

Cooperative Absorption and Luminescence in Cr³⁺-Doped EuAlO₃

J. P. van der Ziel and L. G. Van Uitert

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 30 April 1973)

Absorption and emission involving exchange-coupled nearest-neighbor Cr³⁺ and Eu³⁺ ions have been observed in Cr³⁺-doped EuAlO₃ at the sum of the chromium ²E_g and europium ⁷F₁ energies. Weak absorption at the difference energy has also been observed. The latter is the inverse of the previously studied europium terminated chromium emission. The intensities of the Eu³⁺ sideband transitions vary with the strength of the exchange-induced electric dipole moment.

I. INTRODUCTION

Some time ago we reported the observation of coupled-ion luminescence in Cr³⁺-doped EuAlO₃.^{1,2} In this process an excited Cr³⁺ ion decays by simultaneously transferring part of its excitation energy to a neighboring Eu³⁺ ion and emitting the balance as a photon. Coupled-ion luminescence has been observed from several other Cr³⁺-rare-earth systems³⁻⁵ and for Gd³⁺-Yb³⁺ pairs.⁶

Here we report two new coupled-ion effects in EuAlO₃: Cr³⁺ which are observed in absorption, as well as a new emission effect. In the first case, which we will call sum-energy absorption, both Cr³⁺ and Eu³⁺ are initially in their respective ground states (Cr³⁺ in ⁴A_{2g} and Eu³⁺ in ⁷F₀) and are excited to either of the ²E_g levels in the case of Cr³⁺ and to one of the crystal-field-split ⁷F₁ levels in the case of the neighboring Eu³⁺ [Fig. 1(a)]. The absorption occurs at approximately the sum of the single-ion energies and is an example of cooperative absorption.⁷ In the second case, shown in Fig. 1(b), which we will call difference-energy absorption, the Cr³⁺ ion initially is in the ground ⁴A_{2g} state and the Eu³⁺ ion is in an excited ⁷F₁ state while in the final state the Cr³⁺ ion is in the excited state and the Eu³⁺ has returned to the ⁷F₀ ground state. This is the inverse of pair emission discussed previously.^{1,2} The absorption occurs approximately at the difference between the single-ion energies. We will show that the absorption processes are related to the exchange interaction between the Cr³⁺ and Eu³⁺ ions. The new emission lines are due to the inverse of the sum-absorption mechanism discussed above. The effect is weak due to the required thermal population of the Eu³⁺ ⁷F₁ level.

II. EXPERIMENTAL

The crystals used in this investigation were grown in a PbO-PbF₂-B₂O₃ flux by slow cooling of the melt. Typical crystals had dimensions of several mm.

The space group of orthorhombic EuAlO₃ is D_{2h}¹⁶

and the unit cell contains four EuAlO₃ units.⁸ The Cr³⁺ ions substitute on the four Al³⁺ sites which have C_i symmetry. The four europium sites have C_s symmetry. Because of the low symmetry, the site axes are not simply related to the crystal axes,⁹ and it thus is difficult to determine the polarization accurately. However, in agreement with a center of inversion, the R lines at 13707.5 and 13744 cm⁻¹ appear to have predominantly magnetic dipole polarization. The spectra were recorded electronically using a 1-m Czerny-Turner spectrometer and a S-20-response phototube. Appropriate glass filters were used to flatten the spectral response of the system. The emission spectrum was excited with light from a 500-W Hg lamp which was filtered by 5 cm of saturated copper sulphate solution and appropriate glass filters.

III. RESULTS AND DISCUSSION

A. Sum-Energy Absorption

Cooperative absorption involving transitions terminating on the ²E_g levels and the three crystal-field-split levels of ⁷F₁ are shown in Fig. 2. The crystal field splits the J=1 levels into three components which may be identified with the x, y, and z axes of the Eu³⁺-ion-site coordinate frame.¹⁰ Rather than a single absorption line for each cooperative transition, there are four for the y level of ⁷F₁, three well-resolved lines for the z level, and one broad line which contains at least three unresolved components for x level. The sum-absorption lines occur with the same displacements in energy above R₁ and R₂, and on the average these displacements differ only slightly from the 280-(y), 358-(z), and 471-(x) cm⁻¹ ⁷F₁ energies of isolated Eu³⁺ in this crystal.^{1,10}

More than one line occurs because the crystal field of an Eu³⁺ ion which has a Cr³⁺ ion as a near neighbor is perturbed by this ion, and consequently the energy levels will differ slightly from the levels of Eu³⁺ ions having only Al³⁺ neighbors. As shown in Fig. 3 the eight Eu³⁺ ions nearest a Cr³⁺ ion are oriented along the <111> axes and interact

