STARK EFFECT OF 4*f* STATES AND LINEAR CRYSTAL FIELD IN BaClF:Sm^{2+}

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The effects of an externally applied electric field on optical transitions of 3*d* ions have been studied in ruby,[1] and in the isoelectronic systems $Cr_2O_3:V^{2+}$ and $Cr_2O_3:Mn^{4+}$.[2] In all these cases there was found to be an energy shift of the *R* lines which depended linearly on the applied field. In this note we wish to report the first observation of an external Stark effect on 4*f* states. The system studied was BaClF:Sm^{2+}, and the "electric effect" was found to be of the same order of magnitude for the 4*f* states as that previously found for the 3*d* states. In order to explain the Stark effect and the intensities of some of the transitions, we invoke an odd-parity potential term which varies linearly with electron distance.[3] By using such a term, we have obtained a relation between the Stark splitting and the oscillator strength for some of the transitions.

We chose BaClF:Sm^{2+} for the study of the external Stark effect on 4*f* states since a number of conditions expected to contribute to the effect are favorable. The Sm^{2+} ion replaces a Ba^{2+} which occupies a site of C_{4v} = 4-mm symmetry,[4] a site that lacks a center of inversion. The Sm^{2+} is ninefold coordinated, and the coordination polyhedron is that of an antiprism having an extra Cl above the center of four other coplanar Cl. The odd-power crystal-field potential terms may be expected to appreciably admix the nearby 5*d* configuration with the states of 4*f*. Finally, there are many sharp line transitions between ^5D_J and $^7F_{J'}$ states which can be conveniently studied in both emission and absorption.[5]

The Stark-effect study was performed by observing the change in the fluorescent spectrum of the $^5D_J \rightarrow {}^7F_{J'}$ transitions of Sm^{2+} as the external field was varied. The crystals, about 3 mm×3 mm×1 mm thick, were placed in contact with and between two flat electrodes and were immersed in liquid He at 4°K. A potential difference was applied to the two electrodes from a dc high-voltage supply, and fields up to about 120 kV/cm could be applied before arcing across the sample occurred. The spectra were photographed using a 3.4-m Jarrel-Ash spectrograph in high order having a limit of resolution ≈0.04 Å. The direction of observation was always perpendicular to the field direction $\vec{\epsilon}$, and spectra were measured for $\vec{c} \parallel \vec{\epsilon}$ and $\vec{c} \perp \vec{\epsilon}$, where the crystal $\vec{c}$ axis is parallel to the fourfold axis of the group C_{4v} = 4 mm.

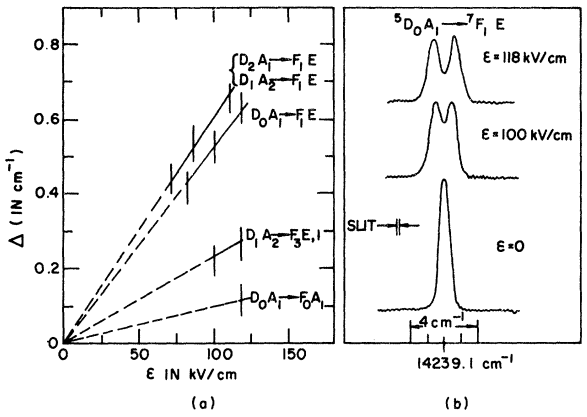

FIG. 1. Observed Stark splitting Δ (in cm^{-1}) as a function of applied electric field. (a) Plot of splitting energy versus applied field for several transitions. Data taken from 4°K fluorescent spectra. The vertical bars represent the approximate linewidths. (b) Densitometer recording of the $D_0A \rightarrow F_1E$ emission line at 4°K in zero field, ϵ = 100 kV/cm, and ϵ = 118 kV/cm taken from the plate and uncorrected for intensity differences due to different exposure times.

When the field was applied perpendicular to $\vec{c}$ no change in the fluorescent spectrum was observed up to ϵ = 120 kV/cm, whereas for $\vec{\epsilon} \parallel \vec{c}$ we found that many of the lines were split into doublets, centered about the ϵ = 0 position, the splitting energy between the lines, Δ, being linear with applied field. The splitting as a function of applied field is shown in Fig. 1, which also contains a profile of one line in various fields. The transitions involved are explained by reference to the partial energy-level diagram shown in Fig. 2.

