the pulse. It should be noted that the observing oscilloscope would not have noted any oscillations in the current or voltage at frequencies above several megacycles per second.

We should like to thank M. A. Lampert and Dr. L. S. Nergaard for many helpful discussions of plasma effects in solids.

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[1] M. C. Steele and M. Glicksman, J. Phys. Chem. Solids 8, 242 (1959).

[2] W. Bennett, Phys. Rev. 45, 890 (1934).

[3] M. Glicksman and M. C. Steele, Phys. Rev. 110, 1204 (1958).

[4] Bezbatchenko, Golovin, Ivanov, Kirillov, and Iavlishkii, Doklady Akad. Nauk S.S.S.R. 111, 319 (1956) [translation: Soviet Phys. Doklady 1, 640 (1957)].

[5] Butt, Carruthers, Mitchell, Pease, Thonemann, Bird, Blears, and Hartill, Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy (United Nations, Geneva, 1958), Vol. 32, p. 42.

[6] M. Kruskal and J. L. Tuck, Proc. Roy. Soc. (London) A245, 222 (1958).

[7] M. Rosenbluth, Los Alamos Scientific Laboratory Report LA-2030 (unpublished).

[8] L. Tonks, Phys. Rev. 56, 360 (1939).

[9] P. C. Thonemann and W. T. Cowhig, Proc. Phys. Soc. (London) B64, 345 (1951).

[10] H. Ehrenreich, J. Phys. Chem. Solids 2, 131 (1957).

[11] M. A. Leontovich and S. M. Osovets, Atomnaya Energ. 1, No. 3, 81 (1956)[translation: Soviet J. Atomic Energy 1, 371 (1956).

[12] M. C. Steele and M. Glicksman, Bull. Am. Phys. Soc. Ser. II, 3, 377 (1958).

[13] M. C. Steele, Bull. Am. Phys. Soc. Ser. II, 4, 28 (1959).

MULTIPLET STRUCTURE OF EXCITONS IN CdS*

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A band model has been proposed recently by a number of authors[1,2] to explain the optical reflection and luminescence excitation spectra of CdS,[3,4] wurtzite structure. The model assumes a *p*-like valence band and an *s*-like conduction band with the extrema at $\vec{k}=(0,0,0)$, in the reduced zone. The *p*-like valence band is split by the crystal-field and spin-orbit effects into three bands. Using these assumptions, optical selection rules may be derived from the symmetry properties associated with the bands. The individual bands may be tentatively assigned by interpreting the polarization effects observed in the experiments with use of the selection rules. The assignment of the extrema to be at $\vec{k}=(0,0,0)$ is not unique since other symmetry points of the zone have group properties, as far as the selection rules are concerned, isomorphic with those at $\vec{k}=(0,0,0)$. In terms of the model, the extrema at $\vec{k}=(0,0,0)$, Fig. 1, indicate the energy splittings and the symmetry assignments as deduced from experiments in this laboratory[5] as well as elsewhere.[3,4] The upper valence band symmetry assignment of Γ_9 is indicated by the fact that at 4.2°K the edge luminescence is completely polarized perpendicular to the *c* axis.

This note is to report on the line absorption spectra near the absorption edge of CdS single crystals at 4.2°K and on the possible interpretation using this model. The absorption spectra were taken of single crystal platelets grown by the vapor phase sublimation method. The samples used were free of visible streaking often observed in platelets of this material. Further, the samples were not subject to any kind of surface preparation, such as polishing, etching, or cleavage. Since the *c* axis of the crystal lay in the plane of the platelet, orientation was easily

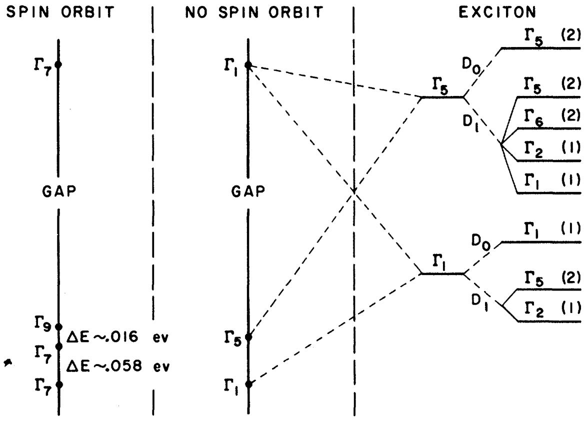

FIG. 1. Band structure at $\vec{k}=(0,0,0)$ of wurtzite CdS, and the possible exciton levels when spin-spin interactions are included.

accomplished by using light incident normal to the plane of the platelet, whereupon the location of the *c* axis was obtained using the birefringent property of hexagonal crystals. The crystal thicknesses were determined either with a microscope or by interference patterns.