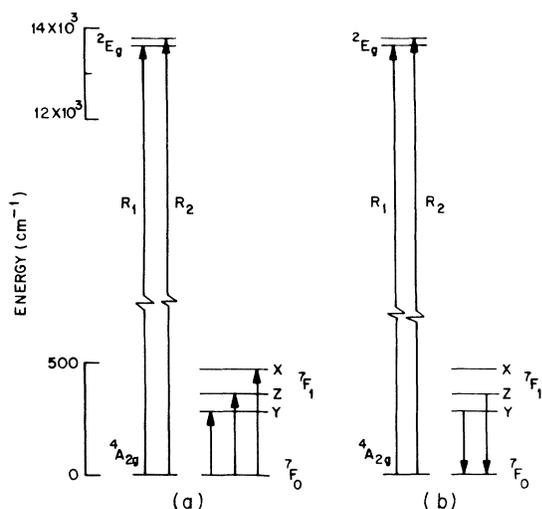


FIG. 1. The Cr^{3+} and Eu^{3+} energy levels involved in cooperative absorption. The arrows denote the observed transitions of the coupled system for the sum-energy sidebands (a) and the difference-energy sidebands (b).

with the Cr^{3+} ion through three oxygen ions with a $\text{Eu}^{3+}-\text{O}^{2-}-\text{Cr}^{3+}$ bond angle of approximately 90° . Since the Cr^{3+} has inversion symmetry, there are four distinct crystal-field environments for these Eu^{3+} ions with two ions belonging to each type.

The wave function of the coupled system can be written in the usual product form. The symmetry of the problem indicates that the appropriate linear combinations of the wave functions involve only the two excited Eu^{3+} ions of the same type, and the wave functions have even or odd parity under in-

version through the Cr^{3+} site. In the initial state the ions are in their respective ground states and the wave function

$$|l, {}^4A_{2g}m\rangle = |l, {}^7F_0, {}^4A_{2g}m, {}^7F_0\rangle \quad (1)$$

has even parity. Here l is the Eu^{3+} -pair type and m is the z component of Cr^{3+} spin. In the final state the Cr^{3+} ion is in the $\kappa=u, v$ state of 2E_g with spin component m and the Eu^{3+} ions are in one of the 7F_1 states with $\mu = x, y$, or z . The wave functions are

$$|l, \mu, {}^2E_g\kappa m, \pm\rangle = [|l, {}^7F_0, {}^2E_g\kappa m, {}^7F_1\mu\rangle \pm |l, {}^7F_1\mu, {}^2E_g\kappa m, {}^7F_0\rangle] / \sqrt{2}, \quad (2)$$

where the \pm refers to the parity under inversion. The dipole moment resulting from the exchange interaction is

$$\vec{P} = \sum_k \sum_j \sum_i \vec{\pi}(\text{Cr}, i; \text{Eu}_k, j) \vec{S}(\text{Cr}, i) \cdot \vec{S}(\text{Eu}_k, j), \quad (3)$$

where the k sum is over the europium ions neighboring the chromium ions, the j sum is over the electrons of this ion, and the i sum is over the Cr^{3+} electrons.

Equation (3) has the same origin as the dipole moment used to explain two-magnon absorption and magnon sidebands¹¹ in magnetically ordered crystals. The dipole moment has odd parity under inversion, and it has matrix elements only to the odd-parity state of Eq. (2). There will thus be one cooperative transition to the odd-parity final state for each type of Eu^{3+} neighbor. It is gratifying that four transitions are observed for the y component of 7F_1 . The crystal-field perturbation of the z and x components is apparently not large enough to

