

Anomalous Absorption-Edge Shift in the Metamagnetic Temperature Range of HgCr_2S_4

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The shift of the optical absorption edge in metamagnetic HgCr_2S_4 is studied as a function of temperature and magnetic field. The large red-shift of the band edge with decreasing temperature is due to short- and long-range magnetic order in the crystal. Its temperature dependence can be explained by the variation of the spiral spin structure with temperature. The magnetic field dependence of the band edge at temperatures below 20 K is interpreted in terms of the conical-spin structure. Its ferromagnetic component which is parallel to the external magnetic field is strongly temperature-dependent. Our results and a recent neutron diffraction study indicate that HgCr_2S_4 has a critical temperature of 60 K.

I. INTRODUCTION

IN 1964, Busch and co-workers¹ observed an anomalous red-shift of the absorption edge of ferromagnetic europium chalcogenides.^{2,3} Harbeke and Pinch reported a very similar effect in CdCr_2Se_4 (Ref. 4) and in CdCr_2S_4 . This effect was also reported by Busch.⁵ The europium chalcogenides as well as the chromium-chalcogenide spinels are semiconductors and a blue-shift of the absorption edge with decreasing temperature is expected. But all these ferromagnetic semiconductors with the noted exception⁴ of CdCr_2S_4 show a strong red-shift with decreasing temperature when the Curie temperature is approached. This red-shift is observed up to temperatures well above the Curie-Weiss temperature θ .

HgCr_2S_4 is a particularly attractive material for the study of the correlation between magnetic and optical properties. The magnetic properties of HgCr_2S_4 have been investigated by Baltzer *et al.*⁶ This compound is one among the few transition-metal spinels with magnetic ions only on the octahedral sites in which the ferromagnetic interaction between nearest neighbors (nn) dominates the antiferromagnetic next-nearest-neighbor (nnn) exchange interaction. In contrast to CdCr_2S_4 , CdCr_2Se_4 , and HgCr_2Se_4 which become ferromagnetic at their respective Curie temperatures and remain ferromagnetic down to 4.2 K, HgCr_2S_4 has been found to be a metamagnet.⁶ At 4.2 K and in a field of 10 kOe almost the full magnetic moment of $6\mu_B$ /molecule is measured which is to be expected for a ferromagnetic spin configuration, whereas for 300 Oe, only about $0.1\mu_B$ /molecule are measured. There is, however, an increase of the magnetic moment under

external fields. In a field of 300 Oe, it starts increasing at 27 K, and a maximum of $1.1\mu_B$ /molecule is reached at 33 K. The 300-Oe magnetization curve then tails out to about 60 K. Magnetization measurements in fields below 300 Oe have not been reported so far. Hastings and Corliss⁷ have shown by neutron diffraction measurements that the magnetic structure of HgCr_2S_4 in zero magnetic field below 60 K is a simple spiral structure and that ferromagnetic order can be induced by external magnetic fields. In a recent letter,⁸ the anomalous shift of the absorption edge in zero magnetic field and for temperatures between 20 and 360 K has been reported. The present study is a continuation of the aforementioned work and extends into the particularly interesting metamagnetic temperature range where the spin order can be changed by external fields. The shift of the band edge is studied not only as a function of temperature but also as a function of magnetic field and orientation with respect to the magnetic field and the polarization of the incident light.

II. EXPERIMENTAL

Optical-absorption studies were performed on single crystals of HgCr_2S_4 grown by vapor transport.⁸ Plane parallel samples with their major faces oriented along (111) and (001) planes were prepared for transmission experiments by conventional grinding and polishing techniques. They had a thickness of 33 and 20 μ , respectively. These platelets (area approximately $0.5 \times 0.5 \text{ mm}^2$) were glued with GE-7031 low-temperature cement on a copper sample holder which was attached to the cold finger of a variable temperature cryostat. With this cryostat, which uses a novel technique⁹ for temperature control, the sample temperature could be continuously controlled between 3.6 and 300 K. The sample temperature could be maintained to better than $\pm 5 \text{ mK}$ below 10 K and to $\pm 20 \text{ mK}$ in the range around

¹ G. Busch, P. Junod, and P. Wachter, *Phys. Letters* **12**, 11 (1964).

