S and M_S selection rules follow from a simple argument. Spin-orbit coupling applied as a static perturbation within the excited configuration $s_1 p_2$ lifts the rule $\Delta S = 0$ for electric

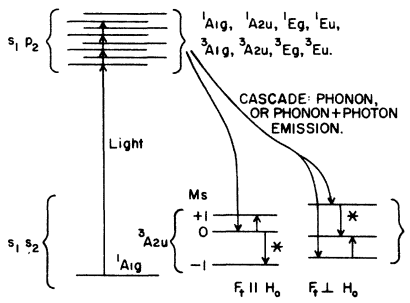

FIG. 2. Level and optical pumping scheme suggested for F_t centers, regarded as exchange-coupled F-center pairs along (100) axes. Levels named from D_{4h} representations. $s_1 s_2$ means Heitler-London configuration with each electron in F-center–like ground state; $s_1 p_2$ means one electron is promoted to first excited F-center state. Zeeman and dipole-dipole splittings, omitted in $s_1 p_2$ states, are much exaggerated in the $s_1 s_2$ triplet. The specific optical pumping routes into the low triplet noted may explain the inverted ESR lines (starred) that are observed.

dipole transitions from the $^1A_{1g}$ ground state. Or, optical excitation to singlet $s_1 p_2$ states may be followed by lattice-modulated spin-orbit coupling that induces $\Delta S = 1$. In any case, the tetragonal symmetry allows orbital moments along z, but not normal to z, to be freely generated, using the Π-like E states. Spin-orbit coupling connects ^1E_u to ^3E_u and ^1E_g to ^3E_g, with selection rules $\Delta S = \pm 1$ and $\Delta M_S = 0$, using spin quantization along z, appropriate to the case $H_0 \parallel F_t$. If spin is quantized along an axis normal to z, for $H_0 \perp F_t$, the M_S rule is correctly written $\Delta M_S = \pm 1$, agreeing with Fig. 2.

We hope soon to have observations also with polarized and with monochromatized light. The optical pumping efficiency seemed seriously reduced in our samples by the strong absorptance in the near uv, only a fraction of which is probably due to the F_t bands. The CaO F band, which ought to be much stronger, ought to partly overlap the F_t peaks if our models for these centers are right. Though the F bands are not yet isolated in the alkaline earth oxides,[7,8] there is an estimate of 3.8 eV for CaO, near a known 3.6-eV peak.[7] There may be ways (e.g. certain heat treatments) to increase the relative F_t-center density. F_t centers have not so far been identified in SrO. Quite recently, J. E. Wertz has told us (unpublished) of finding an F_t-like ESR spectrum in MgO, with $\Delta H_{max} = 416$ G.

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[1]G. V. Skrotskii and T. G. Izumova, Usp. Fiz. Nauk 73, 423 (1961) [translation: Soviet Phys.—Usp. 4, 177 (1961)]; D. P. Devor, I. J. D'Haenens, and C. K. Asawa, Phys. Rev. Letters 8, 432 (1962).

[2]J. E. Wertz, J. W. Orton, and P. Auzins, Discussions Faraday Soc. 31, 140 (1961).

[3]J. C. Kemp and V. I. Neeley, J. Phys. Chem. Solids 24, 332 (1963).

[4]H. Seidel, Phys. Letters 7, 27 (1963).

[5]An alternative is that the F_t center is in fact merely the F' center (two electrons in one O vacancy), discussed by V. I. Neeley, thesis, University of Oregon, 1964 (unpublished); by V. I. Neeley and J. C. Kemp, Bull. Am. Phys. Soc. 8, 484 (1963); by J. E. Wertz, G. S. Saville, L. Hall, and P. Auzins, Proc. Brit. Cer. Soc. 1, 59 (1964); and also by Wirt C. Ward and Eugene B. Hensley, Bull. Am. Phys. Soc. 10, 307 (1965) (they use the term F^2). The weak electron-electron coupling in the F_t points against this, unless the F' is a rather distorted structure.

[6]Heitler-London wave functions for the M center are described by R. A. Evarestov, Vestn. Leningr. Univ., Ser. Fiz. i Khim. 22, 39 (1963); the symmetry there is D_{2h}.

[7]Neeley, reference 5; Neeley and Kemp, reference 5.

[8]Wertz, Saville, Hall, and Auzins, reference 5.