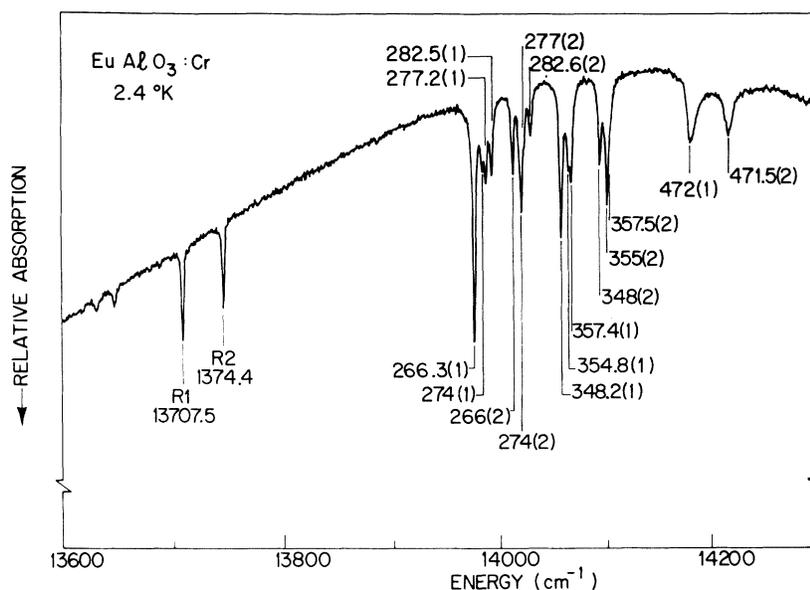


FIG. 2. Absorption spectrum of Cr^{3+} in EuAlO_3 . The energies of the terminal $\text{Eu}^{3+} {}^7F_1$ levels above the R_1 and R_2 energies are given for each pair line and are denoted by the bracketed 1 and 2. The groups of lines at ~ 280 , 358 , and 471 cm^{-1} terminate on the y , z , and x components of 7F_1 , respectively.

separate the four-line patterns completely.

The energy difference of the even- and odd-parity states derives from the off-diagonal matrix element which transfers excitation from one Eu^{3+} ion to the second ion of the same type. The splitting due to this resonant interaction is the two-ion analog of the Davydov splitting in concentrated crystals.¹² Because of the relatively large separation between Eu^{3+} ions of the same type we conclude that this splitting, which will depend on the Eu^{3+} type, is too small to account for the observed splitting between the odd-parity states.

The absorption strength depends strongly on the type of pair, and for the well-resolved lines is generally quite different for the transitions of the two 2E_g components. Multiple lines were also observed in pair luminescence,^{1,2} and for a given crystal-field component of 7F_1 the relative intensities as well as the separation from the R lines are the same in cooperative absorption and pair luminescence. Because the lines overlap, it is not possible to separate the contributions of each pair type; however, the total integrated absorption for each component of 7F_1 , which is given in Table I, reflects these differences. In agreement with the theory, the magnetic dipole strengths of the R lines are equal to within experimental error. The cooperative absorption is predominantly electric dipole and is significantly more intense than the R lines and this is consistent with the exchange-induced-dipole-moment mechanism.

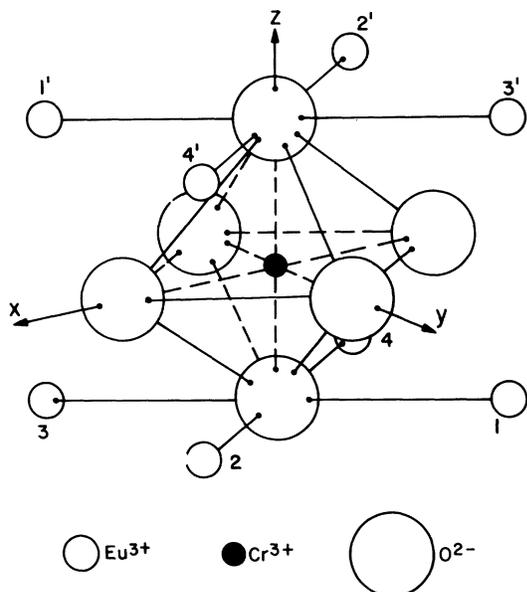


FIG. 3. Crystal structure of EuAlO_3 near the Cr^{3+} ion. The Eu^{3+} sites labeled k and k' are related by inversion through the Cr^{3+} site. The distortion of the oxygen octahedron is not shown.

TABLE I. Integrated absorption strengths of the R lines and the sum-energy pair-absorption lines involving the three components of 7F_1 . The absorption is normalized to unity R_1 absorption, and the values are accurate to within ± 0.1 .

	2E_g	7F_1		
		y	z	x
R_1	1.	6.69	4.53	2.36
R_2	0.97	3.73	3.47	1.40

In the discussion of cooperative luminescence of this compound we showed that the exchange-induced dipole moments associated with the three t_{2g} Cr^{3+} orbitals must be different in order to have a nonvanishing total dipole moment.² Furthermore, the contribution to the dipole moment which is isotropic in the Eu^{3+} orbitals has an equal strength for each component of 7F_1 , but is in general different for the two 2E_g states. However, the individual components do not have equal intensities, and this also shows up in the total intensities in Table I. These differences are attributed to the anisotropy effects of the $4f^6$ orbitals of the Eu^{3+} ion, and we see from Table I that the anisotropy is different for the two 2E_g states. The spatial anisotropy of the single $3d$ - and $4f$ -electron wave functions is thus an important factor in the spin-dependent-dipole-moment mechanism.