The lines are split by an applied field for the same reasons given to explain the Stark effect of the ruby *R* lines. In BaClF there are two Ba^{2+} sites in the unit cell related by a center of symmetry; the applied field thus points in the (local) positive *z* direction at one site and

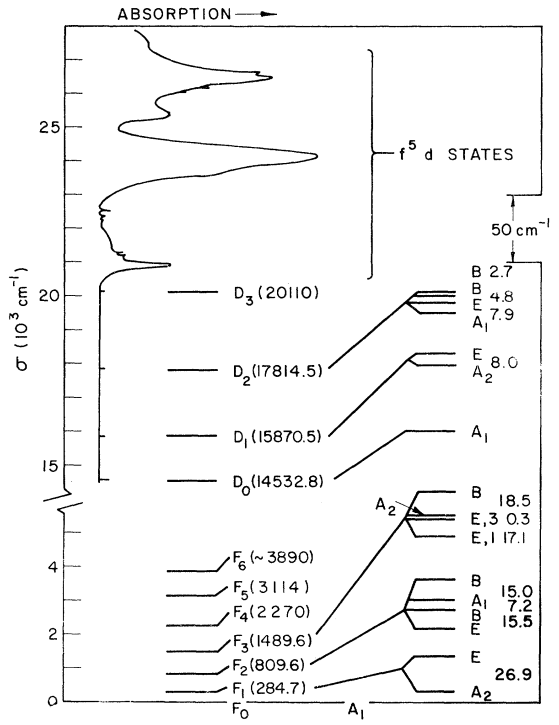

FIG. 2. Energy-level diagram showing some of the ^7F_J and ^5D_J levels. The bands above 20 000 cm^{-1} in the absorption spectrum shown are due to transitions from $^7F_0$ to states of the f^5d configuration. Note that the wave-number scale on the right refers to the crystal-field levels shown to the right.

in the (local) negative z direction in the related site. The lines originating from these two sites thus have an energy shift in opposite directions and as a result one observes a splitting. Simple group theory considerations may be used to show this result and also to show that for $\vec{\epsilon} \perp \vec{c}$ there should be no first-order (in ϵ) splitting. In this latter case, the field $\vec{\epsilon}$ formally destroys (at least) the fourfold symmetry element and the doubly degenerate E states of C_{4v} become pairs of nondegenerate states in the lower symmetry group. If there were a splitting first order in ϵ when $\vec{\epsilon}$ is perpendicular to $\vec{c}$, then $\langle E1 \mid \Gamma(\epsilon_{x,y}) \mid E1\rangle = -\langle E-1 \mid \Gamma(\epsilon_{x,y}) \mid E-1\rangle \neq 0$, where $\Gamma(\epsilon_{x,y})$ is the representation of the vector $\vec{\epsilon} \perp \vec{c}$ and $\mid E1\rangle$, $\mid E-1\rangle$ are the degenerate pair of states transforming like E. $\Gamma(\epsilon_{x,y}) = E$ in C_{4v} and the direct product $E \times E \times E$ does not contain A_1, therefore the matrix elements are zero and the absence of a first-order effect is proven.

The shift δ of a $4f$ state is given by

$$\delta(SLJ) = e\epsilon_{\text{eff}} \sum_d \{\langle fSLJ \mid z \mid dSL'J'\rangle \langle dSL'J' \mid V_{\text{odd}} \mid fSLJ\rangle \times (E_f^{\,0} - E_d^{\,0})^{-1} + \text{c.c.}\} \quad (1)$$

for an effective field ϵ_{eff} at the rare-earth ion parallel with the fourfold z axis. The assumption has been made that the states of the f^5d configuration give the predominant odd-parity admixture to the states of the f^6 ground configuration and they are coupled via the odd-power crystal-field potential terms; the parent configurations are labeled simply by d or f. Equation (1) is, of course, simply the dipole moment of the state SLJ times the effective field, $\delta(SLJ) = \epsilon_{\text{eff}} \mu(SLJ)$. If we (1) assume first-order spin-orbit coupling between the ^7F_J and ^5D_J states of f^6; (2) assume first-order V_{odd} coupling between states (labeled by J) of f^5d and f^6; and (3) neglect V_{even} J-J' mixing within f^5d, we can relate the observed splitting $\Delta(SLJ, S'L'J) = 2\epsilon_{\text{eff}} \mid \mu(SLJ) - \mu(S'L'J) \mid$ of a line due to the transition $SLJ \rightarrow S'L'J$ to the transition dipole moment. Put another way, we use wave functions corrected to first order only in spin-orbit and V_{odd}. With these approximations, a typical term in the expression for the z component of the dipole moment of a transition $fSLJ \rightarrow fS'L'J$ is

$$\sum_k \frac{\langle fSLJ \mid \sum_i l_i \cdot s_i \mid fS'L'J\rangle \langle fS'L'J \mid \sum_i e_i z_i \mid dS'L''J''\rangle \langle dS'L''J'' \mid V_{\text{odd}}^{(k)} \mid fS'L'J\rangle}{[E^0(SLJ) - E^0(S'L'J)][E^0(S'L''J'') - E^0(S'L'J)]}. \quad (2)$$

