

OPTICAL ABSORPTION EDGE OF MAGNETIC SEMICONDUCTORS

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Optical absorption measurements on europium chalcogenides¹⁻³ and on CdCr_2S_4 and CdCr_2Se_4 spinels^{4,5} show that the absorption edge shifts markedly with temperature near the Curie temperature. The effect of a magnetic field on the edge is also greatest near the Curie temperature. In some cases (CdCr_2S_4) photon energy at the edge decreases with increasing temperature, and in others (CdCr_2Se_4 , EuO , EuS , EuSe) this energy increases up to well above T_C , but in all cases the edge shift accompanying increase of the magnetic field strength is in the same direction as that accompanying decrease of the temperature. This Letter will explain these effects as due to deformation potentials and magnetoelastically induced strain.

Figure 1, from Busch,⁶ shows photon energy at the edge versus temperature in the case of EuS . The cadmium-chromium-chalcogenide spinel data are qualitatively similar. Busch et al.,^{1,3,5} attempt to relate the excess, magnetic part of the energy shift to the magnitude of the magnetization. Argyle, Suits, and Freiser² ascribe the effect in EuSe to exchange splitting of an excited state, involving charge transfer of an f electron from one Eu ion to a $5d$ orbital of another. Rys, Helman, and Baltensperger⁷ em-

ploy a somewhat different atomic model from Argyle, Suits, and Freiser and invoke the exchange energy to shift the conduction-band edge. Harbeke and Pinch³ perceive that the magnetic energy is also involved in the edge shift of CdCr_2Se_4 . Haas, van Run, Bonders, and Albers⁸ suggest that the shift is proportional to the magnetization below T_C and depends upon the susceptibility above.

The dependence of absorption edge (and, in some cases, of anomalies in the electronic transport properties) on temperature and magnetic field can be understood by means of deformation potentials and magnetoelastic coupling. Lacking knowledge of the band structure, let us assume that there is some set of valleys populated by the majority carrier. There may be one valley at Γ , or a set of equivalent ones through the Brillouin zone. In the local $(\xi\eta\zeta)$ coordinate system of each valley we can define symmetry strains $\tilde{\epsilon}_1 = \epsilon_{\xi\xi} + \epsilon_{\eta\eta} + \epsilon_{\zeta\zeta}$; $\tilde{\epsilon}_2 \equiv \epsilon_{\zeta\zeta} - \frac{1}{3}\epsilon_1$. Considering only rigid-band energy shifts, the energy of a strained valley is

$$E(k, \epsilon) = E(k, 0) + \tilde{\Xi}_1 \tilde{\epsilon}_1 + \tilde{\Xi}_2 \tilde{\epsilon}_2. \quad (1)$$

It is nonessential but simplifying and reasonable to envision ellipsoidal valleys, particularly at low carrier densities. $\tilde{\Xi}_1$ and $\tilde{\Xi}_2$ are simply related to Ξ_d and Ξ_u , the deformation potentials defined by Herring and Vogt⁹: $\tilde{\Xi}_1 = \Xi_d + \frac{1}{3}\Xi_u$; $\tilde{\Xi}_2 = \Xi_u$. Suppose we now transform the strains to a representation in the macroscopic cubic coordinate system. The scalar invariant $\tilde{\epsilon}_1$ goes into itself, the volume strain ϵ_1 . The several $\tilde{\epsilon}_2$ go into various linear combinations of symmetry strains, with no projection on ϵ_1 . Were there no other states available, $\tilde{\Xi}_1$ would have little significance. For then, under volume strain, the energy of the valleys would rise by $\tilde{\Xi}_1$, but the Fermi level would rise by the same amount, since the number of carriers in the valleys would be conserved. This will rarely be the case in nondegenerate semiconductors. We take it that there are some other states in thermal equilibrium with the band of carriers, and when the volume is strained, carriers transfer between the two.

The question reduces to how the volume strain depends upon temperature and magnetic field.

