Photo-Induced Paramagnetic Resonance of Chromium in Zinc Sulfide Crystals*

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The optical excitation, stimulation, and quenching spectra of the paramagnetic resonance of $3d^5$ substitutional chromium in zinc sulfide single crystals have been measured. From these data the energy of the ground state of the chromium acceptor is estimated both when unoccupied and when occupied by a positive hole. In addition, the energies of gallium donors and copper acceptors have been verified by photo-ionization of these impurities in ZnS:Cr, Cu, Ga crystals, followed by capture of the carriers by the chromium, which is measured by the changes in the paramagnetic resonance. Finally, the characteristics of gallium-chromium pairs are considered.

I. INTRODUCTION

IN several IIB-VIB compound semiconductors, specifically ZnS, ZnSe, ZnTe, and CdTe, chromium has been found to be a deep acceptor. In the charged state, when it has accepted an electron, the chromium exhibits the characteristic paramagnetic resonance of the ^6S state of the $3d^5$ configuration.[1–4] For ZnS the resonance was shown to be photo-induced by near ultraviolet (3650 Å) radiation.[1] In this case, the Fermi level lies below the chromium level which therefore contains a positive hole. This un-ionized acceptor with the $3d^4$ configuration can trap a photoexcited electron to form the $3d^5$ configuration which is observable by paramagnetic resonance. The ion core of the un-ionized acceptor corresponds to the free Cr^{+2} ion, whereas the ion core of the charged acceptor, from which the positive hole has been ionized, corresponds to the Cr^+ ion. The Cr^{2+} behaves as an electron trap whose depth below the conduction-band edge has been estimated to be approximately 0.4 eV.[1] These identifications of charged states do not depend on any assumption regarding ionic or covalent character of IIB-VIB semiconductors.

We wish to report the results of some electron paramagnetic resonance (EPR) measurements on hexagonal ZnS single crystals containing varying concentrations of Cr, and in some cases also containing Cu and Ga. By observing the intensities of the Cr^+ EPR signals, identified by their characteristic fine structure and a g value of 1.9995, as a function of wavelength of the optical excitation we estimate the energies in the band gap of both the occupied and unoccupied levels of the Cr acceptor. In addition, we detect photo-ionizations of an electron from the Ga donor and of a positive hole from the Cu acceptor by the changes in Cr^+ EPR signal intensities resulting from capture of electrons by Cr^{2+} and of holes by Cr^+.

A Varian V-4500 spectrometer was used in our measurements. The cavity was operated with 100 kc/sec modulation and was slotted to allow optical excitation of the sample. Several types of light sources were used: a 450-W xenon lamp, a 200-W high-pressure mercury lamp, and 100- and 625-W tungsten lamps. After corrections were made for differences in lamp spectra the experimental results were found to be independent of lamp type. A series of Bausch and Lomb grating monochromators, and for higher resolution measurements, a Perkin-Elmer 13 U prism monochromator with quartz and rock salt prisms for different spectral regions, were used to vary the wavelength of the incident radiation. The measurements were made with the crystals at 77°K.

II. PHOTOEXCITATION OF THE CHROMIUM PARAMAGNETIC RESONANCE

Because of the long lifetime of the excited electronic state of the crystal which is responsible for the paramagnetic resonance of Cr^+, the EPR photoexcitation spectrum was determined point-by-point. The signal was first quenched with infrared from the high-pressure mercury lamp passed through a Corning Cs 2-73 filter, and then the change in EPR signal intensity was recorded following irradiation at a particular wavelength from either the mercury, xenon, or tungsten lamps passed through a monochromator. The EPR signal is then again quenched with infrared and the procedure is repeated over the wavelength range of interest. If one does not use point-by-point quenching, the effects of the irradiation are cumulative and the structure in the photoexcitation spectra is not resolved. The infrared ionizes trapped positive holes from other acceptors such as Cu and these valence band holes recombine with the trapped electron on Cr^+ thereby returning the crystal to the unexcited initial state with the chromium present as Cr^{2+}. In accordance with this interpretation of the quenching, 1.1-μ radiation was found most effective with Cu present.[5]

[1] J. Dieleman, R. S. Title, and W. V. Smith, Phys. Letters 1, 334 (1962).
[2] R. S. Title, Phys. Rev. 131, 623 (1963).
[3] G. W. Ludwig and M. R. Lorenz, Phys. Rev. 131, 601 (1963).
[4] R. S. Title, Phys. Rev. 133, A1613 (1964).
[5] P. Jaszczyn-Kopec, J. Gallagher, H. Kallmann, and B. Kramer, Phys. Rev. 140, A1309 (1965) have reported the effect of 1.1μ radiation on the EPR of ZnS:Cu, Cl, Cr powders which they attribute in part to ionization of electrons trapped on Cr^{2+}.

