

Hyperfine structure due to interaction with Ni^{61} has been detected⁽¹⁾ in samples doped with nickel enriched to contain 83 per cent of that isotope. The principal axes of the hyperfine interaction are the same as those of the g -tensor, and one finds the principal values $A_1 = 10.3$, $A_2 \leq 1.6$, $A_3 = 12.2$ (in units of 10^{-4} cm^{-1}) in the directions corresponding to $g_1 = 2.1128$, $g_2 = 2.0294$, and $g_3 = 2.0176$.

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 3. Manganese metal was alloyed to silicon bars $\sim 3 \times 3 \times 10$ mm in dimension held in quartz tubes. The tubes were then evacuated and held at $\sim 1230^\circ\text{C}$ for about 18 hr. The samples were quenched by dropping the quartz tubes into water.
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R.3

SPIN RESONANCE OF DONORS IN CdS*

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1. INTRODUCTION

THE subject of donor centers in cadmium sulfide has been of interest from two viewpoints. First it appears that such centers play an important role in luminescence phenomena and secondly they are, of course, important in connection with the semi-conduction properties of CdS. One of the most widely studied of these donor centers is that due to the incorporation of chlorine into cadmium sulfide. It is found that this impurity gives rise to a donor level 0.03 eV below the conduction band. The center arises from the substitution of a singly negative chlorine ion for the doubly negative sulfur ion. This leaves a net positive charge in this region which can bind an additional electron. The center thus has a negatively charged core (due to Cl^-) with a surrounding positively charged region. The electron bound to such a center would be expected to show paramagnetic resonance. At 300°K the centers are essentially completely ionized and the crystals

may have fairly high conductivity. At 4°K the free electrons are bound at the Cl^- centers so that the crystals are highly insulating and spin resonance experiments can be carried out quite easily.

2. EXPERIMENTAL METHODS AND RESULTS

In the experiments reported here an X band paramagnetic resonance spectrometer was used, operating at about 9300 Mc/s . Samples were placed along the axis of a cylindrical cavity operating in the TE_{011} mode. Straight crystal detection was used with 5 kc/s magnetic field modulation and lock-in detector.

Crystals of CdS with added chlorine were measured at 4°K , and a large spin resonance signal was observed. Since CdS has hexagonal crystal structure, long needlelike crystals were used so that the C axis of the crystal could be oriented with respect to the magnetic field. For such crystals a single line was observed with a g value dependent upon orientation of the C axis, as shown in Fig. 1.

The measured g values are $g_{\perp} = 1.78$, $g_{\parallel} = 1.79$.

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The line width is approximately 8 G. No hyperfine structure was observed. The resistivity of these crystals was about $1 \Omega \text{ cm}$ at room temperature. This indicates a carrier concentration 10^{17} electrons/cm³.

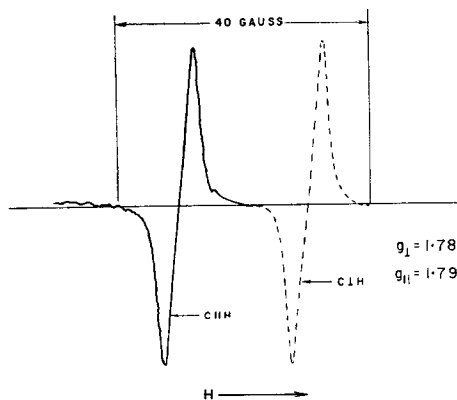


FIG. 1. Observed spin resonance spectrum of a CdS:Cl crystal at 4°K.

Measurements were also made on CdS crystals of higher resistivity to check that the signal was indeed associated with the presence of the donor center. Samples with resistivities in the range of 10^5 to $10^6 \Omega \text{ cm}$ were measured and no signal could be detected. This means that any signal was at least 1000 times smaller than the signal observed for the CdS:Cl sample.

3. DISCUSSION

The foregoing experiments indicate that the chlorine center in CdS does give rise to a paramagnetic resonance absorption. The major points of interest concern the observed g value, its magnitude and the observed anisotropy. A rigorous quantitative treatment of this would be quite involved, but some semi-quantitative observations can be made which are of interest.

As a model for this center we may note some similarity to the F center in the alkali halides. In the case of the F center important contributions to the g value arise from the fact that the electron wave function extends over neighboring potassium ions.^(3, 4) The essential theoretical problem is the evaluation of the wave function at these neighboring ions. In the case of the chlorine center a similar situation should arise with extension of the wave function onto neighboring cadmium ions.

