

Edge Emission and Zeeman Effects in CdS

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Some of the sharp, characteristic emission lines, observed in "blue" and "green" edge-fluorescence spectra of CdS platelets, have been examined experimentally at low temperatures ($\sim 1^\circ\text{K}$). Zeeman effects, in magnetic fields up to 45 000 G, have been studied in doublets of previously reported lines, as well as in several new lines. In particular, the magnetic splitting of I_6 (a characteristic "blue" emission line appearing at 4869.14 Å) has been studied as a function of magnetic field orientation (angular orientation of c axis with respect to field direction). In accordance with the Thomas-Hopfield analysis, arguments are presented for the association of I_6 with a bound exciton complex; this line was observed to split linearly as a function of field strength and a g value of -1.76 ($c \perp H$) is reported. Several zero-field split lines (fluorescent doublets) have been studied as a function of field orientation: I_1 (4888.47, 4888.18 Å), I_2 (4867.17, 4866.98 Å), and I_3 (4861.66, 4862.25 Å). The lines I_1 (doublet) and I_2 (doublet) were observed to split linearly as a function of field strength and a g value of -1.77 ($c \perp H$) is reported for I_1 . In particular crystals, pronounced thermalization effects have been observed in the fluorescent singlets I_1 (4888.47 Å), I_2 (4867.17 Å) and I_6 , i.e., line thermalization was observed as a function of magnetic splitting at constant temperature. Two sharp, long-wavelength lines have also been observed, namely I_6 (5068.54, 5069.18 Å) and I_7 (5084.81 Å). The polarization and magnetic splittings of I_6 and I_7 are reported.

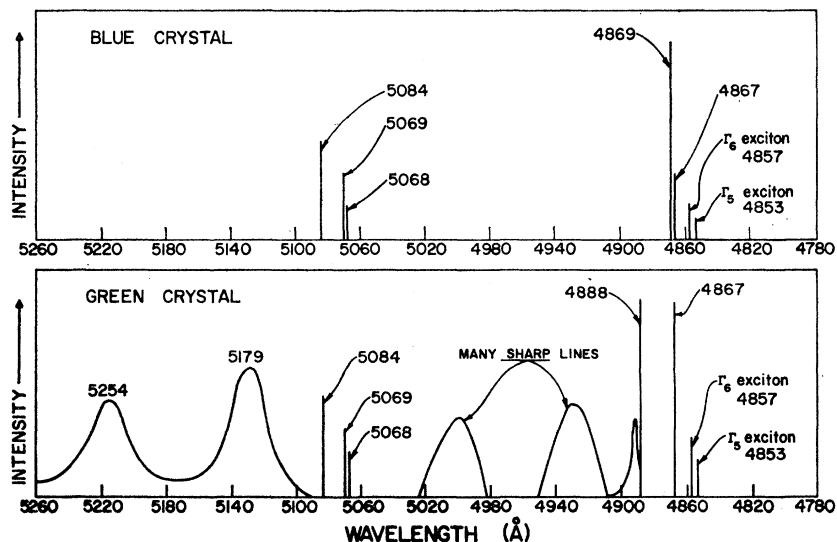
I. INTRODUCTION

In a previous study¹ of CdS edge fluorescence, two distinct types of crystals were observed and their emission was classified as blue emission ("blue crystal") and green emission ("green crystal"). This classification was based primarily on fluorescence color and, to a lesser extent, on presence, absence and grouping of certain lines. The essential features of the two types of crystals are diagrammed in Fig. 1. The "green emission" type of crystal is characterized by a set of broad green peaks, the first of which appears at 5179 Å (4.2°K); these peaks are phonon assisted, i.e., successive peaks are separated by the longitudinal optical phonon energy. Two sharp lines are dominant in this

type of crystal, namely, the 4888 and 4867 Å lines; many other sharp, less intense, lines are observed in these crystals, some of which are contained in the two "envelopes" marked "many lines" (Fig. 1). Thomas and Hopfield^{2,3} have observed and identified many of the CdS emission lines by studying the Zeeman effect in the optical transitions. In particular, they have shown that the transitions are associated with exciton complexes. From the magnetic field splittings of the lines, together with intensities, they have successfully associated specific transitions with specific centers, such as excitons bound to neutral donors or acceptors or charged donors, etc.

