SPECTRAL HOLEBURNING AND THE STARK AND ZEEMAN EFFECTS IN $SrF_2:Sm^{2+}$

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We have observed narrow (40 MHz) persistent spectral holeburning in $SrF_2:Sm^{2+}$ for Sm^{2+} ions in perturbed cubic sites. The transition studied is $^7F_0 \leftrightarrow {}^5D_0$ between the f-electron states. Stark effect measurements show a linear splitting with a coefficient of 0.006 MHz/V cm^{-1} and the splitting pattern shows that the site has C_{4v} symmetry. The C_{4v} perturbation is very weak and leads to unresolved splittings of cubic T_{1g} levels of $\sim$2 cm^{-1}. The nonlinear Zeeman effect was studied using holeburning and the coefficient of 1.04 Hz/G^2 shows that the predominant magnetic coupling is in the ground state as found recently for $CaF_2:Sm^{2+}$.

Spectral holeburning due to photoionization of Sm^{2+} in cubic sites of CaF_2 has recently been reported [1]. Holeburning was observed in the lowest optical transition $4f^6A_{1g} \rightarrow 4f^55dA_{1u}$ which was made allowed by an external magnetic field. We have extended this work to a study of Sm^{2+} in SrF_2 which for the present purposes differs in two important respects from the CaF_2 system. In the first place the lowest optical transition is between $4f^6$ states of the same parity ($^7F_0 \leftrightarrow {}^5D_0$), the $4f^55d$ levels lying $\sim$500 cm^{-1} higher [2]. Secondly, while the $^7F_0 \leftrightarrow {}^5D_0$ transition is forbidden in cubic sites, some ions occupy noncubic sites leading to very weak absorption in zero field [2]. An external magnetic field cannot induce electric dipole intensity in this system. Although the electronic levels have a very different nature in CaF_2 and SrF_2 and the lifetimes of the lowest excited states also differ strongly (2 μs in CaF_2, 10 ms in SrF_2) holeburning is again observed with comparable efficiency to the case of CaF_2.

The absorption and emission spectra of $SrF_2:Sm^{2+}$ have been studied by Kaiser and Wood [2]. The dominant Sm^{2+} site is substitutional for Sr^{2+} with O_h symmetry. The energy level diagram for these sites is given in fig. 1. All of the allowed $4f^6 \leftrightarrow 4f^6$ electronic transitions are magnetic dipole (m.d.) and the $4f^6 \leftrightarrow 4f^55d$ are electric dipole. The $^5D_0A_{1g}$ level has m.d. transitions allowed only to T_{1g} levels of the ^7F_J manifolds. Forced electric dipole phonon sidebands are observed, associated with the forbidden origins of $^5D_0 \leftrightarrow {}^7F_J$.

In addition to the transitions allowed in cubic symmetry, Kaiser and Wood [2] noted a number of weaker lines in the emission spectrum which they characterized as "forbidden". Of particular interest here is a very weak fluorescence line at 6838 Å which is in the region of the rigorously forbidden $^5D_0 \leftrightarrow {}^7F_0$ origin. We show here that this is a resonance line of an ion in a perturbed site which exhibits persistent spectral holeburning. Stark effect measurements on the holes identify the symmetry of this site as C_{4v}.

A sample of $SrF_2:Sm^{2+}$ 5 × 3 × 0.7 mm with a (100) axis normal to the large face, was placed in a Stark cell with stainless steel electrodes such that the Stark field $E_S \parallel (100)$. Thin (0.1 mm) mylar spacers were used around the sample to prevent charge injection and the possibility of breakdown at crystal defects. A tunable cw dye laser of bandwidth $\sim$1 MHz