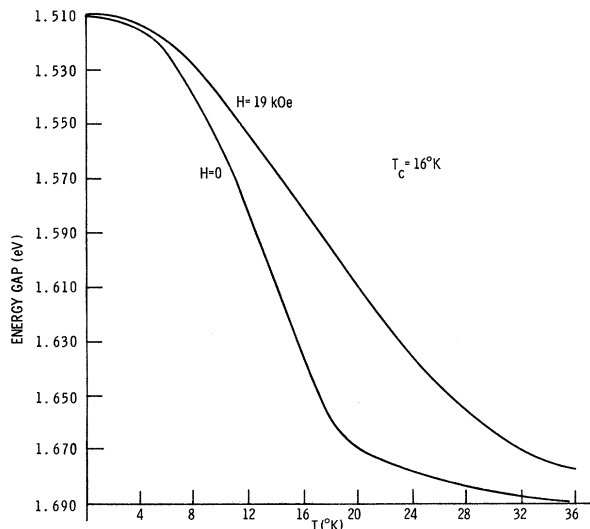


FIG. 1. Band edge of EuS as a function of temperature [after Busch (Ref. 6)]. Note the long tail above T_C , even in zero field, a characteristic of the scalar correlation function.

The relevant part of the Hamiltonian is¹⁰

$$\mathcal{H} = -2 \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j - \epsilon_1 \sum_{\langle ij \rangle} D_{ij} \vec{S}_i \cdot \vec{S}_j + \frac{1}{2} (C_{11} + 2C_{12}) \epsilon_1^2. \quad (2)$$

The D_{ij} are derivatives of J_{ij} with respect to volume strain. Calculating the free energy and minimizing with respect to strain,

$$\epsilon_1(T, H) = \frac{\sum_{\langle ij \rangle} D_{ij} \langle \vec{S}_i \cdot \vec{S}_j \rangle (T, H)}{(C_{11} + 2C_{12})}. \quad (3)$$

The gap width and absorption edge then vary as

$$E_g(\epsilon, T) = E_g(0, T) + [\bar{\Xi}_1 / (C_{11} + 2C_{12})] \times \sum_{\langle ij \rangle} D_{ij} \langle \vec{S}_i \cdot \vec{S}_j \rangle (T, H). \quad (4)$$

The shift in gap width can have either sign, depending upon the product

$$\bar{\Xi}_1 \left(\sum_{\langle ij \rangle} D_{ij} \right),$$

but the correlation functions decrease with increasing temperature and with decreasing field strength, as observed, and are most field dependent near T_C , as observed.

We estimate that the size of the energy shift is also as observed. Although such low-symmetry magnetostrictions as λ_{100} and λ_{111} , which come from the strain dependence of the anisotropy energy, are small, the magnetic volume strain, arising from the exchange energy, is large. Integrating the magnetic thermal expansion down to 0°K, a typical value of $\epsilon_1(0)$ is 10^{-2} , as in EuO.¹¹ Since a typical deformation potential is about 10 eV, Eq. (4) suggests $\delta E_g \approx 0.1$ eV. It will be seen in Fig. 1 that the 0°K energy shift is ~ 0.2 eV.

The right-hand side of Eq. (4) looks like the magnetic energy,

$$U = \sum_{\langle ij \rangle} J_{ij} \langle \vec{S}_i \cdot \vec{S}_j \rangle,$$

as conjectured^{2,4,7}; it is exactly proportional to it when there is only nearest-neighbor exchange and magnetoelastic coupling.¹⁰ In this case magnetic contributions to the specific heat, thermal-expansion coefficient, and temperature derivative of the gap width should all be proportional:

$$C_v \sim \alpha_T \sim \frac{dE_g}{dT} = \frac{\bar{\Xi}_1 DNZ}{2(C_{11} + 2C_{12})} \frac{d \langle \vec{S}_i \cdot \vec{S}_j \rangle}{dT}. \quad (5)$$

Proportionality of C_v and α_T has been demonstrated in EuO.¹¹ Another nearest-neighbor candidate is CdCr₂Se₄ ($J_1 \gg J_2$),¹² but for this material neither C_v nor α_T are reported. Whether or not the interactions are nearest neighbor, the magnetic parts of the volume strain and energy gap should be proportional.

The easiest evaluation of the scalar correlation function, $\langle \vec{S}_i \cdot \vec{S}_j \rangle$, is by molecular-field theory, which is a bad model on which to calculate this two-particle quantity. It gives, for neighbors at whatever distance,

$$\langle \vec{S}_i \cdot \vec{S}_j \rangle \sim m^2(T, H) \quad (6)$$

with $m(T, H)$ the reduced magnetization.