In the other type of crystal ("blue crystal") the

FIG. 1. Diagram of some characteristic emission lines in "blue" and "green" CdS crystals at 4.2°K and below. Lines are drawn to represent some of the fluorescence lines at the appropriate wavelengths. While intensities are generally represented by line heights, intensities are not meant to be quantitatively comparable. Many variations between predominantly blue and predominantly green fluorescence have been observed in CdS, i.e., "blue-green" fluorescence. For example, a strong "blue-crystal" spectrum may contain a weak I_1 line (4888 Å) and low-intensity broad-green peaks, while a strong green crystal spectrum may contain a weak I_6 line (4869 Å) in addition to the strong I_2 line (4867 Å) and intense broad green peaks. The I_6 (zero-field split into 5068 and 5069 Å components) and I_7 (5084 Å) lines, usually observed in "blue crystals," are observed in some "blue-green crystals."



¹ L. S. Pedrotti and D. C. Reynolds, Phys. Rev. 120, 1664 (1960).

² D. G. Thomas and J. J. Hopfield, Phys. Rev. Letters 7, 316 (1961).

³ D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).

broad green peaks are missing, as well as the sharp 4888 Å line (see caption, Fig. 1.). Interestingly the dominant sharp transition in the blue crystal is the 4869.14 Å line; in some of these crystals, as much as 85% of the total fluorescence (intensity) appears in this dominant line. Based on the Thomas-Hopfield exciton complex analysis, we have tentatively identified the 4869 transition.

In some crystals ("blue" and "green") both the 4888.47 Å line and the 4867.17 Å line appear as doublets (zero field). The behavior of these doublets in a magnetic field will be discussed; moreover, the zero-field splitting of the 4861.66 Å emission line will be reported.

A few sharp lines have been observed at relatively long wavelengths (5068 Å and longer). One of these lines (zero-field split) is interesting in that it is preferentially polarized in the mode $E\parallel c$. As a consequence of lattice symmetry, intrinsic transitions are allowed for $E\perp c$, i.e., in the wurtzite symmetry, the Γ_9 valence band is strongly active only for the $E\perp c$ mode of polarization, while the Γ_7 bands (B and C) are active for both modes. (The energy band structure of the wurtzite lattice at $\mathbf{k}=0$, group theoretically deduced, has been reported by many investigators⁴ and is reproduced in Fig. 2.) Since the center involved is energetically close to a band, one would expect it to reflect the band symmetry so that the corresponding optical transition would obey the $\Gamma_7 \leftrightarrow \Gamma_9$ selection rule. The behavior of these long wavelength lines in a magnetic field, as well as the polarization of their emission, is discussed in the text.

For purposes of identification, we have adopted, for mutually observed lines, a nomenclature due to Thomas and Hopfield² (I_1 , I_2 , etc.). This notation has been extended for additional lines. All of the emission lines we have studied are listed in Table I.

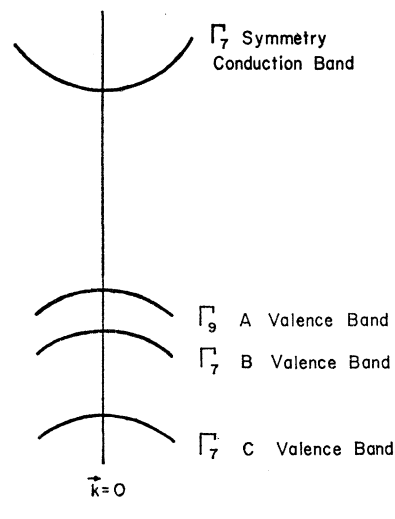


FIG. 2. CdS band extrema in the k_z direction in the neighborhood of $\mathbf{k}=0$. The A -, B -, and C -band notation is due to Thomas and Hopfield (See Refs. 3 and 7).

⁴ See, e.g., J. L. Birman, Phys. Rev. Letters 2, 157 (1959).

II. EXPERIMENTAL

The crystals used in these experiments were of the platelet type, varying in thickness from 1–50 μ . The samples were glued on one end (relatively strain-free) to a sample holder which was in turn placed in the tip of a glass helium Dewar. The mounting was arranged so that the samples were immersed in liquid He. Provision was made for pumping on the liquid He (high-speed mechanical vacuum pump) and temperatures were measured by means of vapor pressure thermometry, using an oil manometer. All of the experiments were carried out at approximately 1.2°K. The Dewar tip was inserted between the pole pieces of a large, conventional dc electromagnet (Pacific Electric Motor), with a pole spacing of $\frac{5}{16}$ in. For a power input of 30 kW (100 A, 300 V), this magnet generated a maximum field strength of 45 000 G; this was the highest field strength used in any of the experiments. A 500 W Hg lamp (Osram high pressure), filtered to remove the visible radiation, was used for fluorescence excitation. The crystal fluorescence was focused on the slit of a Bausch and Lomb 2-m grating spectrograph, having a reciprocal dispersion of 2 Å/mm in first order. The spectral resolution ranged from 0.02 to 0.4 Å. All of the spectra were photographically recorded on Kodak 103 aF plates. The effective spectrographic aperture was about $f/16$ and exposure times ranged from 10 sec to 30 min for strong lines and up to 1 h for very weak lines in some crystals.

