The effect of this mixing is to increase the transition probability for the polarization $x-iy$ and decrease it for $x+iy$. To first order, the change for this one center is $(I_+-I_-)/I \simeq 4\epsilon$. There is no change in the energy of the emission to first order in ϵ.

In the case where $\langle S_z\rangle = 0$, the spin-orbit contribution cancels for an average over all centers, while the orbital Zeeman contribution does not. The resultant circular polarization can be written

$$\Delta = -\frac{4g_{\mathrm{orb}}\beta H_z}{\delta E}, \qquad (3)$$

where $g_{\mathrm{orb}} = |\langle 2p_y|L_z|2p_x\rangle|$. This result has the same form as the observed effect

$$\Delta_{\mathrm{exp}} = -(6\pm 1)\times 10^{-8}H_z, \qquad (4)$$

where H is given in gauss. Since δE was estimated to be ~0.016 eV from the Stark effects in emission, this would imply that $g_{\mathrm{orb}} \simeq 0.04$. Such a strong reduction of the orbital g value is not unusual for color centers. It might result from countercirculating current on the neighboring ions,[6] or from even-parity Jahn-Teller distortion,[7] or both.

The authors wish to thank J. A. Davis for advice and for the use of his experimental equipment.

Note added in proof.—After this Letter was submitted, a paper by Mollenauer et al.[8] appeared reporting the indirect observation of ESR in the relaxed excited state of the F center. Although the behavior we observe is quite different from theirs, and we measure orbital rather than spin g values, the two experiments are consistent. They were able to detect microwave-induced spin flips at resonance in the excited state because the normal spin memory of the F center in a single excitation cycle is very high (~99%). However, it is possible to quench the spin polarization by intense optical pumping if the spin-lattice relaxation time T_1 is sufficiently long compared with the recycling time. We have verified that the spin polarization is destroyed under the conditions of our experiment in KF. This was demonstrated by monitoring the magnetic circular dichroism of the F absorption band as a function of pumping-light intensity. A detailed account of this work will be published elsewhere.

---

[*] Work supported primarily by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-3464, Technical Report No. NYO-3464-20. The Advanced Research Projects Agency is also thanked for the use of central facilities of the Materials Science Center at Cornell University, MSC Report No. 1204.

[1] L. D. Bogan, L. F. Stiles, Jr., and D. B. Fitchen, Phys. Rev. Letters 23, 0000 (1969).

[2] L. D. Bogan, thesis, Cornell University, 1968 (unpublished).

[3] C. H. Henry and C. P. Slichter, in Physics of Color Centers, edited by W. B. Fowler (Academic Press, Inc., New York, 1968), p. 351.

[4] B. R. McAvoy, D. W. Feldman, J. G. Castle, and R. W. Warren, Phys. Rev. Letters 6, 618 (1961).

[5] D. Schmid and V. Zimmerman, Phys. Letters 27A, 459 (1968).

[6] D. Y. Smith, Phys. Rev. 137, A574 (1965).

[7] F. S. Ham, Phys. Rev. 138, A1727 (1965).

[8] L. F. Mollenauer, S. Pan, and S. Yngvesson, Phys. Rev. Letters 23, 683 (1969).

OPTICAL PROPERTIES OF SINGLE-CRYSTAL FILMS OF $CdCr_2S_4$

S. B. Berger and L. Ekstrom
RCA Laboratories, Princeton, New Jersey 08540

(Received 10 November 1969)

We report on the preparation and optical properties of single-crystal films of $CdCr_2S_4$. The present data show no large blue shift associated with magnetic ordering near the Curie temperature contrary to that previously observed in bulk $CdCr_2S_4$ data. A large red shift correlated to the magnetic ordering is observed for a peak in the highly absorbing region. The weakness and narrowness of this absorption is inconsistent with that expected for band-to-band transitions resulting in unbound electrons and holes. We suggest an exciton model to explain this absorption.

The absorption edges of magnetic semiconducting chromium chalcogenide spinels are known to shift dramatically near the Curie point.[1-4] The usual shift is to lower energies (red shift) with increasing magnetic order (decreasing temperature); however, a large opposite blue shift was observed for $CdCr_2S_4$.[1] Several models have been proposed to explain these large magnetic shifts[5-10]; however, the need to simultaneously account for both senses of shifts has placed a severe constraint on theory. The most recent theory[9] can explain the opposite shifts in terms of valence-band to exchange-split conduction-band transitions. The direct transition would show a red shift as found in previous descriptions,[5,6] but a spin-fluctuation–assisted indirect transition would exhibit an apparent blue shift. Other models have incorporated the effects of volume magnetostriction coupled with the deformation potential[7] on band transitions and of an exchange-split valence band[8] or excited state[10] in charge-transfer transitions to Cr levels. All these models have been constructed in a special effort to account for both senses of large magnetic shifts.[11]