B. Sum-Energy Luminescence

Four weak luminescence bands are observed between 13 960 and 14 110 cm^{-1} at liquid-nitrogen temperature. The spectrum is similar to the absorption spectrum shown in Fig. 2 and is the inverse of this type of pair absorption. Initially the Cr^{3+} is in the 2E_g state and the neighboring Eu^{3+} is in the y or z component of 7F_1 . The luminescence terminates with both ions in their respective ground states. Relative to the R lines the pair-emission intensity decreases as the temperature is lowered and is similar to the temperature dependence of the 7F_1 level population. At 77 °K the pair-emission intensities range from ~ 6 to 0.4% of the R -line parents, and are in reasonable agreement with the relative emission calculated using the 2E_g and 7F_1 populations at this temperature and the integrated absorption given in Table I.

C. Difference-Energy Absorption

This is the inverse of the pair emission discussed in Refs. 1 and 2. The spectral dependence of the absorption is similar to the emission spectrum, and the absorption is observed only when the 7F_1 levels are populated. The temperature dependence of the strongest pair absorption, which involves the lowest-energy 2E_g level and the y component of 7F_1 ,

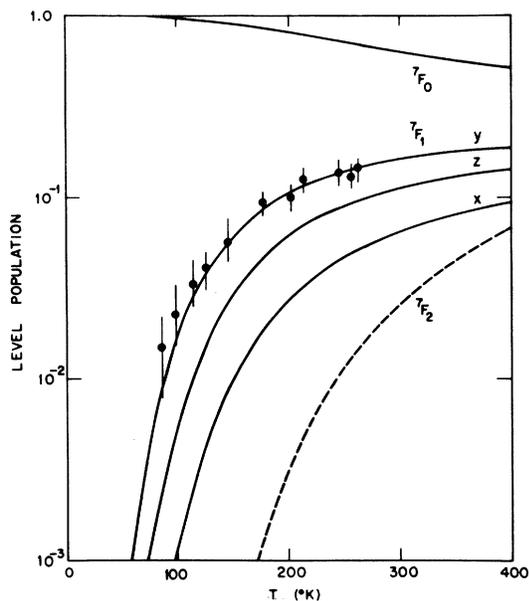


FIG. 4. The calculated population of the 7F_0 and 7F_1 levels as a function of temperature. The average population of the five 7F_2 levels at $\sim 1000\text{ cm}^{-1}$ is shown by the dashed line. The points show the measured temperature dependence of the energy difference pair absorption which involves the y component of 7F_1 . The error bars indicate the experimental uncertainty.

relative to the R_1 -line absorption is shown by the points in Fig. 4. The data are in good agreement with the temperature dependence of the y -level population. Pair absorption was also observed for the y component and the higher 2E_g level as well as for the z component and both 2E_g levels. These absorption lines are considerably weaker than the absorption plotted in Fig. 4, and at the higher temperatures the thermally broadened absorption overlaps the spectrum of nearest-neighbor Cr^{3+} pairs.¹³ These lines also have temperature dependence which are characteristic of the populations of the 7F_1 crystal-field levels involved in the absorption.

The integrated emission intensities of the energy-difference pair lines, normalized to the integrated R -line emission, were obtained from the luminescence spectrum at 77°K and are shown in Table II. The relative strength of most of the energy-difference pair lines are in good agreement with the strength of the sum-energy absorption given in Table I. The major discrepancy involves the x - R_2 component. The emission intensity of this line is relatively weak, and the accuracy of this measurement was not very high. In plotting the data of Fig. 4 we find that the ratio of the pair absorption to the R -line absorption is 6 ± 1 times larger than the calculated population of the y level. This factor is just the ratio of the dipole strengths of the pair line and R lines and is in reasonable

agreement with the value of the ratio of 6.95 obtained from the luminescence data (Table II).

For the case of energy-difference pair absorption, the single-ion quantum numbers change by $\Delta S = -1$ for the Cr^{3+} ion and $\Delta J = -1$ for the Eu^{3+} ion, and for the sum-energy absorption the changes are $\Delta S = -1$ and $\Delta J = +1$. In emission the quantum numbers change by $\Delta S = 1$ and $\Delta J = \pm 1$. We have shown that when the population effects are taken into account, the dipole strengths are the same for each transition involving the same 2E_g and 7F_1 levels. This is a peculiarity of our pair system which does not occur in the spin-wave-sideband spectrum of antiferromagnets. It results from the fact that, unlike an antiferromagnet, the levels of the Cr^{3+} ion remain Kramers's doublets in this crystal.