The spectrograph used to observe the spectra was a large Hilger Littrow mounting with glass optics, providing a dispersion of about 9 A/mm, with a resolution for emission lines of about 0.4 A.

In considering these spectra, as pointed out by Gross,[6] some lines are variable from crystal to crystal, especially if individual crystals are subjected to surface deterioration or prolonged heat treatment. Thus, if one considers only the indicated lines of Fig. 2 (numbered 1-5) which appear in all spectra, or are not present due to progression to thinner samples, one observes 5 sharp lines in the region between 4890 A and 4850 A.

One may arrive at a possible interpretation of these lines by considering them all as possible ground-state excitons originating from the Γ_5 valence level. Initially, consider the valence band split by the crystal field into the twofold degenerate Γ_5 band and the nondegenerate Γ_1 band. Assuming the conduction band has a Γ_1 symmetry, any excitons formed of the two states have the symmetry of the direct product of the valence and conduction band symmetries. This means, of course, that the symmetry of the exciton band will be Γ_5. Now suppose we include spin-spin interaction between the hole and the electron making up the exciton. This means that we generate triplet and singlet states by forming the direct product of Γ_5 with D_0 (singlet) and D_1 (triplet). Here in the irreducible representations of the hexagonal group C_{6v},[7,2] D_0 transforms as Γ_1, and D_1 transforms as $\Gamma_2+\Gamma_5$. Thus we are led to the levels indicated in Fig. 1. As has been pointed out by Overhauser,[8] if the spin-orbit splitting of such a *p*-like valence band is of the same magnitude as the exciton Coulomb and exchange energies, the selection rules prohibiting transitions to "triplet" states are relaxed. In fact, the transition probabilities may be significant. Thus we should like to suggest that the five indicated lines should be ascribed to the ground states of different terms in the exciton spectra. This interpretation may be further borne out by the Zeeman splitting of CdS lines indicated in photographs published by Gross.[9] The degeneracies, indicated in Fig. 2, of the exciton levels show that upon splitting by a magnetic field, the lines will either be split into only two components or not at all. Although Gross's photograph indicates that the line at 4857 A is split into two components, unfortunately his plate does not cover the necessary spectral range nor is the magnetic field orientation and polarization of the light given. Thus, due to the group-theoretical selection rules, an unequivocal interpretation cannot be made with relation to the magnetic line splittings observed by Gross.

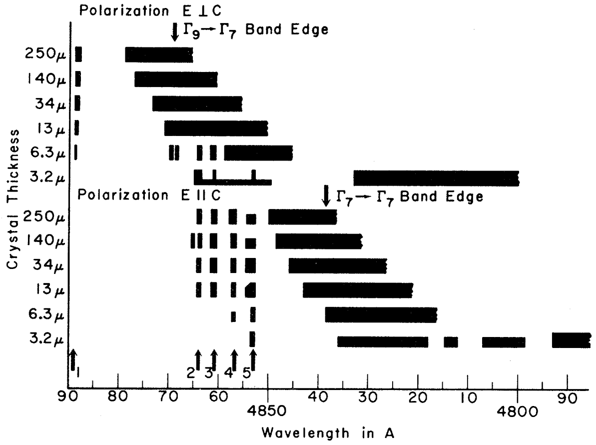

FIG. 2. Wavelengths (in air) of the line absorption spectra for six crystals of different thicknesses at 4.2°K. Also indicated are the respective polarizations of the light relative to the hexagonal axis, the positions of the start of the continuous absorption for each crystal, and the approximate location of the band to band transition wavelengths. The graph has been constructed to show the line width; the varying amplitudes are only to be considered relative to other lines observed in the same crystal.

The lines at wavelengths shorter than 4840 A probably are exciton levels due to transitions from the Γ_1 valence band. In this case the observed lines probably do not involve triplets because of the absence of the spin-orbit mechanism to relax the optical selection rules. More probably the lines are analogous to the hydrogenic excitons observed in Cu_2O, deviations from the Balmer-like spectra due to nonspherical energy bands.[10]

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[1] J. Hopfield, Bull. Am. Phys. Soc. Ser. II, 3, 409

(1958), and J. Phys. Chem. Solids (to be published).