III. RESULTS

A. I_5 Line (4869.14 Å)

We have studied the Zeeman splitting of the I_5 line in fields up to 45 000 G. The data reported here are for crystals showing strong "blue emission," with approximately 85% of the total emission intensity appearing in the I_5 line. In these crystals, the broad green bands and the I_1 line were totally absent; the I_2 line was present but of very low intensity. The intensity of the I_5 line varies appreciably from crystal to crystal and is quite low in "green crystals." The g value of the

TABLE I. A list of the CdS emission lines reported in the text.

Line	Wavelength (Å)	Energy (eV)	Active for
I_1	4888.47	2.53585	$E\perp c$
I_1 (doublet)	4888.47	2.53585	$E\perp c$
	4888.18	2.53600	$E\perp c$
I_2	4867.17	2.54695	$E\perp c$
I_2 (doublet)	4867.17	2.54695	$E\perp c$
	4866.98	2.54705	$E\perp c$
I_3	4861.66	2.54984	$E\perp c$
(zero-field split)	4862.25	2.54953	$E\perp c$
I_5	4869.14	2.54592	$E\perp c$
I_6	5068.54	2.44576	$E\parallel c$ (strong)
(zero-field split)	5069.18	2.44545	$E\parallel c$
I_7	5084.81	2.43793	unpolarized

split I_5 line is -1.76 for the orientation $c \perp H$. In the orientation, $c \parallel H$, no splitting is observed, indicating that in this orientation the g value of the hole is approximately equal to the g value of the electron. The splitting of the I_5 line as a function of magnetic field orientation ($\cos\theta$) is shown in Fig. 3. The g values of the lines reported here were determined from detailed exciton-complex-analyses due to Thomas and Hopfield^{2,3}; the expected magnetic splittings of two such complexes are shown diagrammatically in Fig. 4. The observed linear splittings,⁵ line multiplicities and optical selection rules agree very well with the theory.

Thomas and Hopfield³ have observed that the intensities of the magnetically split I_1 and I_2 lines (multiplets) are independent of both magnetic field strength and temperature (range: 1.6 to 4.2°K) when viewed in fluorescence. We have observed intensity variations in the multiplets of both the I_1 and I_2 lines as a function of magnetic field. The intensity variation is not the same in all crystals; in some crystals, the multiplet intensities are approximately equal. In the case of the I_1 line ($c \perp H$ orientation) the low-energy line of the multiplet is always the most intense when a difference is observed. One would expect such an intensity difference to result from thermalization of the upper state (high-energy state of the split pair). This intensity difference or variation (variation with field strength at low temperature) is what one would expect for an exciton bound to a neutral acceptor site, in agreement with the assignment of Thomas and Hopfield (see Fig. 4). Intensity variations are also observed for the I_2 fluorescent multiplets in the same orientation as above ($c \perp H$). In general, the crystals show an I_2 multiplet whose high-energy component is the more intense. Such intensity behavior suggests the association of the I_2 line with an exciton bound to a neutral

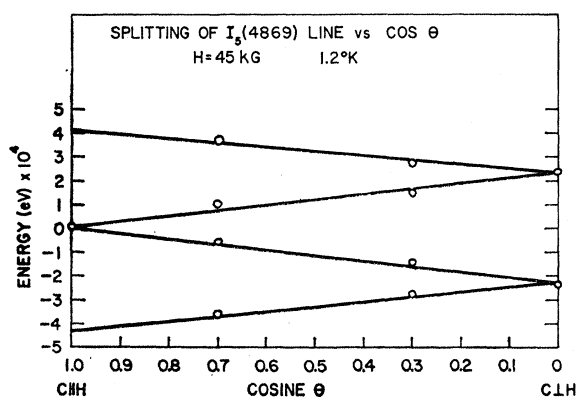
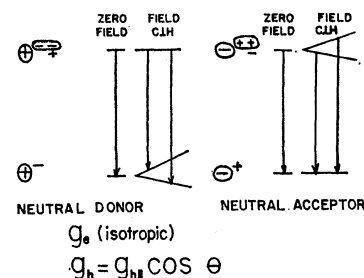


FIG. 3. Splitting of the emission line I_5 as a function of $\cos\theta$ in a field of 45 000 G and at a temperature of 1.2°K. Here, as in subsequent plots, θ is the angle between the crystalline c axis and the direction of the magnetic field. The zero of energy is taken to be the center of each group of lines.