In this Letter we report the first preparation of single-crystal films of a chromium chalcogenide spinel, $CdCr_2S_4$. We emphasize the fact that no large magnetic blue shift is found. This observation removes the constraint previously placed on theoretical models by the magnetic blue shift in bulk $CdCr_2S_4$ data. We also note the presence in a strongly absorbing spectral region of an absorption with a large magnetic red shift. The narrowness and weakness of this absorption is distinctly inconsistent with band-to-band transitions to continuum states and thereby eliminates an explanation in terms of split-band models.

The films were prepared by an open-tube vapor-phase technique using ultrahigh-purity He as the carrier gas.[12] For deposition, a mixed stream of Cd, S_2, and $CrCl_3$ was passed through a nozzle which directed the flow onto the substrate of oriented sapphire or magnesium aluminate held at about 740°C. Deposition times were typically 2 hours, which resulted in films of 1 to 2 μm thickness. The films were analyzed by Debye-Scherrer x-ray powder techniques for phases present, and by low-angle electron diffraction for crystallinity.

Figure 1 contains spectra taken at room temperature, at 86°K (just above the Curie temperature $T_C = 84°$K observed for bulk $CdCr_2S_4$), and near 4.2°K. These data extend to much higher extinction coefficients than previous bulk-sample studies.[1,2] For example, the bulk data cut off at about 0.775 and 0.70 μm at 300 and 4.2°K, respectively. The spectral structure observed in bulk samples near 1.62 eV (0.765 μm) was broadened in the films but evident above the background. The intensity of this absorption is too small to be seen in Fig. 1. Three peaks A, C, and D, and edge B are labeled in Fig. 1. At very low temperatures, A is comprised of peaks A_1 and A_2 on which C, the magnetic red-shifting peak, is superimposed. Linearly polarized spectra were measured with magnetic fields of 0.8 and 2.5 kOe in the film plane at about 77 and 4.2°K. Circularly polarized spectra were obtained with magnetic fields, normal to the film plane, of 2.5 kOe near 77°K and 5 and 10 kOe at 2°K. Figure 2 contains spectra for $\Delta m = 0$ and ± 1 (where m represents the component of total angular momentum in the magnetization direction) taken at liquid-He temperatures. Absorption A is comprised of transitions active in all polarizations with regions of selective polarization which are evidenced by peaks in the spectra. At 77°K, absorption C is predominantly right-circularly polarized ($\Delta m = +1$). The peak at 0.66 μm in the $\Delta m = +1$ spectrum taken at 2°K and shown in Fig. 2 is ascribed to absorption C on the basis of its similar polarization activity.

The oscillator strengths f of the absorptions labeled A, C, and D in Fig. 1 have been determined using a Gaussian line-shape approximation, neglecting reflection corrections and assuming two ions per formula unit. The sample thickness was estimated from the observed interference

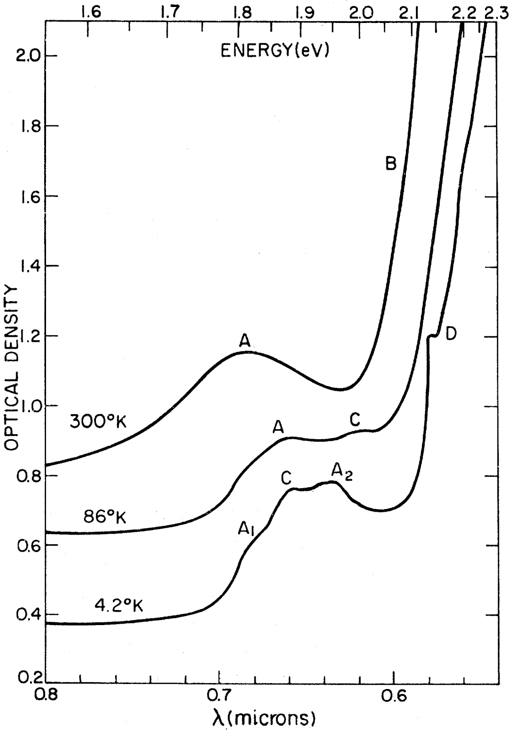

FIG. 1. Relative optical absorption spectra of 7×10^{-5}-cm-thick single-crystal film of $CdCr_2S_4$ at various temperatures. (The spectra are displaced by about 0.2 optical density for clarity.)