² G. Busch and P. Wachter, *Physik Kondensierten Materie* **5**, 232 (1966).

³ P. Wachter, *Helv. Phys. Acta* **41**, 1249 (1968); M. J. Freiser, F. Holtzberg, S. Methfessel, G. D. Pettit, W. M. Shafer, and J. C. Suits, *ibid.* **41**, 832 (1968).

⁴ G. Harbeke and H. Pinch, *Phys. Rev. Letters* **17**, 514 (1966).

⁵ G. Busch, B. Magyar, and P. Wachter, *Phys. Letters* **23**, 438 (1966).

⁶ P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, *Phys. Rev.* **151**, 367 (1966).

⁷ J. M. Hastings and L. M. Corliss, *J. Phys. Chem. Solids* **29**, 9 (1968).

⁸ G. Harbeke, S. B. Berger, and F. P. Emmenegger, *Solid State Commun.* **6**, 553 (1968).

⁹ H. W. Lehmann and E. Meier, *J. Sci. Instr. (J. Phys. E)* (to be published).

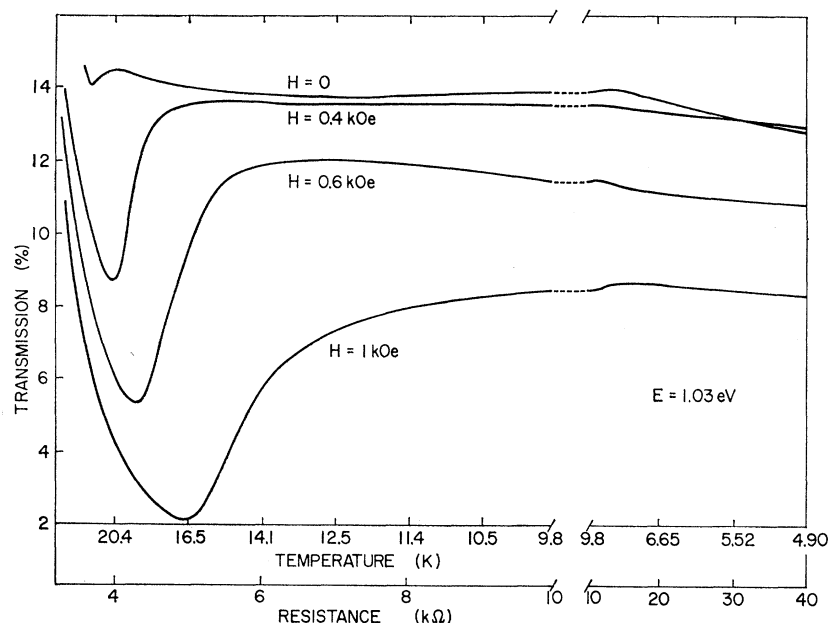


FIG. 1. X-Y recorder graph of optical transmission versus temperature at constant energy ($E=1.03$ eV) with magnetic field as a parameter. Note the two different scales on the X axis.

30 K. The temperature was interpolated between the reading of two Allen-Bradley 1-k Ω , $\frac{1}{10}$ -W carbon resistors which were attached just above and below the sample. The difference between the two readings never exceeded 0.2 K. The carbon resistors were calibrated at the temperature of boiling He and N₂, respectively. The Clement formula was used for evaluating the intermediate temperatures. The resistances were measured either with a Wheatstone bridge (constant-temperature measurements) or with a Keithley-610B electrometer (variable-temperature measurements). The measurements above room temperature were performed in a very similar manner. The crystal was again mounted on a copper block which could be heated in vacuum or inert-gas atmosphere up to 900 K. The temperature was measured with a Chromel-Alumel thermocouple.