In the case of the F center theoretical considera-

tions⁽⁴⁾ lead to the expression of the following form for the shift in g value from the free electron value ($\Delta g \cong -0.007$ for the F center)

$$\Delta g \propto \frac{1}{E_F} \sum_{\alpha i} \langle F | \alpha_i \rangle \lambda_{\alpha} \quad (1)$$

E_F = excitation energy for F center

$\langle F | \alpha_i \rangle$ measures the magnitude of the F center wave function overlap with the core orbitals on surrounding ions

λ_{α} is the spin-orbit coupling parameter for the core orbital.

The application of the above type of expression to the CdS:Cl problem involves the evaluation of many factors in detail, however it is interesting to note the direct dependence of Δg upon E_F . In the case of the F centers, E_F is of the order 2 eV. In the case of CdS:Cl this value would be 0.03 eV, or less. This then has a large effect on Δg . This factor alone would indicate that Δg for CdS:Cl should be about 60 times as large as for the F center. It is seen that $\Delta g \cong -0.2$ for CdS:Cl which is in fact about 30 times as large as for the F center. Needless to say the other factors in (1) will also be quite different but the above considerations illustrate the importance of excitation energy in connection with Δg .

The anisotropy in g is of special interest in that the following point is involved. CdS has the typical wurzite lattice structure and is thus quite similar to ZnS. In the case of ZnS, however, a sulfur site is surrounded by a tetrahedron of zinc ions and all the zinc ions are equidistant from the sulfur site, the distance being 2.33 \AA .⁽⁵⁾ For the case of CdS, however, there is a distortion of the tetrahedron and the distances to nearest cadmium ions are not equal, being 2.51 \AA and 2.53 \AA .⁽⁵⁾ On ZnS the complex of zinc ions around a sulfur site should show cubic symmetry even though the lattice is not cubic. In the case of CdS, the difference in ionic distances may be sufficient to cause the anisotropy in g . This point can perhaps be checked by calculation. On the other hand, if the wave function of the donor electron extends significantly beyond nearest neighbor cadmiums, this could also introduce the anisotropy in g .

The lack of hyperfine structure precludes the direct identification of the spin resonance with the

chlorine by this means. This lack is, however, not surprising. In this case the chlorine core is already negative and would tend to minimize the interaction of the additional electron with the chlorine nucleus. Hyperfine interaction with the cadmium may be expected but the extent of this is not known.

It was noted that with the power available in the X band spectrometer, about 25 mW, and with a cavity Q of 2000, there were no apparent saturation effects. This indicates that the spin lattice relaxation time is quite short (10^{-6} or less). This is consistent with the large amount of orbital motion implied by the large Δg .

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R.4 CYCLOTRON RESONANCE IN CADMIUM SULFIDE*

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1. EXPERIMENTAL

PRELIMINARY experiments on cyclotron resonance in CdS have been performed at liquid air and liquid helium temperatures using 1.25 cm microwaves. Free charge carriers were excited using visible and infrared light separately or in combination. In initial experiments polarized light was not used and the infrared light was that transmitted by quartz and germanium therefore in the 2–3 μ range.

CdS samples selected from those grown by D. C. Reynolds of Wright Air Development Center showed no visible edge luminescence at low temperature and were selected on that basis since they proved to have the highest mobility of free carriers. A typical sample grown by the vapor-phase reaction was about $2 \times 1 \times 0.01$ mm and was a plane containing the c axis of the hexagonal structure.

Despite strong visible light and infrared photoconductivity at 78°K, very poor photoconductivity was found at liquid helium temperatures. The sample was mounted near one end of a tapered quartz light pipe and the light from a 1000-watt tungsten projection lamp was focused into the

other end. Ultraviolet and infrared sources were also used and various filters were available. Following earlier techniques of cyclotron resonance in semiconductors,⁽¹⁾ light was chopped at 90 c/s. Microwave magnetoconductivity changes at that frequency were recorded following a narrow band amplifier and phase sensitive detector. In samples showing high mobility, triggered light experiments demonstrated that photoconduction easily followed the 90 c/s alternation of light intensity.

2. RESONANCE RESULTS

Microwave magnetoconductivity of CdS at 78°K gave evidence that infrared produced carriers with a mobility of about 2×10^5 cm²/V-sec and that visible light produced carriers with a mobility about one-fifth as large. Infrared quenching of the visible light photoconductivity was demonstrable in some samples as in earlier d.c. experiments.⁽²⁾

At temperatures of 1.2 to 4.2°K the following cyclotron resonance observations were made using linearly polarized microwaves.† In several samples,

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† Insufficient carrier concentrations were produced in the circular polarization system used. This system if successful would allow determining carrier sign directly as described in DRESSLHAUS *et al.*⁽¹⁾