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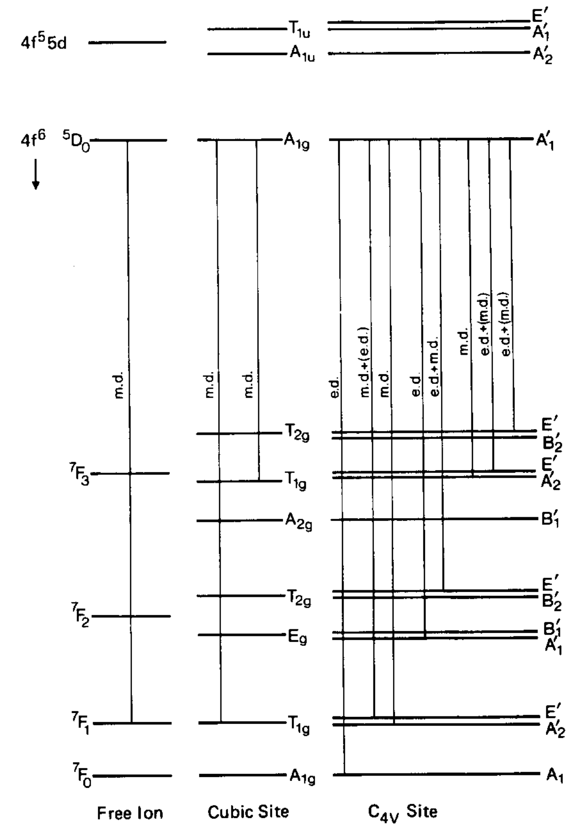

Fig. 1. Energy level diagram for $SrF_2:Sm^{2+}$. The majority O_h sites exhibit only magnetic dipole transitions and the ${}^7F_0 \leftrightarrow {}^5D_0$ transition is rigorously forbidden. In perturbed C_{4v} sites a very small (~1 cm^{-1}) splitting of the T_{1g} levels is observed. Splittings of other degenerate cubic levels are not observed because transitions from ${}^5D_0$ are allowed to only one component.

and a power of 10 mW was weakly focused (0.5 mm ϕ) into the sample. Holes were burned by irradiation for ~5 s, and probed by scanning an attenuated laser (X 10^{-2}) to measure the excitation spectrum. Fluorescence spectra were analyzed with a 1 m double monochromator. Excitation spectra of the weak 6838 Å line in absorption were obtained by monitoring the ${}^5D_0 \leftrightarrow {}^7F_1$ emission in the vicinity of 6950 Å with a 1/4 m monochromator.

A typical hole spectrum is shown in fig. 2 for zero applied electric field, E_S, and for a field of 19 kV/cm. In zero field the hole width was 40 MHz. A single unshifted hole was observed for the probe laser electric field $E_L \perp E_S$ and a doublet splitting for $E_L \parallel E_S$. The holes split linearly (fig. 3) with a coefficient of 0.006 MHz/V cm^{-1}, showing that the site is noncentrosymmetric. The observed splitting and intensity pattern is

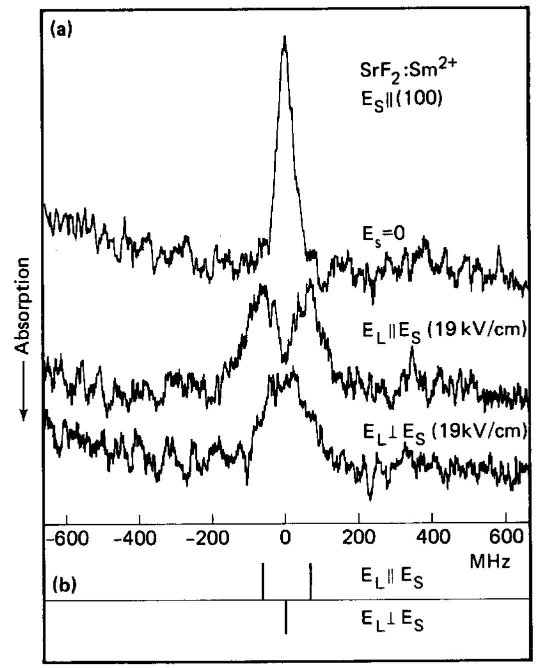

Fig. 2. Holeburning spectrum of the 6838 Å transition in zero field and for a Stark field of 19 kV/cm ‖ (100). The intensity pattern is that of a C_{4v} site.