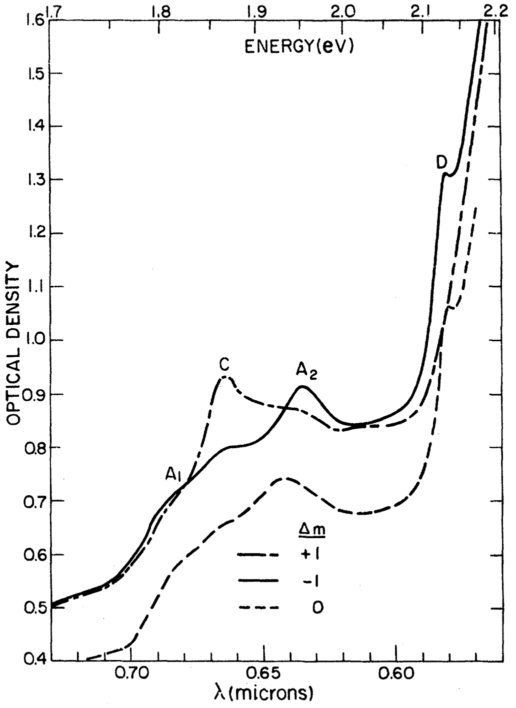

FIG. 2. Polarized optical spectra of 7×10^{-5}-cm-thick single-crystal film of $CdCr_2S_4$ taken in magnetic fields as described in the text. (The $\Delta m = \pm1$ spectra are displaced by 0.12 to higher optical density.)

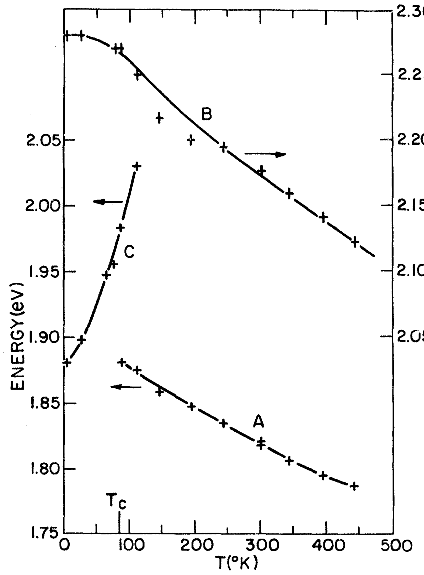

FIG. 3. Temperature dependencies of three spectral features shown in Fig. 1 for $CdCr_2S_4$.

spacings as a function of wavelength in the nonabsorbing region using a refractive index of 3.[13] The half width at half-maximum absorption was determined for *A* from the low-energy side of the peak where absorption *B* has least overlap. The *f* number determined in this was was 2×10^{-3} and is temperature independent to within experimental error. For absorptions *C* and *D*, the *f* number was obtained from circularly polarized spectral data taken at 2°K. The determination of the *f* number for *C* depends on its unique polarization activity relative to *A*, and for *D*, on its absence in the $\Delta m = +1$ spectrum at 2°K. The *f* numbers for *C* and *D* are 10^{-4} and 10^{-5}, respectively. This *f* number for *C* agrees with its intensity at higher temperatures. The oscillator strength for *B* is not obtainable from these data, but is obviously very large since the maximum absorption coefficient is much greater than 6×10^{-4} cm^{-1} and the width at half-maximum absorption appears large.

The temperature dependence of the energies of the maxima of absorptions *A* and *C*, and the energy of *B* at optical density 2 (above that in the nonabsorbing region, $\alpha \sim 3\times10^4$ cm^{-1}), are plotted in Fig. 3. The temperature dependences of *A* and its low-energy edge are similar and approximately linear above 100°K with a differential coefficient of about -3×10^{-4} eV/°K. This value agrees with that on bulk $CdCr_2S_4$ above 150°K. However, no large magnetic blue shift is observed in our data below 150°K, contrary to the bulk-sample observation. We believe that the bulk-sample data were complicated by the presence of more than one absorption. The temperature independence of the energies of the crystal-field peaks at 0.765 and 0.68 μm (see below) and the blue shift of absorption *A*, which is unrelated to magnetic order, gave the appearance of a large rapid shift near the Curie point. In fact, the peak at 0.765 μm rides the absorption tail of peak *A*. This peak became apparent in the bulk data only when *A* moved to higher energies with decreasing temperature. Unfortunately, this occurred near the ordering temperature of $CdCr_2S_4$ and led to confusion with large magnetic shifts. The additional shift observed upon application of a magnetic field in the bulk-sample data may reflect a much smaller magnetic blue shift.[14] The superposition of *C* on *A* in the present data makes it difficult to determine the center of *A*, thereby precluding detection of a smaller shift. Absorption edge *B* behaves essentially the same as *A* as a function of temperature with a differential coefficient of about -4×10^{-4} eV/°K and also exhibits no large magnetic shift. The points at 145 and 190°K appear low for edge *B* in Fig. 3. This may be a manifestation of the appearance of absorption *C* or the $^2T_{1g}$ crystal-field transition on the absorption edge. Absorption *C* most strikingly does show a large magnetic shift near the Curie point. The magnitude of the magnetic shift cannot be obtained from these data because the absorption is seen only below about 110°K. The temperature dependence of the energy of peak C is quite similar to that for the red-shifting absorption edge of $CdCr_2Se_4$ which suggests a magnetic shift of about 0.2 eV.

