

Table II. Relaxation times of Cr in TiO₂.^a

Transition	Axis	Frequency (kMc/sec)	Resonant field (gauss)	Temp. (°K)	T ₂ (sec)	T ₁ (sec)	
1/2	3/2	z	23.79	3505	78	5.3×10 ⁻⁹	4×10 ⁻⁴
1/2	3/2	z	23.79	3505	4.2	5.3×10 ⁻⁹	4×10 ⁻²
1/2	3/2	x	23.79	6750	4.2	4.9×10 ⁻⁹	5×10 ⁻²

^aThe conversion factor needed to go from linewidth to T₂ is obtained by using the slope of the calculated curves for energy level vs magnetic field.

c.w. methods³ are given in Table II. These are order-of-magnitude estimates; the large possible error arises almost entirely from uncertainty about the radio-frequency field distribution within the cavity. The dielectric constant of TiO₂ is very large, anisotropic, and temperature-dependent. Thus, mode distortion in the cavity due to the sample is difficult to estimate and further study will be required to fix more accurately the values of T₁.

Because some of the resonance lines are very narrow, the four-line hyperfine structure due to Cr⁵³ (9.55% of natural Cr) is easily observed. The hyperfine splitting is described by adding to the spin-Hamiltonian terms of the form $A_z I_z S_z + A_x I_x S_x + A_y I_y S_y$.

A splitting of 50 gauss between the outer of the four hyperfine lines was observed along all three axes and at both frequencies used. One can show theoretically that the over-all splitting measured in this way is equal to $3A/g\beta$ independent of D, E or H, as long as these are large compared to A. The observed splittings of 50 gauss show that $A_x = A_y = A_z = 0.0015 \text{ cm}^{-1}$. This is in good agreement with measurements on other Cr-doped crystals⁴ and a further support of the theory of configurational interaction. Because the inner hyperfine lines were not completely separated from the strong resonance due to the Cr⁵², it was not possible to detect quadrupole effects. The distances between the four hyperfine lines were equal to within 10%.

The narrow lines and long relaxation times of Cr³⁺ in TiO₂, together with the high dielectric constant and good mechanical properties of the crystal, indicate that it may be a very effective material for use in a solid-state maser. With 1 mw of power incident on a cavity with a Q of approximately 1000, we observed saturation parameters of about one at 78°K and 100 at 4.2°K. The

voltage reflection coefficient was about 0.5.

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POLARIZATION OF FLUORESCENCE IN ZnS AND CdS SINGLE CRYSTALS

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The polarization of impurity fluorescence has been observed in both ZnS and CdS crystals. The specimens were obtained by vapor phase growth and in the case of ZnS have been deliberately doped with Cu and Mn. Plate-like crystals with the c axis in the plane were used for the measurements.

The fluorescence was excited by filtered 3650A radiation incident perpendicularly to the plate surface. Natural or plane polarized radiation

Table I. Data on the polarization of fluorescence.

Type	Impurity in mole %	Fluorescence emission peak (Å)	Structure	$p(0^\circ)$	$p(90^\circ)$	$p_n(0)$
1 ZnS:Cu	0.02	4500	hex	-0.03	0.20	-0.12
2 ZnS:Cu	0.02	4500	hex	-0.10	0.20	-0.16
3 ZnS:Mn	1.0	5800	cub	-0.03	0.07	-0.05
4 ZnS:Mn	0.1	5800	cub	-0.03	0.02	-0.03
5 CdS(?)		~6200	hex	-0.52	0.51	-0.50

could be used. The measurement of fluorescence was made along the exciting beam direction by means of a photomultiplier and an analyzer. Filters were used to prevent the exciting radiation from reaching the photomultiplier.

The amount of polarization is defined by $p(\theta) = [(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})]_{\theta}$, where I_{\parallel} is the intensity measured with the analyzer parallel to the polarizer and I_{\perp} with the analyzer perpendicular to the polarizer. θ is the angle between the exciting electric vector \vec{E} and the c axis of the crystal. For unpolarized excitation [amount of polarization denoted by $p_n(\theta)$], θ is the angle between the principal direction of the analyzer and the c axis.

Table I summarizes the results of the measurements for several crystals and Fig. 1 gives the full p vs θ curves for crystals 2 and 5. The CdS crystal was not grown in our laboratory and the nature and content of its impurity was not known. The accuracy of the polarization measurements is ± 0.02 .

The following features are to be noted:

(a) For $\theta = 0$ the values of p and p_n are negative and for $\theta = 90^\circ$ they are positive. This means that the fluorescence is polarized preferentially in the direction perpendicular to the c axis under any conditions of excitation.

(b) The largest value of p is obtained for crystal 5 which has hexagonal structure and a high degree of perfection. The ZnS:Cu crystals are also hexagonal but exhibit a certain amount of stacking disorder.

(c) For the CdS crystal, the amount of polarization p is nearly independent upon the nature of excitation (polarized or unpolarized). For ZnS we have, in general, $|p(0)| < |p_n(0)|$.

(d) The values of p for ZnS:Mn are significantly smaller than for ZnS:Cu. Since these crystals are predominantly cubic (with disorder) we cannot say whether this is a characteristic of the Mn center or of the structure.