⁵ The lines I_5 , I_1 (doublet) and I_2 (doublet) split linearly as a function of magnet field strength.

Fig. 4. Bound exciton complex states (holes from the top valence band only) showing the expected magnetic field splittings of the neutral donor and acceptor species for the case, $c \perp H$.



donor site (after Thomas and Hopfield). In Fig. 4, one can follow the reasoning which suggests that I_2 arises from an optical transition involving the neutral donor complex. There are, however, notable exceptions to this general intensity behavior; in particular, we have observed some crystals where the low-energy line of the I_2 multiplet was the more intense component. Such exceptions may prove to be important when one attempts to associate other transitions with specific complexes.

An examination of the I_5 multiplet intensities reveals that the intensity of each split component changes with magnetic field strength at 1.2°K. The general intensity behavior is shown in Fig. 5. Here we have plotted the intensity of the weak component relative to that of the strong component, normalizing the strong component to unity for each field strength. The orientation is, as above, $c \perp H$. The intense component of I_5 is the low-energy line; hence, one can conclude (from the data) that the I_5 line arises from a transition involving an exciton bound to a neutral acceptor site (see Fig. 4). Thomas and Hopfield report that they observe only one transition that can be associated with a neutral acceptor site, namely the I_1 transition. Not unlike the I_2 line, we have observed exceptions in the general intensity behavior of the I_5 components (intensity versus field strength). For example, in some crystals we have observed an intensity reversal in the I_5 com-

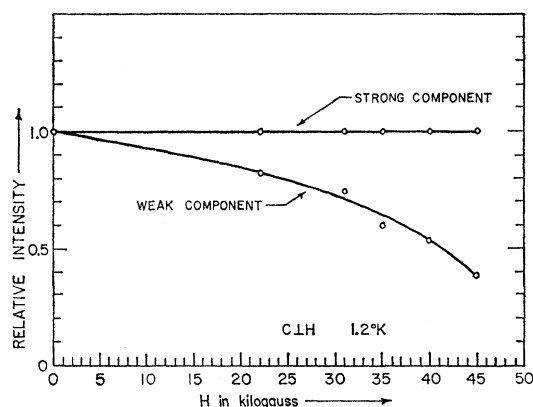


FIG. 5. Intensity comparison of the I_5 (4869) line components as a function of magnetic field strength at 1.2°K for the orientation $c \perp H$. The low energy or strong component is normalized to unity in this plot.

ponents, i.e., the high-energy component was more intense than the low-energy component. In the region of I_5 , and to shorter wavelengths, many emission lines (not reported here) are observed. Some crystals show many lines in this region ($\lambda < 4869 \text{ \AA}$) while others show only a few. The overlapping of some of these lines with the split components of the lines under observation (I_2 , I_3 , and I_5) could give rise to apparent line intensities that are false. In support of the "overlap" possibility, consider the following: intensity-reversals (function of field) have never been observed for the I_1 line components and I_1 (a sharp line) has no other sharp lines nearby. At any rate, our identification of the I_5 line (exciton bound to a neutral acceptor site) is rendered somewhat tentative by the observed intensity reversal in this line's components.

B. Long Wavelength Lines, I_6 and I_7

A group of relatively long wavelength emission lines have been observed in some crystals ("blue" and "green"). The spectral positions of these sharp, narrow lines ($< 0.1 \text{ \AA}$ half-width) are shown in Fig. 1 (see Table I for exact wavelength). These lines, which we have labeled I_6 and I_7 , are particularly distinguished by their polarization characteristics: I_6 is polarized preferentially in the mode $E \parallel c$, while I_7 is practically unpolarized.⁶ Figure 6 shows a densitometer trace of the more intense lines for the two different modes of polarization. It is interesting to note that the red emission from CdS:Cu crystals is polarized preferen-

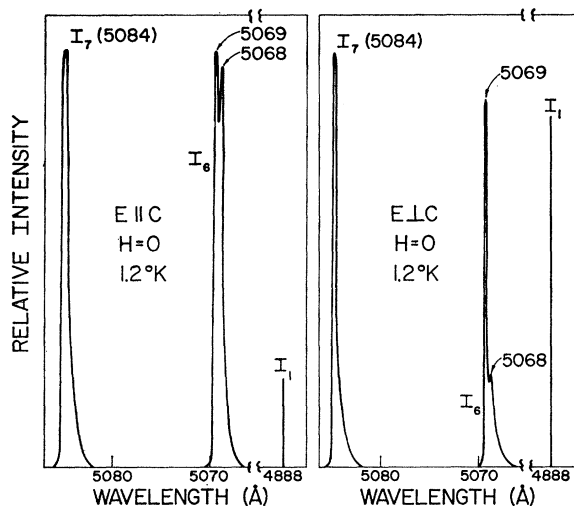


FIG. 6. Intensity comparison of the lines I_6 (5068, 5069), I_7 (5084) and I_1 (4888) for the polarizations $E \parallel c$ and $E \perp c$ at 1.2°K , $H=0$. The half-widths of the lines I_6 and I_7 are actually less than the half-width of the I_1 line (a line is drawn to represent I_1).