One attempt at a more accurate treatment of the scalar correlation function, a two-spin cluster theory,¹³ has been employed in describing some of the magnetic properties of EuO¹¹ and of cadmium- and mercury-chromium-chalcogenide spinels.¹² Figures 2 and 3 show the application of this analysis to CdCr₂Se₄, which has only B - B nearest-neighbor interactions ($Z = 6$), and a Cr³⁺ spin of $S = \frac{3}{2}$. In Fig. 2 the reduced correlation function is shown versus temperature for several field strengths. The curves are qualitatively similar to the absorption edge data of Harbeke and Pinch⁴ on CdCr₂Se₄, after subtracting off a uniform background due to electron interaction with acoustic phonons. Although the Z and S parameters for the europium chalcogenides

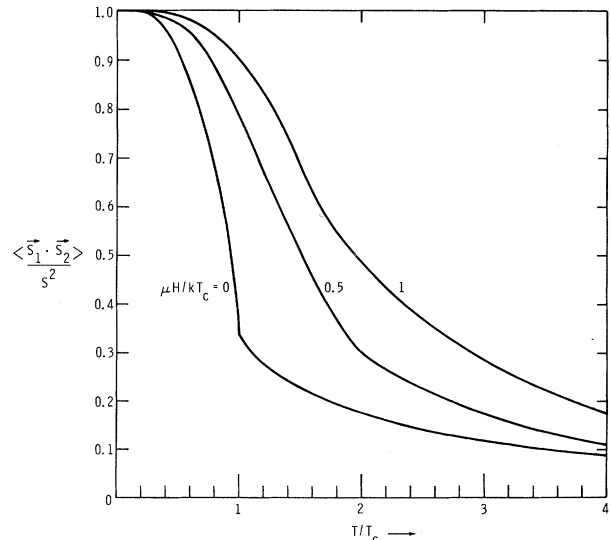


FIG. 2. Calculated temperature dependence of the reduced correlation function for several field strengths. Only nearest-neighbor interactions are assumed, with $Z = 6$. Spin $S = \frac{3}{2}$. These parameters are appropriate to CdCr₂Se₄.

are quite different from those of the spinels, to which Figs. 2 and 3 apply, it is apparent that the theoretical analysis is also reproducing the absorption-edge behavior of EuS depicted in Fig. 1. In any case the correspondence cannot be made precise, since the absorption edge is somewhat arbitrarily defined. [Harbeke and Pinch adopt $\ln(I_0/I) = 3$ as a criterion.] Figure 3 shows the field dependence at a number of temperatures. At small fields the curves show a linear field dependence below T_C and quadratic dependence well above. The effect of the field is greatest near T_C , as has been observed in measurements of the optical absorption edge. Note that the linear slope appears to extend above T_C , as illustrated by the curve where $T/T_C = 1.06$. This is misleading; it really means that close above T_C , the power series in H^2 , which represents the scalar correlation function, is only slowly convergent, with the H^4 term having a negative coefficient. True linear response above T_C is forbidden in zero field by time-reversal invariance. Such a pseudolinearity was observed in the forced volume magnetostriction of Gd, which involves the same correlation function.^{10,14,15}

In summary, we have shown that magnetoelastic coupling can account for the temperature and magnetic field behavior of the optical absorption edge of magnetic semiconductors of the rare-earth chalcogenide and cadmium-chromium-chalcogenide spinel families. The calculated temperature and field dependence reproduce the observed behavior and the amplitude of the calculated energy gap shift is of the observed magnitude.

Finally, let us speculate on the effects of shift of the band edge on the electrical and magnetic

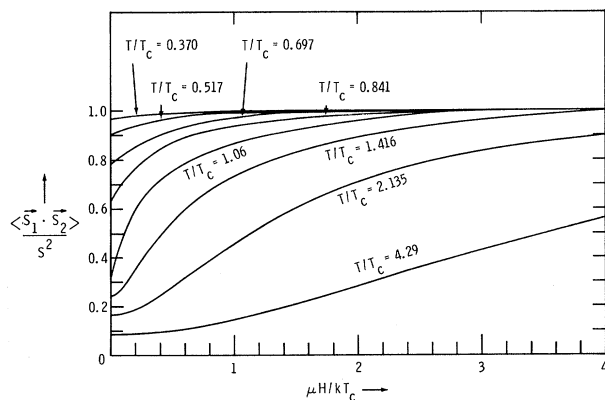


FIG. 3. Calculated magnetic field dependence of reduced correlation function for a number of temperatures. $Z = 6$ neighbors; $S = \frac{3}{2}$.