Observations along the c axis were made on several ZnS:Cu and ZnS:Mn specimens grown with the c axis perpendicular to the plane of the plate. Invariably p and p_n were found to be zero.

The observed polarization cannot be due to the dichroism of the lattice since in both ZnS and CdS the absorption coefficients are larger for the direction perpendicular to c . This would make c the direction of preferential polarization. This point was checked directly by observing the degree of polarization of transmitted unpolarized light of about the same wavelength as the fluorescence. p was found to be very small (of the

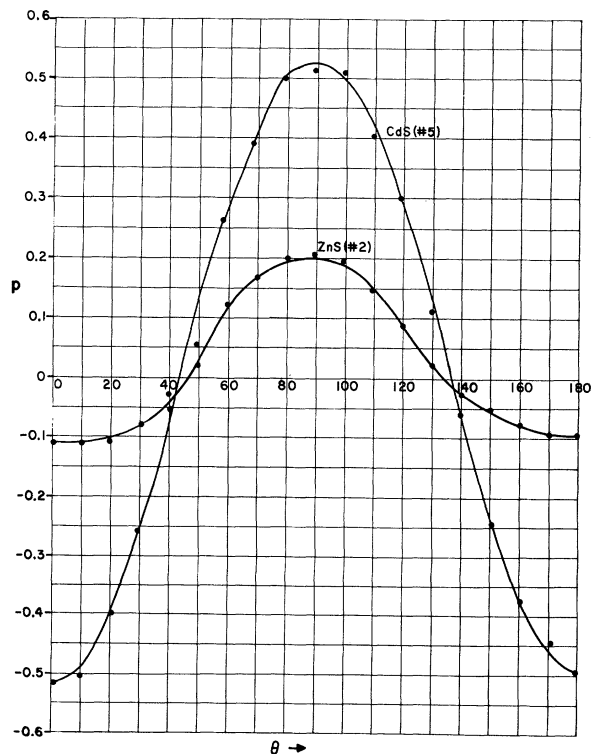


FIG. 1. Polarization factor p vs the azimuth θ for a ZnS:Cu and a CdS crystal. For $\theta = 0$ the exciting electric vector is parallel to the "c" axis.

order of experimental error) and of opposite sign to that observed in fluorescence. The phenomenon must thus be due to the centers themselves.

The fact that natural light produces polarized emission shows that the elementary oscillators cannot be randomly oriented.¹ Following the dipole theory as applied to the fluorescence in alkali halides²⁻⁴ and diamond,⁵ we can try to represent the centers as an array of oscillators all aligned along some direction in the crystal. The polarization depends then upon the elements of a polarizability tensor. It can be shown quite generally that such a model cannot account for the observed results.

We can also discard the possibility of the dipoles being oriented along the 12 equivalent directions in the wurtzite lattice. Such an array of dipoles would give rise to a nonvanishing mean square dipole moment only along the *c* axis and hence would lead to preferential polarization along *c*. A similar result is obtained in case of centers having the *c* axis as one of the principal axes of their polarizability tensor (common α_{zz} components) but randomly oriented principal axes in the *x-y* plane. None of these models can be salvaged by assuming that the exciting radiation is subject to a dichroic absorption by the lattice.

It is possible that experimental results can be accounted for by the introduction of separate absorption and emission oscillators, such as have been postulated by Feofilov² and others,¹⁻⁶ in order to explain the dispersion of *p*. Nevertheless, for a fixed excitation wavelength anisotropic (in particular linear) oscillators are sufficient to explain the results in the halides. The centers in ZnS and CdS must therefore have essentially different features. Our results are qualitatively very similar to those obtained by Dutton⁷ on the polarization of edge luminescence in CdS. We have also observed that the green electroluminescence (involving band to band recombination⁸) of CdS crystals is polarized preferentially perpendicular to *c*. Values of *p* up to -0.3 have been measured although the instability of emission makes it very difficult. As shown by Birman in the accompanying Letter,⁹ the polarization in all these cases is consistent with the Lambe-Klick model of luminescence.

More detailed work on the effect of crystal structure, crystal disorder, and type and level of doping on the polarization of fluorescence is under way. It is becoming evident that it may

provide fundamental information on the nature of luminescent centers and processes.

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POLARIZATION OF FLUORESCENCE IN CdS AND ZnS SINGLE CRYSTALS

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The polarization of the fluorescence at 6200Å in CdS and at 4500Å and 5800Å in ZnS is reported in the accompanying Letter,¹ along with the failure of various simple dipole theories to account for these results. Since a dipole-type model was able to account for color centers in the halides, and the localized centers in diamond, it was indicated that the CdS and ZnS centers in question may be of an essentially different type.¹ We shall suggest that the 6200Å emission in CdS, and probably the 4500Å in ZnS, be interpreted on the basis of the Lambe-Klick model² and shall make certain predictions based on this explanation which, if verified, will substantiate the interpretation. The 5800Å Mn emission in ZnS apparently requires a more complex interpretation, which is not surprising in view of the complexity of the ground and excited states of Mn⁺⁺.

In Fig. 1 we show valence and conduction bands for zinc blende (ZB) and wurtzite (W) structures