In Fig. 1 is shown the change in Cr^+ EPR signal as a function of the wavelength of the photoexcitation. There are two maxima: one at 4350 Å, the other at 3850 Å. These maxima are observed with tungsten and mercury lamps, as well as with the xenon lamp used in obtaining the actual data in Fig. 1. The sample was ZnS:Cr, Cu. We attribute the 4350 Å Cr^+ EPR photoexcitation peak to pumping electrons from the compensated Cu^+ level to the conduction band, followed by trapping at Cr^{2+}, thereby increasing the intensity of the Cr^+ EPR signal. The 3850 Å Cr^+ EPR photoexcitation corresponds to pumping positive holes from the Cr^{+2} to the valence band, thereby increasing the intensity of the Cr^+ EPR signal. In a crystal containing Ga as well as Cu and Cr there is some excitation of the Ga A-center[6] EPR signal with 3850 Å radiation. This can be explained on the basis of the trapping of valence-band holes at the A-center acceptor. The presence of both Cu and Ga in this crystal is confirmed by the observation

FIG. 1. Photoexcitation spectrum for EPR signal of Cr^+ in ZnS crystals.
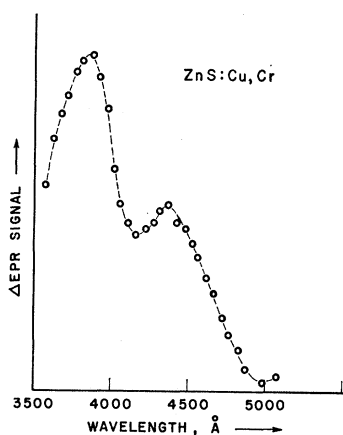
of the EPR signal characteristic of Cu-Ga pairs.[7] We conclude therefore that the chromium acceptor level Cr^{2+}, from which positive holes can be pumped to the valence band, lies 3.2 eV above the valence band edge as shown in Fig. 2.

III. PHOTOQUENCHING AND PHOTO-STIMULATION OF THE CHROMIUM PARAMAGNETIC RESONANCE

Following the optical pumping of the positive hole from the Cr^{2+} to the valence band, the Cr^+ impurity system will polarize the lattice so that the acceptor state relaxes to a different electronic energy. In order to determine the acceptor level unoccupied by a positive hole, we measured the spectrum for optical de-excitation or quenching of the intensity of the Cr^+ EPR signal. This is shown in Fig. 3. In this experiment a ZnS:Ga, Cr crystal was used for which the Cr^+ EPR signal was

[6] H. D. Fair, Jr., and R. D. Ewing, Bull. Am. Phys. Soc. 10, 475 (1965).

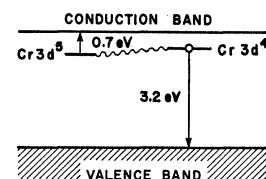[7] H. D. Fair, Jr., R. D. Ewing, and F. E. Williams, Phys. Rev. Letters 15, 355 (1965).

FIG. 2. Band-theory model of states and optical transitions of chromium in ZnS.

present without ultraviolet excitation, although the signal could be enhanced with ultraviolet radiation. We interpret this to mean that the Fermi level lies near the Cr^+ level. The data of Fig. 3 indicate that maximum quenching of the Cr^+ EPR signal occurs at 1.6μ, and we conclude on the basis of this analysis that the chromium acceptor level when unoccupied by a positive hole lies 0.7 eV below the conduction band edge as also shown in Fig. 2. This energy is in agreement with the infrared absorption of ZnS:Cr.[8] It should be noted that the photoinduced component of the Cr^+ EPR signal apparently cannot be quenched by 1.6-μ radiation. Within the framework of the above interpretation, this result can be understood by considering the Ga donors. It is necessary that these donors trap some of the conduction electrons photo-ionized from the Cr^+ in order to detect this transition. Otherwise the electrons are retrapped at the Cr^{2+} sites giving no net effect. If then, the crystal is first excited by ultraviolet radiation the Ga donors will not be empty and thus the 1.6-μ transition cannot be observed by changes in the EPR signal. On the other hand, there is some possibility that an excited state of the Cr^+ or a state of an associated donor is involved in the 1.6-μ transition, in which case the 0.7 eV is a lower limit for the energy of the ground state of Cr^+ with respect to the conduction band edge. Photoconductivity measurements are in progress to determine more directly whether the 1.6-μ transition is to the conduction band edge.