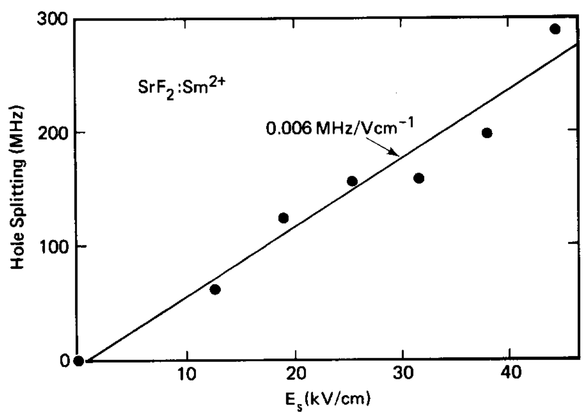

Fig. 3. Stark splitting as a function of field showing the linear dependence and the small coefficient consistent with a weakly perturbed cubic site.

that expected for electric dipole transitions in a center of C_{4v} symmetry [3]. However, as the holes split, they also broaden somewhat suggesting that there may be small deviations from exact C_{4v} symmetry. The linear Stark coefficient is much smaller than observed for f–f transitions of Pr^{3+}:LaF_3 where a value of 0.3 MHz/V cm^{-1} was found [4]. This reflects the fact that the linear effect arises from the C_{4v} symmetry, and the strength of the C_{4v} perturbation is very small as discussed below.

The persistent holeburning also enabled us to measure the nonlinear Zeeman effect of the perturbed site transition at 6838 Å. A hole was burned in zero field and it shifted quadratically with the applied field (fig. 4). Since the u levels do not contribute to the nonlinear Zeeman effect it is straightforward to calculate the shift, in the f-electron approximation. The ground state shift is 0.98 Hz/G^2 and the $^5D_0$ shift –0.08 Hz/G^2 giving a net calculated value of 0.90 Hz/G^2, in reasonably good agreement with the observed value of 1.04 ± 0.05 Hz/G^2. As in CaF_2:Sm^{2+} the dominant contribution comes from the off diagonal Zeeman coupling between $^7F_0$ and $^7F_1$.

Since the magnetic field does not couple g and u levels, in the cubic approximation the only magnetic field enhancement of the intensity of the $^7F_0 \leftrightarrow {}^5D_0$ transition comes from a magnetic dipole mechanism involving $^7F_0$, $^7F_1$ admixture which did not produce an observable effect up to 50 kG. Higher order effects arising from the weak C_{4v} perturbation are negligible both for the field induced intensity and nonlinear Zeeman shift. This is in contrast to the case of CaF_2:Sm^{2+} where the A_{1u} excited level lies lowest [5].

The fluorescence spectrum consisted of several groups of lines to the $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ levels. For the majority cubic sites only transitions to the T_{1g} component of these J levels ($J = 1, J = 3, J = 4$) is allowed and these are the strongest features in the emission. Transitions to other components are observed for the perturbed site when selectively exciting at 6838 Å. We found that one of these lines in each of the $^7F_1$, $^7F_3$ and $^7F_4$ multiplets coincided in *frequency* with the majority site T_{1g} level but was a factor of 2–3 times *broader* (fig. 5). We interpret this as

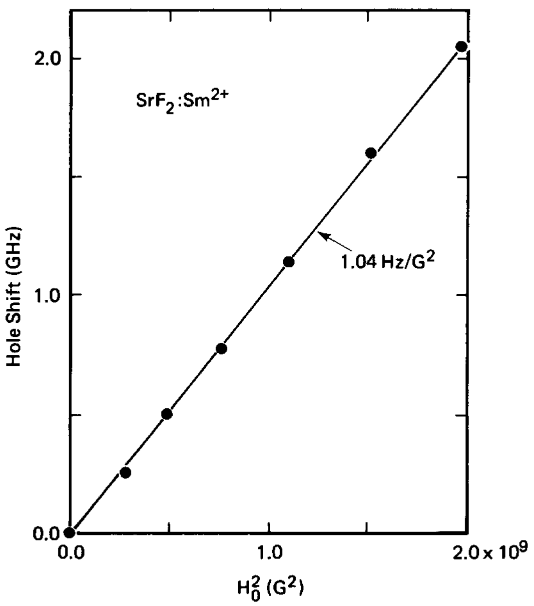

Fig. 4. Nonlinear Zeeman effect measured by the shift of a hole burned in the 6838 Å line.