⁶ Actually, another very weak line (not labeled in Table I and not shown in Fig. 6) appears on the high-energy side of I_6 (5068 component). This line is strongly polarized ($E \parallel c$) but, like I_7 , it shows no Zeeman effects.

tially in the $E \parallel c$ mode⁷; on the other hand, most of the CdS edge-fluorescence is polarized in the mode, $E \perp c$. We have previously observed from Fig. 2 that the optical selection rules allow a $\Gamma_7 \leftrightarrow \Gamma_9$ transition, only for the mode $E \perp c$. Since the centers under investigation lie relatively close to a band, one might expect the transitions (arising from excitons bound to these centers) to reflect the band symmetry and obey the band to band optical selection rules. On the contrary, experimental results show that this is not the case for the long wavelength lines.

Only one of the long wavelength lines reported here shows a Zeeman effect, namely I_6 . The 5068.54 and 5069.18 \AA lines are components of the zero-field-split I_6 line. The zero-field splitting is $3.1 \times 10^{-4} \text{ eV}$. A plot of the splitting of the I_6 components (5068 and 5069) as a function of magnetic field strength ($c \parallel H$) is shown in Fig. 7. The high-energy component (5068) splits nonlinearly with increasing field strength; the low-energy component (5069) also seems to split, but its magnetically split, high-energy component appears to be missing. In zero field, the I_6 components are of approximately equal intensity. With increasing magnetic field, the 5069.18 \AA component shows an appreciable increase in intensity, whereas the magnetically split components of the 5068.54 \AA line decrease with equal intensity as the field increases. The I_6 line is isotropically split in a magnetic field. The isotropic behavior of the split component of this line is observed in Fig. 8. Here we have plotted the splitting of the 5068 component of I_6 as a function of field orientation ($\cos \theta$) at a constant field strength of 45 000 G. The isotropic splitting of this line is not the usual behavior in CdS; equally unusual are the polarized emission characteristics of all of these lines (long wavelength lines). From the data given here, it appears that the I_6 line cannot be identified with any of the molecular complexes described by Thomas and Hopfield.⁸

C. Doublets, I_1 and I_2

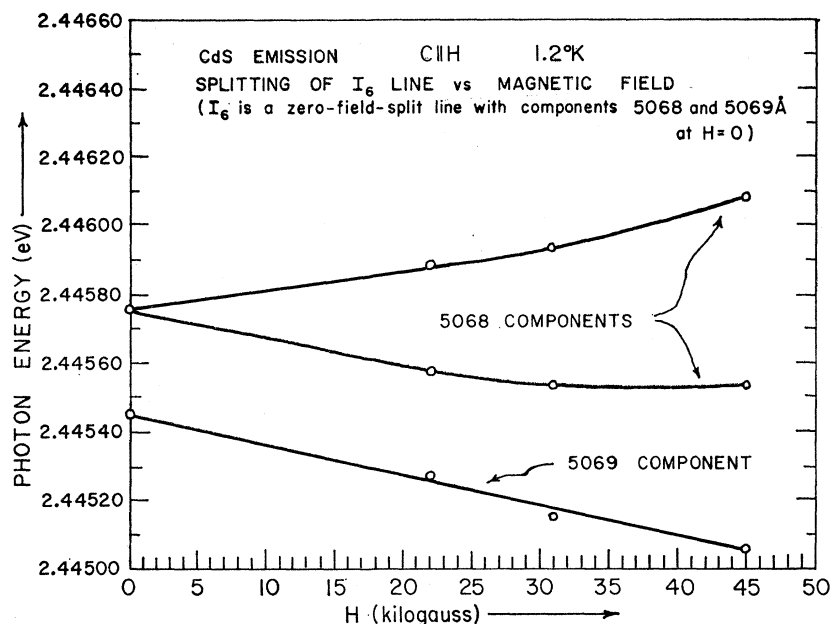
The doublet nature of I_1 ($H=0$), as well as the multiplet structure of I_2 , was first reported by Thomas and Hopfield.⁸ They made a detailed study of the behavior of the I_1 and I_2 singlet lines (fields up to 31000 G) but did not elaborate on the multiplet nature of either line.