The difference-energy pair absorption has recently been discussed theoretically by Altarelli and Dexter.¹⁴ They propose several experiments and suggest that the excited initial state (equivalent to the 7F_1 states for the experiment discussed here) be populated by a second beam of light. For relatively closely spaced energy levels found in many of the rare earths the interlevel relaxation is relatively rapid. It is thus not only difficult to obtain a large population in the excited state, but also to obtain a quantitative measure of this population. These problems are avoided by using thermal excitation. The experiments proposed in Ref. 14 involved calculations based on the electrostatic multipolar interaction. The resulting pair emission would then be considerably weaker than the single-ion absorption. We have shown that, at least in our case and presumably also in others, the exchange-induced-electric-dipole moment can lead to pair absorption which is considerably stronger than the associated single-ion transition.

IV. CONCLUSION

We have now observed the sum and difference sidebands of the Eu^{3+} levels in both the absorption and emission spectrum of the chromium ${}^4A_{2g} \leftrightarrow {}^2E_g$ transitions. The coupling of the two ions was shown to result from the exchange interaction between the Cr^{3+} and the nearest-neighbor Eu^{3+} rather than from electrostatic multipolar interactions.^{1,2} The transition-dipole moment of the pair derives

TABLE II. Integrated emission of the energy-difference pair lines. The pair emission is normalized to unity R_1 and R_2 emission.

	y	7F_1 z	x
R_1	6.95	4.48	2.34
R_2	3.85	3.18	1.01

from the exchange interaction and the anisotropy of the single-electron-single-electron exchange was shown to make a significant contribution to the dipole moment.

ACKNOWLEDGMENT

The assistance of L. Kopf in the course of this work is appreciated.

-
- ¹J. P. van der Ziel and L. G. Van Uitert, *Phys. Rev. Lett.* **21**, 1334 (1968).
²J. P. van der Ziel and L. G. Van Uitert, *Phys. Rev.* **180**, 343 (1969).
³J. P. van der Ziel and L. G. Van Uitert, *Phys. Rev.* **186**, 332 (1969).
⁴J. P. van der Ziel and L. G. Van Uitert, *Solid State Commun.* **7**, 819 (1969).
⁵J. P. van der Ziel, *J. Lumin.* **1**, 807 (1970).
⁶P. P. Feofilov and A. K. Trofimov, *Opt. Spectrosc.* **27**, 291 (1969).
⁷F. Varsanyi and G. H. Dieke, *Phys. Rev. Lett.* **7**, 442 (1961); G. H. Dieke and E. Dorman *Phys. Rev. Lett.* **11**, 17 (1963); J. S. Margolis, O. Stafsudd, and E. Y. Wong, *J. Chem. Phys.* **38**, 2045 (1963).
⁸S. Geller and V. B. Bala, *Acta Crystallogr.* **9**, 8 (1956).
⁹J. P. van der Ziel, F. R. Merritt, and L. G. Van Uitert, *J. Chem. Phys.* **50**, 4317 (1969).
¹⁰L. Holmes, R. Sherwood, L. G. Van Uitert, and S. Hüfner, *Phys. Rev.* **178**, 576 (1969).
¹¹Y. Tanabe, T. Moriya, and S. Sugano, *Phys. Rev. Lett.* **15**, 1023 (1965); K. I. Gondaira and Y. Tanabe, *J. Phys. Soc. Jap.* **21**, 1527 (1966); Y. Tanabe and K. I. Gondaira, *J. Phys. Soc. Jap.* **22**, 573 (1967); N. Fuchikami and H. Ono, *J. Phys. Soc. Jap.* **34**, 360 (1973).
¹²J. P. van der Ziel, *Phys. Rev.* **161**, 483 (1967); J. W. Allen, R. M. McFarlane, and R. L. White, *Phys. Rev.* **179**, 523 (1969).
¹³The nearest-neighbor Cr³⁺ pair spectrum in the isomorphous crystal YAlO₃ has been studied by J. P. van der Ziel, *J. Chem. Phys.* **57**, 2442 (1972).
¹⁴M. Altarelli and D. L. Dexter, *Opt. Commun.* **2**, 36 (1972); M. Altarelli and D. L. Dexter, *Phys. Rev. B* **1**, 5335 (1973).