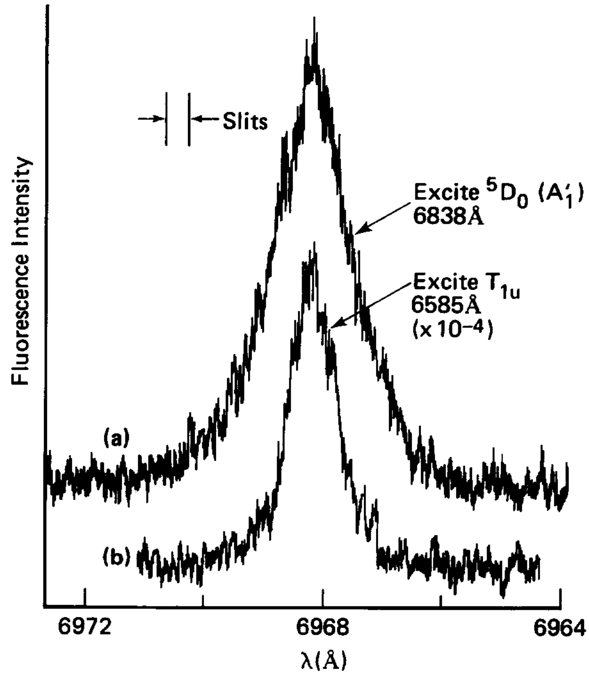

Fig. 5. Emission lines from $^5D_0 \rightarrow {}^7F_1T_{1g}$ transitions. (a) C_{4v} perturbed sites showing a linewidth of 4.9 cm^{-1} which we attribute to an unresolved splitting of the T_{1g} level by the small C_{4v} field. (b) Cubic sites showing a linewidth of 1.7 cm^{-1}.

evidence for the nearly cubic symmetry of the perturbed sites as would be expected for a divalent ion in SrF_2 which has no need for charge compensation in close proximity to the rare earth ion (cf. the case of trivalent rare earths). Transitions from $^5D_0 \to {}^7F_JT_{1g}$ levels perturbed by a C_{4v} field would be allowed, $A_1' \to A_2'$ and $A_1' \to E'$ as magnetic dipole and $A_1' \to E'$ as electric dipole, where the primes denote representations of C_{4v}. For both the cubic and perturbed sites the $^5D_0 \to {}^7F_1$ transition is two orders of magnitude stronger than that to the other ^7F_J levels showing that magnetic dipole transitions still occur in these perturbed sites. We note that for transitions from the $^5D_0$ excited state the *only* cubic representation for which *both* C_{4v} components are allowed is T_{1g} and it is just these transitions which show an anomalous linewidth. We interpret this extra width (1–2 cm^{-1}) of transitions to these perturbed T_{1g} components as an unresolved splitting of T_{1g}. Since shifts of the centers of gravity of the transitions $^5D_0A_{1g}(A_1')$ $\to {}^7F_JT_{1g}(A_2', E')$ for J = 1, 3 and 4 are all less than 1 cm^{-1}, the shift of the $^5D_0A_1'$ level due to its off diagonal coupling to T_{1u} via the C_{4v} field must also be $\lesssim 1$ cm^{-1}. Since the T_{1u} level lies 565 cm^{-1} above $^5D_0$, the off diagonal coupling is less than 20 cm^{-1}. This places an upper limit on the oscillator strength induced by the C_{4v} field of 10^{-3} times that of the $^7F_0 \to T_{1u}$ transition at 6585 Å. We estimated the absorption ratio of cubic to C_{4v} sites by monitoring the $^5D_0 \to {}^7F_1$ emission following excitation of $^7F_0 \to T_{1u}$ (cubic sites) and also $^7F_0A_1' \to {}^5D_0A_1'$ (perturbed sites). This gave a peak absorption ratio of 10^4 which, corrected for the relative linewidths, gives an integrated absorption ratio of 10^5. From this we deduce that the concentration of perturbed sites is at least 1% of the total Sm^{2+} concentration. When fluorescence was excited nonselectively, the cubic site emission from $^5D_0 \to {}^7F_JT_{1g}$ was 10–20 times stronger than that from the perturbed sites. This sets an upper limit on the relative concentration of perturbed sites of ~10%. The nature of the C_{4v} perturbation is unclear, but from its size it appears to arise from a perturber in a distant neighbor position.

In conclusion we have demonstrated the existence of persistent holeburning on the f–f $^5D_0 \leftrightarrow {}^7F_0$ transition of Sm^{2+} ions in perturbed sites of SrF_2. Stark effect measurements show that the sites have C_{4v} symmetry and a nonlinear Zeeman effect arising from $^7F_0$, $^7F_1$ interactions was observed.

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