It was proposed above that some of the ionized Ga donors capture electrons following ultraviolet excitation and therefore an increase in the Cr^+ EPR signal should result from pumping electrons out of these Ga donors
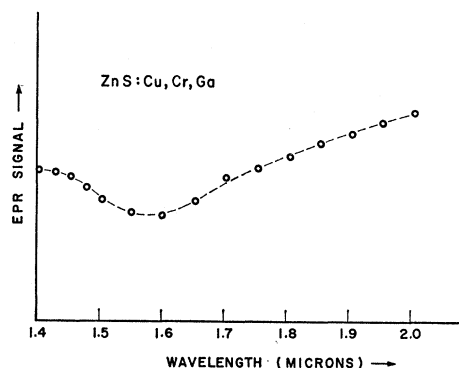

FIG. 3. Photoquenching spectrum for EPR signal of Cr^+ in ZnS.

[8] C. S. Kelley, R. B. Lauer, and F. E. Williams, Bull. Am. Phys. Soc. 11, 85 (1966).

followed by electron capture at Cr^{2+}. We have observed a broad maximum at 3μ in the photoexcited Cr^+ EPR signal which we attribute to optical ionization of Ga donors. The thermal depth of Ga donors has been determined from thermoluminescent measurements as 0.4 eV,[9] and our measurements can be interpreted as evidence for the optical depth being approximately the same value.

IV. THEORETICAL ASPECTS

The energy of the chromium acceptor in zinc sulfide has been estimated by approximate theoretical methods using tight-binding methods.[10] The basic assumption of the calculation is that the conduction band can be approximated in terms of states of the cation. In this way, effects of the crystal field are minimized since the ionization of an electron from the substitutional chromium involves charge transport between equivalent sites. Independently of the ionic-covalent character the ground state of $^6S\,3d^5$ substitutional Cr in ZnS is found to lie within approximately an electron volt of the

conduction band edge. Our experimental results are consistent with the results of the simple theory.

From general theoretical considerations one predicts pairing of Ga donors with Cr acceptors in compensated crystals in which the Fermi level lies near or preferably above the chromium level. In this case these impurities are oppositely charged and attract each other Coulombically. The resulting donor-acceptor pairs would be expected to have unusual properties because the ground states of the Ga and Cr are separated in energy by only 0.3 eV. Among these unusual properties is a predicted far infrared absorption corresponding to the optical transfer of an electron from the Cr to the Ga. Nearer infrared absorption is expected if an excited state of either Ga or Cr is involved, as noted earlier in the discussion of 1.6-μ absorption. Work is in progress to observe the effect of these transitions on the Cr^+ EPR signal and any detectable spin resonance of the photoexcited Cr-Ga pairs.

[9] W. Hoogenstraaten, Philips Res. Rept. 13, 519 (1958).
[10] H. E. Gumlich, R. L. Pfrogner, J. C. Shaffer, and F. E. Williams, J. Chem. Phys. (in press).

Electronic Structure and Superconductivity of Indium-Cadmium Alloys*

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The superconducting transition temperatures (in zero magnetic field) of In-Cd alloys in the range 0–60 at.% cadmium have been measured. T_c decreases from 3.406 to 3.245°K in the tetragonal solid solution and from 3.55 to 3.00°K in the cubic phase, with increasing Cd content. A kink in the T_c-versus-composition curve at 2 at.% Cd is attributed to Fermi-surface–Brillouin-zone interaction. This interpretation is supported by lattice-parameter determinations which show an anomaly at 2% Cd, and also by the magnetic susceptibility measurements of Verkin and Svechkarev. The existence of the superconductivity anomaly at $Z=2.98$ supports a recent hypothesis of Svechkarev concerning the electronic structure of indium. Measurement of reduced resistance ratio $\rho \equiv R_{4.2}°/(R_{273}° - R_{4.2}°)$ show ρ to be linear in Cd concentration x up to the solubility limit at 5 at.% Cd, with a slope of 0.042/(at.% Cd). The data for the tetragonal phase are not linear on a plot of $\Delta T_c/x$ versus $\ln x$, and thus do not fit the present theory of T_c variation in primary solid solutions. At the tetragonal-cubic phase transition, T_c jumps by 10% without change of electron/atom ratio, cell volume, or ionic mass. The superconductivity data are all consistent with the published phase diagram of Heumann and Predel.

INTRODUCTION

I T is not yet possible to theoretically predict the superconducting transition temperature (T_c) of any material from first principles, or even from the values of other electronic properties. Empirical rules[1] have

been successful in many cases, but these have no firm foundation in physics, although attempts[2] have been made to connect them with the microscopic theory.[3] To attack the general problem we have undertaken to measure the composition dependence of T_c in nontransition metal alloy systems, since the electronic structure of these metals is presumably less complicated

[1] B. T. Matthias, in Progress in Low Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.

[2] D. Pines, Phys. Rev. 109, 280 (1958).
[3] J. Bardeen, L. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).