The cryostat was mounted in a 41-mm air gap of a conventional electromagnet with which we could attain magnetic fields of up to 10 kOe. The magnetic field was measured with a Hall probe and a Bell Gaussmeter (Model-110). The magnetic field is perpendicular to the incident light and therefore parallel to the major planes of the sample. The optical absorption was measured with a Zeiss-spectrometer, PMQ II, with a glass prism double monochromator. The resolution was kept at 0.02 eV throughout all measurements. In order to get a high enough light intensity through the relatively small holes (diameter, 0.3 mm), we used a 650-W Sylvania sun gun. The exit slit of the monochromator was either focused on the sample or on the reference hole by means of a 50-mm Leica lens. This type of optical setup keeps the unwanted heating of the sample to a minimum.

The band edge was measured at different temperatures in all three different magnetic states, i.e., paramagnetic, ferromagnetic, or the state of spiral order.

It was found that it neither contains any structure nor is the shape changed between 600 and 4.2 K. Therefore we are able to arbitrarily define the absorption edge as the energy which corresponds to a value of the absorption coefficient $K=1500$ cm⁻¹.

The dependence of the band edge with respect to temperature and magnetic fields was measured in two ways: In one set of measurements, the temperature was held constant, as described above, and the optical transmission was directly plotted on an X-Y recorder as a function of magnetic field at different wavelengths. In a second set of measurements, the sample was cooled down to 4.2 K in the magnetic field in which the band edge should be determined. When the sample had reached this temperature, the cooling was turned off and the sample warmed up slowly without external heating at a rate of 5 K/min. The transmission of the sample at a certain fixed wavelength was directly recorded as a function of temperature on an X-Y recorder. When the sample had reached 25 K, the magnetic field was changed and the sample again cooled to 4.2 K. Then the measurement was repeated. An actual recorder plot of four successive runs is given in Fig. 1. The E_g (band edge)-versus-temperature and magnetic field curves were obtained as follows (the procedure for the second method is given in parenthesis). At a fixed magnetic field (fixed temperature) the energies corresponding to the optical density values which lie closest to the chosen K value of 1500 cm⁻¹ were read from the X-Y plots. The energy value corresponding to $K=1500$ cm⁻¹ was then linearly interpolated between the two values. The energy-gap values interpolated from constant temperature measurements were always within $\pm 0.2\%$ of the values interpolated from variable-temperature measurements.

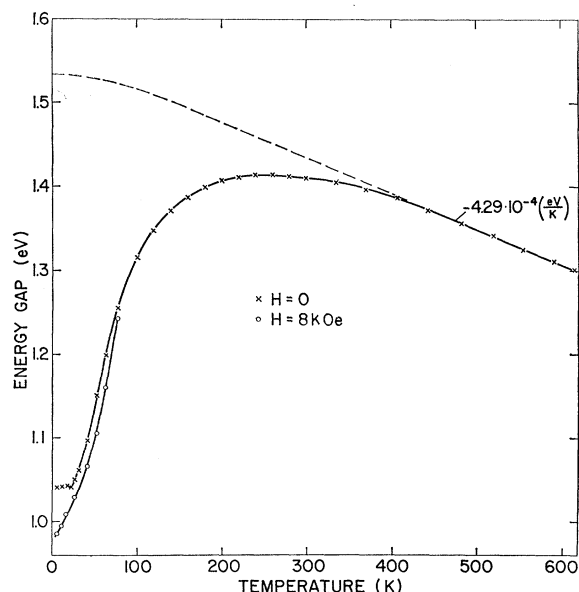


FIG. 2. Energy gap of HgCr_2S_4 as a function of temperature between 4.2 and 600 K for $H=0$ and $H=8$ kOe. Broken line is the estimated paramagnetic energy gap.

In the measurements of the orientation dependence of the optical properties, the sample had a fixed orientation with respect to the magnetic field. As will be seen later, the orientation dependence is small and, therefore, we have chosen only three different orientations with respect to magnetic field: (a) The platelet whose face is parallel to (111) was not particularly oriented; it served to give us the general features. (b) The platelet whose face is parallel to (001) was measured twice. (c) First, the $[110]$ axis was parallel to the magnetic field and, in a second set of measurements, the $[100]$ axis was parallel to H .