properties by alteration of the carrier density. Lehmann¹⁶ has suggested that this alteration, plus spin-disorder scattering, are responsible for the maxima in the transport coefficients (except the Seebeck coefficient⁹) of n -CdCr₂Se₄. Lehmann assumes the ionization energy of the donor level to be effected by its separation from the valence band. As the conduction-band edge shifts to a maximum on raising the temperature to the Curie point, it separates somewhat from the donor levels, and the number of ionized donors decreases. A decrease in carrier density may also play some role in the observed temperature dependence of the reflectivity¹⁷ of the antiferromagnetic semiconductor, p -type MnTe, since the plasma frequency depends upon carrier density.

Magnetoelastic coupling can also affect magnetic properties. Suppose the result of relaxation of the magnetic order were to deionize donors, and suppose that the origin of magnetic coupling were indirect exchange through conduction-electron polarization. The results of raising the temperature would then be cataclysmic for the magnetic order, since reduction of magnetization would dissolve out the glue, further reducing the magnetization. This could produce square magnetization curves, and even first-order transition. When the effect of relaxation of magnetic order was such as to increase the number of carriers, magnetization curves with long tails would result. In both circumstances the susceptibility and other magnetic response would be strange.

The electrical and magnetic properties of the europium chalcogenides are very sensitive to magnetic impurities. A 1% substitution of Gd for Eu in EuSe raises the paramagnetic Curie temperature θ from 9 to 24°K, but has little effect on the ferromagnetic Curie temperature.¹⁸ The magnetoresistance is also changed greatly, and is enormous at 1% substitution¹⁹ of Gd. Kasuya²⁰ has explained these remarkable properties by considering that the extra electron of the gadolinium is localized around the impurity and its nearest-neighbor shell of 12 europium ions. Indirect s - f exchange through this electron aligns the spins within this superparamagnetic "molecule." Thus θ is increased, but not T_C . Such phenomena are not observed in the cadmium spinels, where the s - d exchange is weaker and the spin coupling is primarily superexchange. In either type material, while the transport properties are impurity sensitive, the magnetoelas-

tic properties are not particularly so, and these latter are the principal concern of this Letter.

A lucid colloquium by Dr. Peter J. Wojtowicz stimulated the author's interest in these problems.

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ALBEDO NEUTRON SOURCE FOR HIGH-ENERGY PROTONS TRAPPED IN THE GEOMAGNETIC FIELD*

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An absolute intensity measurement of cosmic-ray neutrons in the atmosphere, in the energy range from thermal to 20 MeV, leads to a value of 0.36 ± 0.06 neutron $\text{cm}^{-2} \text{sec}^{-1}$ for the albedo neutron leakage flux at 42° geomagnetic latitude near solar minimum. The significance of this value for evaluating the contribution of the cosmic-ray albedo-neutron-decay source for the high-energy protons in the inner radiation belt is discussed.

While cosmic-ray albedo neutron decay (CRAND) is probably a source for some of the protons of the inner radiation zone, the measurements reported here, confirming earlier estimates by Boella et al.,¹ indicate that if the theoretical calculations of Dragt, Austin, and White² are correct, CRAND is too small by a factor of 50 to account for the high-energy ($E_p \geq 20$ MeV) inner-zone protons.

The measurements were made in an experiment in which boron plastic-ZnS(Ag) scintillation detectors were flown on balloons to obtain the neutron counting rate from sea level (1030 g cm^{-2}) to 4 g cm^{-2} at 42° geomagnetic latitude near solar minimum. The detection unit was similar to that described by Boella et al.¹: Two detectors, one enriched in B^{10} and one unen-

riched, were flown back to back and the neutron counting rate was obtained by the difference technique. The detection unit was small and lightweight to minimize local neutron production, and it responded to energies from 0.025 eV to 20 MeV.

The measurements carried out enabled two estimates of the CRAND source strength to be made. First, the neutron flux measured closest to the top of the atmosphere near solar minimum was 0.58 neutrons $\text{cm}^{-2} \text{sec}^{-1}$ at 4 g cm^{-2} . Since the flux decreases with increasing altitude near the top of the atmosphere, this measured flux must be an upper limit to the neutron flux at 0 g cm^{-2} .

Second, the measured neutron flux within the atmosphere can be extrapolated to 0 g cm^{-2} . A