The latter quantity is related to the oscillator strength through the equation

$$f(SLJ, S'L'J) = 4\pi mc\sigma\hbar^{-1}e^{-2}[\mu(SLJ, S'L'J)]^2, \quad (3)$$

where σ is the wave number of the transition. Thus, the desired relation is found to be

$$\Delta(SLJ, S'L'J)/\epsilon_{\text{eff}} = 4\mu(SLJ, S'L'J)/a(SLJ, S'L'J), \quad (4)$$

where $a(SLJ, S'L'J)$ is the first-order spin-orbit mixing coefficient of the zero-order states. The value $f = 1.2 \times 10^{-6}$ was experimentally measured for the ${}^7F_0 \rightarrow {}^5D_0$ transition, and from the known energy levels and spin-orbit matrix elements we estimate $a({}^7F_0, {}^5D_0) \approx 0.25$. Finally, taking $\epsilon_{\text{eff}} = \epsilon(\text{applied})$, we calculate $\Delta({}^7F_0, {}^5D_0)/\epsilon \approx 2 \times 10^{-3}$ cm^{-1}/kV cm^{-1}, which is to be compared with the observed shift of 1×10^{-3} given in Table I.

An unexpected feature of this work is the electric dipole strength and Stark shift of the lines involving $J = 0 \nleftrightarrow J' = 0$, $J = 0 \nleftrightarrow J' = 1$, and $J = 1 \nleftrightarrow J' = 1$ transitions (see Table I). We suggest that these intensities and Stark shifts can be explained by a term $V^{(1)} = \mathcal{C}^{(1)} \langle r \rangle C_0^{(1)}$, where $C_0^{(1)} = \sum_i \cos\theta_i$ and $\mathcal{C}^{(1)}$ is a parameter depending on the geometry and charge distribution about the rare-earth ion.

In the study of the isoelectronic Eu^{3+} ion in the trichloride and ethylsulfate hosts by Ofelt[6] and Axe,[3] these transitions were not observed. However, in these two crystals the rare-earth ion is at a site of D_{3h} symmetry which formally does not allow a $V^{(1)}$ term, whereas in the present case the site symmetry C_{4v} in BaClF does allow such a term. One way that the $V_{\text{odd}}^{(k)}$ terms with $k \geq 3$ can explain the intensity would be to require the even-power crystal-field terms to admix $J \geq 2$ components into ${}^5D_0$ or ${}^7F_0$. We believe this admixture would be too small to account for the high intensity of ${}^7F_0 \rightarrow {}^5D_0$, which is comparable to that of ${}^7F_0 \rightarrow {}^5D_2$ (a transition made allowed through the $k \geq 3$ terms). If $V_{\text{even}}^{(k)}$ terms were large enough to eliminate J as a good quantum number in the excited states of f^5d, one can also see that $V_{\text{odd}}^{(k)}$ terms with $k \geq 3$ could account for the nonvanishing intensity of ${}^5D_0 \rightarrow {}^7F_0$. If this were the case, then the equation would not be applicable, and no obvious relation exists between the intensity and Stark splitting of lines due to transitions ${}^5D_J \nleftrightarrow {}^7F_J$.

Summarizing, the arguments in favor of the correctness of a dominant contribution by $V^{(1)}$ to the intensity and Stark splitting are (1) in crystals where the local symmetry excludes such a term, 0-0 and 0-1 transitions are not observed, but are observed in the present case where $V^{(1)}$ is formally allowed; and (2) the Stark shift calculated by using the observed oscillator strength seems to be in reasonably good

Table I. Stark splittings, oscillator strengths, and transition types for a number of ${}^5D_J \nleftrightarrow {}^7F_{J'}$ transitions.