In most crystals, I_1 and I_2 appear as singlet lines ($H=0$); however, we have observed I_1 and I_2 doublets ($H=0$) in a number of crystals (ranging from "blue" to "green"). In the case of I_1 , the singlet line appears at 4888.47 \AA . When this line appears as a doublet, one component is observed at 4888.47 \AA , while the other component (high-energy) appears at 4888.18 \AA . The

⁷ D. M. Warschauer and D. C. Reynolds, Phys. Rev. Letters **3**, 370 (1959).

⁸ D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959); **122**, 35 (1961).

FIG. 7. Splitting of the line I_6 as a function of magnetic field strength at 1.2°K for the orientation $c||H$. Based on the assertion that I_6 is a zero-field-split line, note that the high-energy component of the 5069 Å line is missing.



zero-field separation of the two components is approximately 1.2 cm^{-1} ($1.49 \times 10^{-5} \text{ eV}$). At constant field strength (45 000 G), a plot of the I_1 doublet splitting as a function of magnetic field orientation ($\cos\theta$) is given in Fig. 9. We have observed that the zero-field separation is constant, i.e., it is independent of both orientation ($\cos\theta$) and magnetic field strength (at least up to 45 000 G). In Fig. 9, the doublet I_1 splitting is identical in form to its singlet counterpart, except that here it is splitting as a doublet. From the data ($c \perp H$), a g value of -1.77 is determined.

The I_2 doublet has a zero-field separation of approximately 0.8 cm^{-1} ($9.9 \times 10^{-6} \text{ eV}$). The singlet I_2 line appears at 4867.17 \AA : one component of its doublet appears at this same wavelength, while the other component (high-energy) appears at 4866.98 \AA .

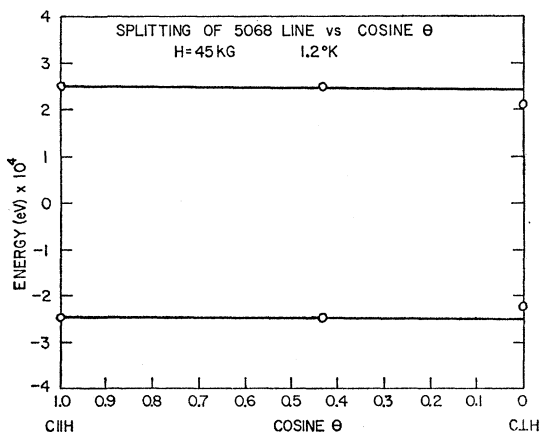


FIG. 8. Splitting of the 5068 Å line (component of I_6) as a function of $\cos\theta$ in a field of 45 000 G at 1.2°K.

The magnetic field dependence of the I_2 doublet is appreciably different from that of the I_2 singlet. In very low fields, $\sim 700 \text{ G}$, another doublet appears on the long-wavelength side of the I_2 doublet. The components of this doublet appear at 4867.42 and 4867.64 \AA , again with a separation of approximately 0.8 cm^{-1} (note that for this satellite doublet, the 700 G is a threshold field, i.e., when $H < 700 \text{ G}$ no line appears, split or unsplit). A plot of the I_2 doublet splitting as a function of magnetic field orientation ($\cos\theta$) at 45 000 G is shown in Fig. 10. Note that the I_2 doublet splitting at $c \perp H$ is the same as that of the singlet I_2 line. At this point, however, the similarity ends and,

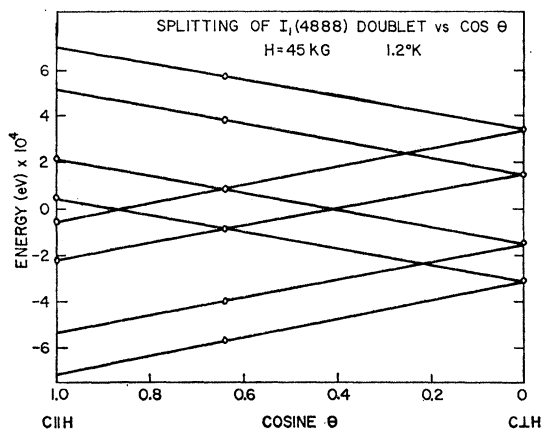


FIG. 9. Splitting of the I_1 emission line multiplet as a function of $\cos\theta$ in a field of 45 000 G at 1.2°K. For the case $\theta=0$ or 90° , note that quartets are observed, while for the case, $0^\circ < \theta < 90^\circ$, sextets are observed and, presumably, octets could be observed at the appropriate θ with sufficient spectral resolution. The zero of energy is taken to be the center of each set of multiplets.