[2] Joseph L. Birman, Phys. Rev. Lett. 2, 157 (1959), and Phys. Rev. (to be published).

[3] D. Dutton, J. Phys. Chem. Solids 6, 101 (1958), and Phys. Rev. 112, 785 (1958).

[4] D. G. Thomas, Bull. Am. Phys. Soc. Ser. II, 4, 154 (1959).

[5] R. G. Wheeler and P. B. Dorain (to be published).

[6] E. F. Gross and B. S. Razbirin, J. Tech. Phys. U.S.S.R. 27, 2173 (1957)[translation: Soviet Phys. (Tech. Phys.) 2, 2014 (1957)].

[7] G. Dresselhaus, Phys. Rev. 105, 135 (1957).

[8] A. W. Overhauser, Phys. Rev. 101, 1702 (1956).

[9] E. F. Gross, J. Phys. Chem. Solids 8, 172 (1959).

[10] G. Dresselhaus, J. Phys. Chem. Solids 1, 14 (1956).

FERRIMAGNETIC RESONANCE LINE WIDTHS AND g-FACTORS IN FERRITES

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A theory of resonance g-factors[1] and line widths[2] for the rare earth garnets which gives reasonable agreement with all available experimental data has recently been developed by Kittel, Portis, and de Gennes. The purpose of this Letter is to extend the above theory to other magnetic systems, in particular the spinel-type ferrites.

The KPdeG theory hinges on the demonstration that (1) a lattice of ions (the rare earths) exhibiting a relaxation frequency high compared to all other frequencies involved in the motion will contribute a precessing magnetization to the system but essentially no coherently precessing angular momentum, and (2) an ion of very high relaxation frequency, exchange-coupled to a precessing low-loss magnetic system, will effectively scatter energy out of a uniform precession and into shorter spin waves.

The extension of the theory rests upon two further observations: (1) that the rapidly relaxing ions need not be sequestered onto a distinct sublattice to exhibit the properties cited above, and (2) that certain ions of very short relaxation time do indeed commonly occur in ferrites.

Any of the transition elements whose lowest lying state in an octahedrally or tetrahedrally coordinated site of cubic symmetry is not an orbital singlet is a candidate for the role played by the rare earth ions in the rare earth garnets. In particular, Fe^{2+}, Co^{2+}, and Mn^{3+} in octahedrally coordinated sites and Fe^{2+}, Ni^{2+}, or Mn^{3+} in tetrahedrally coordinated sites will possess such energy levels, since these ions will then have ground states which are orbital doublets or triplets split only by spin-orbit interaction or crystal field components of lower symmetry. Fe^{2+}, most likely the principal source of line width in ferrites generally, has been observed in the paramagnetic state[3] to have a short relaxation time T_1 even at reduced temperatures ($T_1 = 5\times10^{-9}$ sec at 20°K, $T_1 = 10^{-10}$ sec at 80°K). As pointed out by KPdeG, the relaxation time T_1 is theoretically inversely proportional[4] to H^2 and may be further greatly shortened by the enhancement of the applied field by the exchange fields; i.e., T_1 may be several orders of magnitude shorter in the ferrites than in a diamagnetic host.

Several general features of the available data on ferrites tend to confirm the hypothesis that the KPdeG relaxation process is a dominant one in these materials:

1. Magnetite, Fe_3O_4, which certainly contains Fe^{2+} ions, shows a very wide (2000-3000 gauss) resonance line.

2. Yttrium iron garnet, which should contain exclusively Fe^{3+} ions (ground state, orbital singlet) and essentially no Fe^{2+} ions, shows exceedingly narrow ($\Delta H < 0.5$ gauss) resonance lines.

3. A maximum in line width as a function of temperature is observed in iron-rich manganese and manganese-zinc ferrites. This maximum is characteristic of motionally narrowed resonances and is expected in this case when the relaxation frequency of the spin scattering ion becomes commensurate with the precession frequency of the system.

4. The addition of small amounts of Zn^{2+}, unambiguously divalent, to iron-rich manganese ferrite greatly reduces the observed resonance line width. It is suggested that divalent zinc reduces the concentration of divalent iron.

5. A high degree of correlation exists between large magnetic anisotropy and large resonance line widths (single crystal) in the ferrites. In the present theory the same low-lying energy levels which give rise to magnetic anisotropy[5] tend to