The crystal-field absorptions can be reasonably assigned by comparison with spectra for $NaCrS_2$.[10,15] The similar local environments of chromium octahedra and the occurrence of three absorptions at similar energies with comparable widths and oscillator strengths for $NaCrS_2$ and $CdCr_2S_4$ are the bases for the assignments. The transition from the $^4A_{2g}$ ground state to the $^2T_{1g}$ state is at 1.62 eV (0.765 μm), to the $^4T_{2g}$ state is at 1.82 eV (0.68 μm) (peak A_1), and to the $^2T_{2g}$ state is at 2.14 eV (0.58 μm) (peak D). The latter absorption was observed in $NaCrS_2$ but unassigned. The transition to the ^2E_g state is not observed for $CdCr_2S_4$ and is either too weak to be seen or is broadened into the nearby $^2T_{1g}$ peak. The oscillator strength of peak A_1 is only a small part of that for A and its magnitude lies between those estimated from published data for $CrCl_3$ and $CrBr_3$.[15] The energies of these absorptions are essentially temperature independent as is expected for crystal-field transitions. Peaks A_1 and D can be observed up to temperatures of 90°K. Above this temperature they are obscured by the stronger absorptions.

The remainder of absorption A originates from some other type of transition, since all the Cr^{3+} crystal-field transitions normally found in this energy range are accounted for. The moderate oscillator strength of about 10^{-3} for the rest of A is consistent with indirect band-to-band or weak charge-transfer transitions. Absorption B is much stronger and may correspond to either a direct band-to-band or strong charge-transfer transition. Evidence for both types of transitions in this energy range exist for materials with common ions. For example, the nonmagnetic spinel $CdIn_2S_4$ has a band edge of 2.2 eV at 300°K, and $NaCrS_2$ and $CrBr_3$ have charge-transfer edges at 2.35 and 2.7 eV, respectively.[10,15,16] Obviously a better understanding of the energy-level sequence is required in order to make a more concrete assignment.

The origin of red-shifting absorption C is of fundamental importance in understanding the properties of these materials. We feel that some insight into this problem is possible through comparison of the energies of the red-shifting absorptions for the cadmium and mercury chromium chalcogenide spinels. At room temperature, where the magnetic effects are minimal, these energies are 0.8, 1.3, 1.45, and at least 2.1 eV for $HgCr_2Se_4$,[4] $CdCr_2Se_4$,[1,2] $HgCr_2S_4$,[3] and $CdCr_2S_4$, respectively. The energy difference between pairs of compounds with similar anion are about 0.7 to 0.8 eV, and between pairs of compounds with similar nonmagnetic cation (Hg or Cd) are about 0.5 to 0.6 eV. An additional strong dependence on nonmagnetic cation is reflected in the magnitudes of the red shifts which accompany magnetic order. These shifts are 0.2 and 0.4 to 0.5 eV for the Cd[1,2] and Hg[3,4] spinels, respectively. The strong dependences on ions other than Cr indicate that this transition involves levels with large degrees of anionic and nonmagnetic cationic character. This conclusion is also supported by the existence in this energy range of band-to-band transitions for Cd and Hg containing chalcogenides with similar local environments. The strong polarization found for C in $CdCr_2S_4$ is indicative of a strong spin-orbit interaction which implies Cd orbital involvement. On the other hand, the large magnetic shifts require strong exchange interactions. Typically, couplings of such magnitude are intra-atomic in origin, which implies that the excited electron or hole must have substantial probability on the Cr sublattice. The observation of charge-transfer transitions involving Cr ions in this energy range supports this implication. The small width (0.04 eV) and oscillator strength ($f = 10^{-4}$) of absorption C in $CdCr_2S_4$ is inconsistent with that expected for band-to-band transitions involving unbound states. We suggest that the red-shifting absorption corresponds to a transition to an excitonic state comprised of an electron and hole which, considered together, have substantial probabilities at all three sites (Cd or Hg, Cr, and S or Se). We note that another excitonic model, similar in some ways, has been proposed to explain the magnetic red shifts observed for the europium chalcogenides.[17]