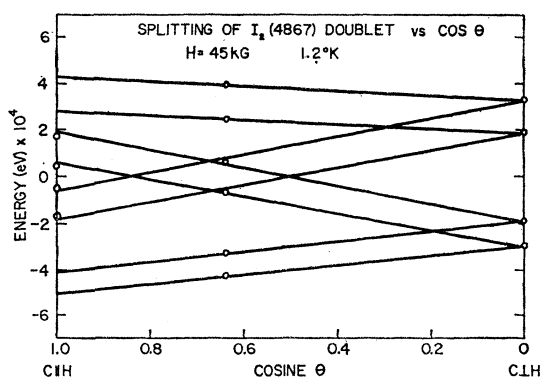


FIG. 10. Splitting of the I_2 emission line multiplet as a function of $\cos\theta$ in a field of 45 000 G at 1.2°K. Sextets are observable at an angle of $\sim 50^\circ$. The zero of energy is taken to be the center of each set of multiplets.

in all other orientations, the two splittings are significantly different. For example, when the crystal is oriented to a $\theta \sim 50^\circ$ ($\cos\theta = 0.643$) the I_2 singlet splits into four components; at this same orientation, the I_2 doublet splits into three sets of doublets.

The I_3 line is a zero-field split or doublet line. This line was previously reported by Thomas and Hopfield,^{2,3} but they have stated that the line is observed only in absorption spectra (they do not report its observation in fluorescence). Thomas and Hopfield have shown that I_3 arises from a transition involving an exciton bound to an ionized donor site; they have made the following observations concerning this line: (1) The low-energy component of the line does not appear in zero magnetic fields. (2) The low-energy component is not observed until a field of 10 000 G is reached, i.e., this component is absent below 10 000 G, since it arises from a forbidden transition to the lower state. (3) The splitting of the line varies nonlinearly with increasing field after 10 000 G; an extrapolation of the splitting to $H=0$ reveals a zero-field splitting of 3.1×10^{-4} eV.

We have observed the I_3 line in fluorescence spectra ("blue-green" crystals) and both components have appeared at zero field. A plot of the I_3 components as a function of magnetic field strength ($c \perp H$) is given in Fig. 11. The zero-field high-energy component of I_3

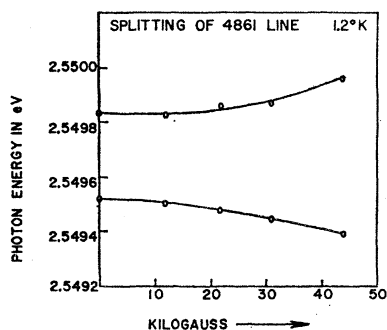


FIG. 11. Splitting of the I_3 emission line as a function of magnetic field strength at 1.2°K for $c \perp H$.

appears at 4861.66 Å (emission), while Thomas and Hopfield report this component at 4861.7 Å (absorption). The measured zero-field splitting of the emission line is 3.14×10^{-4} eV, in very good agreement with the extrapolated splitting (3.1×10^{-4} eV) determined from absorption. The nonlinear splitting observed in emission is also in good agreement with the corresponding absorption measurement.³

IV. DISCUSSION

At present, we are unable to advance a satisfactory explanation for the doublet nature of the I_1 and I_2 lines. One can rule out crystal strain as a source of the zero-field splitting for several reasons: (1) Both lines (and components) are sharp and well-formed (contain no distortions). (2) When either line is observed as a doublet (zero-field split), its component separations are always of the same magnitude; it is unlikely that a uniform strain existed, even in one crystal, much less from crystal to crystal. (3) In some crystals, the I_2 line is zero-field split, while the I_1 line appears as a singlet.

Consider the following argument for the doublet nature of the I_1 line: Suppose, e.g., that this line arose from transitions involving two neutral acceptor centers energetically close together, each with the same g value, resulting in identical splittings. In principle, such a situation could account for the doublet nature of I_1 ; however, one obvious objection to this line of reasoning is that one would not expect two such centers to be present in equal concentrations in a crystal, yet the doublet components always appear with equal intensity. Also, the "two-center" explanation can not account for the I_2 doublet nature, since the magnetic splitting of the I_2 doublet is different from that of the I_2 singlet.