Transition	Wave number (cm^{-1})	Type[a]	Oscillator strength[b] f	Stark splitting Δ/ϵ in cm^{-1}/kV cm^{-1}
$D_0A_1 \nleftrightarrow F_0A_1$	14 532.8	ED	1.2×10^{-6}	1.1×10^{-3}
$\rightarrow F_1A_2$	14 266.0	MD		$<2 \times 10^{-4}$
$\rightarrow F_1E$	14 239.1	ED		5.2×10^{-3}
$\rightarrow F_2E$	13 738.0	ED		None observed
$\rightarrow F_2A_1$	13 715.5	ED		None observed
$D_1E \nleftrightarrow F_0A_1$	15 873.2	ED	5.3×10^{-7}	
$D_1A_2 \nleftrightarrow F_0A_1$	15 865.2	MD	$\approx 1 \times 10^{-8}$	
$D_1E \nleftrightarrow F_1A_2$	15 606.5	ED		
$D_1A_2 \nleftrightarrow F_1A_2$	15 598.3	ED		
$D_1E \rightarrow F_1E$	15 579.5	ED		
$D_1A_2 \rightarrow F_1E$	15 571.3	ED		6.0×10^{-3}
$D_1A_2 \rightarrow F_3E, 1$	14 390.3	ED		2.3×10^{-3}
$D_2E \nleftrightarrow F_0A_1$	17 812.9	ED	5.0×10^{-7}	None observed
$D_2A_1 \nleftrightarrow F_0A_1$	17 805.1	ED	$\approx 1 \times 10^{-7}$	None observed
$D_2E \rightarrow F_1A_2$	17 547.3	ED		
$D_2E \rightarrow F_1E$	17 519.9	ED		
$D_2A_1 \rightarrow F_1E$	17 512.3	ED		6.0×10^{-3}
$D_2A_1 \rightarrow F_3E, 3$ F_3A_2	16 313.5	ED + MD		5.2×10^{-3}

[a]The transition type was determined by studies on the polarized absorption and emission spectra of crystals mounted both with the c axis parallel and perpendicular to the direction of observation. ED means electric dipole and MD means magnetic dipole.

[b]Determined from the integrated absorption lines.

agreement with the experimentally observed Stark splitting.

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OBSERVATION OF PERSISTENT CURRENTS IN A SUPERCONDUCTING CIRCUIT CONTAINING A JOSEPHSON JUNCTION*

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Measurements of the dc superconductive properties of Josephson tunnel junctions have been made by many investigators.[1] The I-V characteristics have always been obtained by potentiometric techniques. This note describes the observation of the superconductivity of a junction by the much more sensitive method of incorporating it in a persistent current loop. That the junction should support a persistent current equal in magnitude to the maximum indicated by the I-V characteristic is not immediately evident. In the latter case, the boundary conditions for the wave function are determined by the external current source, while in the former case the wave function must be single valued around the loop.[2] In addition, measurements on hard superconductors have revealed systems in which no measurable resistance can be detected by potentiometric measurements but which will not support stable persistent currents.[3] The measurements described below show that superconducting loops containing Pb-Pb_xO_y-Pb junctions will support persistent currents equal to the maximum supercurrent obtained from the I-V characteristic.

The junction was made by vacuum evaporating two lead strips at right angles to each other onto a glass microscope slide. The first strip was allowed to oxidize in oxygen for 14 hours at 20°C before evaporating the second strip. The strips were 0.1 mm wide and about 2000 Å thick.

The experiment was performed at 4.2°K with the junction in the circuit shown in Fig. 1. With the exception of the junction and the leads from the liquid-helium region, all portions of the circuit were made of 2-A Buss fuse wire (diameter 0.7 mm). The composition of the wire was

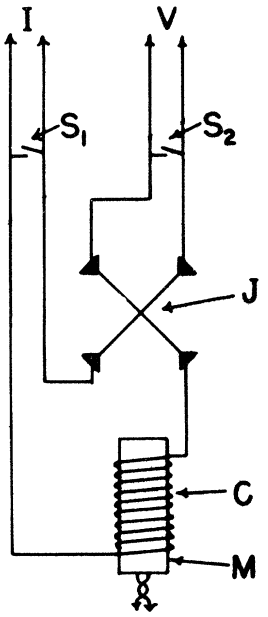

FIG. 1. Schematic diagram of junction and circuit. I: current leads; V: voltage leads; S_1 and S_2: mechanical switches; J: tunneling junctions; C: superconducting coil; M: magnetometer and aluminum shield.