ELECTRON-SPIN RESONANCE OF A PHOTOSENSITIVE $^2S_{1/2}$-STATE GALLIUM CENTER IN ZnS

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Fair, Ewing, and Williams[1] have recently reported that ZnS single crystals and powders, doped simultaneously with gallium and copper, exhibit a characteristic ESR spectrum at 77°K, under optical illumination, peaked at 450 mμ. We have repeated the experiment and we will show that the paramagnetic center responsible is a $^2S_{1/2}$-state Ga^{2+} ion, and not some kind of photoexcited donor-acceptor pair, as postulated by Fair, Ewing, and Williams.

The spectrum consists of four sharp lines, a few gauss in width, and extends from 1780 to 6200 G at 9.1 Gc/sec. Two of these lines were barely detectable in samples doped with 98% enriched Ga^{71}. From this, it can be concluded that the large spread of the spectrum arises from a large hyperfine interaction, $A\vec{I}\cdot\vec{S}$, of the unpaired electron spin $\vec{S}$ with the nuclear spin $\vec{I}$ of the gallium isotopes Ga^{69} (60.2%) and Ga^{71} (39.8%), both having nuclear spin $I=\frac{3}{2}$. The $^2S_{1/2}$ state of Ga^{2+}, where the unpaired electron is localized in an almost pure 4s orbital, can well account for the large hyperfine structure observed. The spectrum is described in terms of the spin Hamiltonian

$$\mathcal{H}=g\beta\vec{H}\cdot\vec{S}+g_n\beta_n\vec{H}\cdot\vec{I}+A\vec{I}\cdot\vec{S}, \qquad (1)$$

where the first two terms represent the electronic and nuclear Zeeman energy, respectively. The eigenvalues of this Hamiltonian are given by the Breit-Rabi formula.[2] The two lines occuring at H_1 and H_2, which are observed for each gallium isotope, are the $(F=1,\ m_F=-1) \rightarrow (F=2,\ m_F=-2)$ and $(F=2,\ m_F=-2) \rightarrow (F=2,\ m_F=-1)$ transitions, see Fig. 1, which occur at

$$\nu=\Delta\nu[\tfrac{1}{2}(1-x_1+x_1^2)^{1/2}+\tfrac{1}{2}(1-x_1)-g_n\beta_nH_1/h\Delta\nu],$$

$$\nu=\Delta\nu[\tfrac{1}{2}(1-x_2+x_2^2)^{1/2}-\tfrac{1}{2}(1-x_2)+g_n\beta_nH_2/h\Delta\nu], \qquad (2)$$

where

$$x_i=(g\beta-g_n\beta_n)H_i/h\Delta\nu,$$

and $\Delta\nu=2A$ is the zero-field splitting. Zhitnikov and Kolesnikov[3] have interpreted the ESR spectrum of $^2S_{1/2}$-state neutral copper atoms, trapped in organic matrices, in the same way.

The evaluation of the experimental data by means of Eqs. (2) gives

$$g=2.0006\pm0.0003,$$

$$\Delta\nu(Ga^{69})=12.395\pm0.002\ \text{Gc/sec},$$

$$\Delta\nu(Ga^{71})=15.747\pm0.002\ \text{Gc/sec}.$$

The ratio of the zero-field splittings of the Ga^{71} and Ga^{69} is 1.2704, which corresponds to the ratio of their nuclear moments, 1.2706. The validity of the Breit-Rabi formula for the problem under study was verified by evaluating the ESR spectra obtained for three different microwave frequencies, 8742, 9102, and 9404 Gc/sec.

Comparison is invited with the hyperfine-structure data of the isoelectronic neutral copper

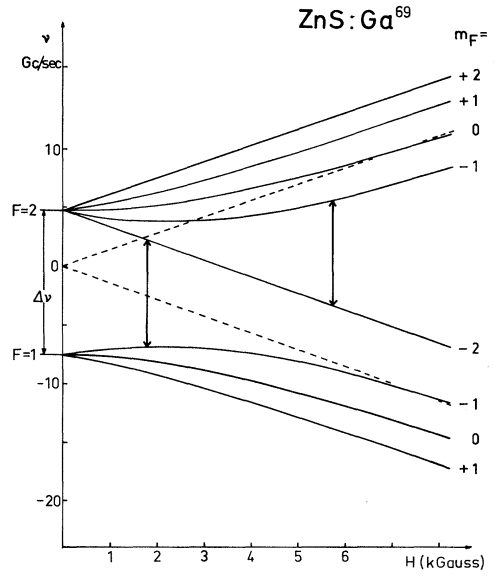

FIG. 1. Breit-Rabi diagram for the Ga^{69} center in ZnS, showing the field position of the two lines observed. The broken lines indicate the Zeeman splitting in the absence of hyperfine structure.

isotopes which have been determined by atomic-beam measurements.[4] The zero-field splitting extrapolated for the free Ga^{69} and Ga^{71} ions is 10 625 and 13 500 Gc/sec. These values will underestimate the true zero-field splitting of the free Ga^{2+} ion because the wave function of the unpaired 4*s* electron will be somewhat more localized at the gallium nucleus, as a result of its greater charge. On the other hand, the cubic crystalline field of the ZnS lattice will admix some 4*g* character to the wave function of the unpaired electrons and the Fermi contact interaction A will be decreased. A further reduction of A results when some localization of the unpaired electron on the surrounding sulfur and zinc ligands is admitted.

It remains to discuss the question how the gallium center is incorporated in the ZnS lattice. The most straightforward model for its paramagnetic modification is a Ga^{2+} ion on a cubic Zn^{2+} site, in the ionic picture. However, we do not know whether the charge state of the center in the absence of optical excitation is Ga^{3+} or Ga^{+}, both being diamagnetic. Fair, Ewing, and Williams have observed no photoconductivity under 450-mμ illumination which preferentially creates the paramagnetic center. This would favor the Ga^{3+} charge state for the diamagnetic form of the center since the mobility of holes in ZnS, split off by optical ionization of the Ga^{3+} ion, is much less than that of electrons, split off from a Ga^{+} ion.

Finally, we want to mention that the ESR spectrum of the Ga^{2+} center was also observed in samples not purposely doped with copper. We have no experimental evidence that a copper ion is present in the vicinity of the paramagnetic gallium center. The ESR spectra observed are isotropic and can be very precisely described, within the small limits of experimental error, by the spin Hamiltonian (1) which is characteristic for an $S=\frac{1}{2}$ center in cubic symmetry. If defect association should occur, the ESR spectrum could no longer be described by an isotropic A.

We wish to thank F. Friedrich for preparation of the samples.

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

[2]See, for instance, N. F. Ramsey, Molecular Beams (Clarendon Press, Oxford, 1956).

[3]R. A. Zhitnikov and N. V. Kolesnikov, Soviet Phys.–Fiz. Tverd. Tela 6, 3307 (1964) [translation: Soviet Phys.–Solid State 6, 2645 (1965)].

[4]Yu Ting and Hin Lew, Phys. Rev. 105, 581 (1957).