Thomas and Hopfield³ have explained the zero-field splitting of I_3 . For the case $c \perp H$, states with antiparallel spins ($1s \Gamma_5$ states) are mixed with states whose spins are parallel ($1s \Gamma_6$ states); the zero-field splitting arises from a spin-spin exchange interaction. Since I_6 (Table I and Figs. 6-8) is a zero-field split line, one would tend to assume that this line arises from an exciton bound to an ionized center. The zero-field splitting of this line is almost identical to the zero-field splitting of I_3 ; however, the details of the I_6 splitting do not conform to the specification of an exciton bound to an ionized donor or acceptor. From the polarized emission of the long-wavelength lines (Fig. 6), it appears that the centers are polarized (polarized centers as opposed to band polarizations). Such a polarization could be responsible for the unusual isotropic splitting of the I_6 component, observed when this splitting is examined as a function of magnetic field direction (Fig. 8).

Given in Table II are the approximate binding

energies of excitons to the various centers associated with the lines I_1 , I_2 and I_3 (after Thomas and Hopfield⁸). As can be seen from this table, the exciton binding energy is greater than the exciton-to-center binding energy for all the complexes; consequently, the complex should dissociate before the exciton dissociates. On the other hand, a different situation may be operative for the I_6 line (take the 5068 component, e.g.). Assuming that this line arises from an exciton complex, one observes that the exciton-to-center binding energy (0.109 eV) is greater than the exciton binding energy (0.028 eV); hence, the exciton would dissociate before the complex could undergo a mole-

TABLE II. Binding energies of excitons to various centers.

Complex	Line (\AA)	Energy (eV)	Binding energy: exciton to center (eV)
Neutral acceptor	$I_1(4888)$	2.53595	0.018
Neutral donor	$I_2(4867)$	2.5471	0.007
Ionized donor	$I_3(4861)$	2.5499	0.001

Note: The ground-state exciton Γ_6 (4857 \AA) has a binding energy (hole to electron) of 0.028 eV.

cular-like dissociation. Such a situation might account for the observed polarization and magnetic field behavior of I_6 .

Quadrupole Interactions of Vanadium and Manganese in Corundum*

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Hyperfine fields and quadrupole interactions have been measured for divalent vanadium and quadrivalent manganese in corundum by electron-nuclear-double-resonance (ENDOR) spectroscopy. This work, together with previous work on trivalent chromium, provides a study of electronic properties of dilute impurities in an isoelectronic sequence. The results show that the internal magnetic field due to the paramagnetic electrons is the same for all ions and equal to about -200 kG. The quadrupole interaction is -0.021 Mc/sec for V^{2+} and 0.138 Mc/sec for Mn^{2+} . This is to be compared with a value for the host aluminum nuclei of 0.180 Mc/sec. A theory based on the point-charge model is unable to account for this result in any simple way. The possible influence of covalent bonds on the observed field gradients is discussed.

INTRODUCTION

THE system of transition-ion impurities in corundum has been the subject of many experimental and theoretical investigations.¹ The interest in this system is understandable since ruby, the best known example, was the first solid material to be used both for the maser and for the laser. Considerable progress has been achieved in the understanding of the optical and microwave absorption of impurity ions in this material. For the case of ruby the basic analysis of the optical spectrum was done by Sugano and Tanabe.² Using crystal-field theory, enlarged parametrically to include covalency effects, they were able to explain the observed optical spectra, at least as regards the position of the spectral lines. The calculation of transition probabilities, together with some of the subtler points of the structure of the energy levels, was somewhat less satisfactory. For example, a straightforward calculation of the splitting of the ground state gave the wrong sign. Including certain

third-order terms in the perturbation expression gave the right sign, but it was obvious that the theory, when applied to such fine details of the spectra, was inadequate.

In recent years a number of experiments have been directed to the determination of the magnitude of the trigonal component of the crystalline field. The measurements of Weakliem and McClure³ attempted a determination of the trigonal field through measurements of splittings in the optical spectra of a series of transition metal ions in corundum. Their results indicate that the trigonal field is different for different ions. Since the trigonal field should only depend on the environment of an ion and not on the ion itself, they postulated that impurity ions do not assume a true substitutional position in the Al_2O_3 lattice, but rather are slightly displaced along the "c" axis. This displacement varies with ion, causing the observed variation of the trigonal field. Such a distortion does not lower the symmetry, since the symmetry at the substitutional position is only C_3 , the same symmetry as any position on the "c" axis.

* A preliminary account of this work was presented at the March 1963 meeting of the American Physical Society. See Bull. Am. Phys. Soc. 8, 212 (1963).

¹ For a general review of the subject see the article by D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 399.

² S. Sugano and Y. Tanabe, J. Phys. Soc. Japan 13, 880 (1958).

³ H. A. Weakliem and D. S. McClure, Suppl. J. Appl. Phys. 33, 347 (1962). See also the article by D. S. McClure, J. Chem. Phys. 36, 2757 (1962).