In summary, no large magnetic blue shift exists in the spectrum of $CdCr_2S_4$. Instead a large magnetic red shift is observed. We believe that there exists no basic difference between the optical spectra of $CdCr_2S_4$ and the other chromium chalcogenide spinels. Only the relative positions of the absorptions for the various compounds differ. For $CdCr_2S_4$, in distinction to the other compounds of this group, crystal-field absorptions and absorption A lie lower than the red-shifting absorption. Finally, we feel that our data on single-crystal films of $CdCr_2S_4$ taken in conjunction with these on bulk samples of the other magnetic chromium chalcogenide spinels is consistent with an exciton model for the magnetic red shift.

The authors gratefully acknowledge the able assistance of E. Trezciak in the preparation and characterization of the films, W. C. Roth for electron-diffraction analyses, and C. C. Neil in taking circular-polarized spectra. One of us (S.B.B.) is indebted to Dr. H. Weakliem and Dr. S. Freeman for stimulating discussions and to Dr. P. J. Wojtowicz for critical reading of this manuscript.

---

[1] G. Harbeke and H. L. Pinch, Phys. Rev. Letters 17, 1090 (1966).

[2] G. Busch, B. Magyar, and P. Wachter, Phys. Letters 23, 438 (1966).

[3] G. Harbeke, S. B. Berger, and F. P. Emmenegger, Solid State Commun. 6, 533 (1968).

[4] H. W. Lehmann and F. P. Emmenegger, to be published.

[5] F. Rys, J. Helman, and W. Baltensperger, Physik Kondensierten Materie 6, 105 (1967).

[6] C. Haas, Phys. Rev. 168, 531 (1968).

[7] E. Callen, Phys. Rev. Letters 20, 1045 (1968).

[8] J. Goodenough, J. Phys. Chem. Solids 30, 261 (1969).

[9] R. M. White, Phys. Rev. Letters 23, 858 (1969).

[10] K. W. Blazey and H. Rohrer, Phys. Rev. 185, 712 (1969).

[11] A magnetic shift is one associated with magnetic ordering and occurs near a Curie or Néel point.

[12] L. Ekstrom and E. Trezciak, to be published.

[13] The refractive index of $CdCr_2Se_4$ has been measured and is 3.02 ± 0.03. P. F. Bongers and G. Zanmarchi, Solid State Commun. 6, 291 (1968).

[14] G. Harbeke, private communication.

[15] A. L. Companion and M. Mackin, J. Chem. Phys. 42, 4219 (1965).

[16] J. F. Dillon, H. Kamimura, J. P. Remeika, and C. E. Olsen, in Proceedings of the International Conference on Magnetism, Nottingham, England, 1964 (The Institute of Physics and The Physical Society, London, England, 1965), p. 367.

[17] J. C. Suits, B. E. Argyle, and M. J. Freiser, Phys. Rev. Letters 15, 822 (1965); A. Yanase and T. Kasuya, J. Phys. Soc. Japan 25, 1025 (1968).

THEORY FOR THE GIANT SUSCEPTIBILITIES OF DILUTE MAGNETIC ALLOYS

K. H. Bennemann
University of Rochester,* Rochester, New York 14627

and

J. W. Garland
University of Illinois, Chicago, Illinois 60637, and Argonne National Laboratory, Argonne, Illinois 60439

and

F. M. Mueller
Argonne National Laboratory,† Argonne, Illinois 60439

(Received 10 September 1969)

The giant susceptibilities and their suppression by small magnetic fields observed for dilute La–rare-earth alloys are explained quantitatively by assuming clustering of localized spins.

Many experiments on dilute alloys containing transition-metal or rare-earth impurities[1-4] have demonstrated ordering of the localized spins. Although the spin ordering is known to arise essentially from the Ruderman-Kittel indirect exchange coupling, it has been shown by Hilsch and Korn[1] that the magnetic properties of dilute magnetic alloys depend sensitively on the distribution of the localized spins. This is further demonstrated by the giant susceptibilities recently observed for LaGd, LaGdIn, and similar alloys.[3] It was shown that the giant susceptibilities depend sensitively on the concentration of paramagnetic impurities and that they can be suppressed by small magnetic fields.[3] From the experimental results obtained for a variety of dilute alloys in which clustering of magnetic impurities has been studied carefully,[1] Hilsch and Korn reached the conclusion that these anomalous magnetic properties[3] result from clustering of local spins.

In the following we present a simple theory for