III. RESULTS

Figure 2 shows the temperature dependence of the absorption edge with and without magnetic field between 4.2 and 600 K. The band edge reaches a maximum at 260 K ($E_g = 1.414$ eV) and then decreases with decreasing temperature. It levels off below 22 K and is 1.040 eV at 4.2 K. At temperatures above 260 K, the E_g -versus- T curve remains nonlinear up to approximately 450 K. At even higher temperatures, the band edge decreases linearly with increasing temperature with a temperature coefficient of -4.29×10^{-4} eV/K. The general shape of the E_g -versus- T curve, at least for $T > 22$ K, is the same as found in ferromagnetic semiconductors.^{3,4} It has an inflection point at about 60 K. Up to this temperature, satellites in certain neutron diffraction lines could be observed.⁷ The inflection point in the E_g -versus- T curves of ferromagnetic semiconductors is usually found at the Curie temperature where long-range order sets in (see, e.g., Ref. 4).

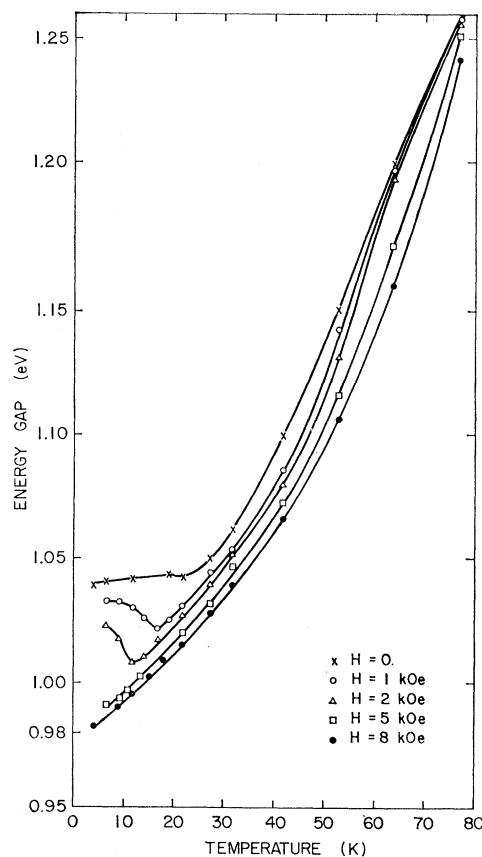


FIG. 3. Energy gap of HgCr_2S_4 as a function of temperature between 4.2 and 78 K with magnetic field as a parameter.

The application of a magnetic field shifts the band edge further toward the red as exemplified by the 8-kOe curve in Fig. 2. In fields of 10 kOe, this effect can be seen up to 150 K.

Figure 3 shows the temperature dependence of the band edge as a function of temperature with the mag-

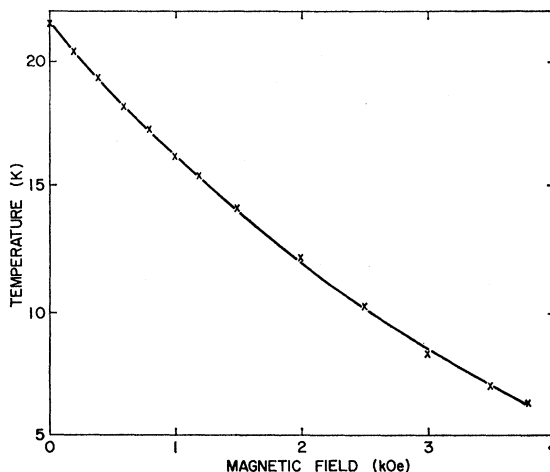


FIG. 4. Temperature of minimum in the band-edge-versus-temperature curve as a function of magnetic field.

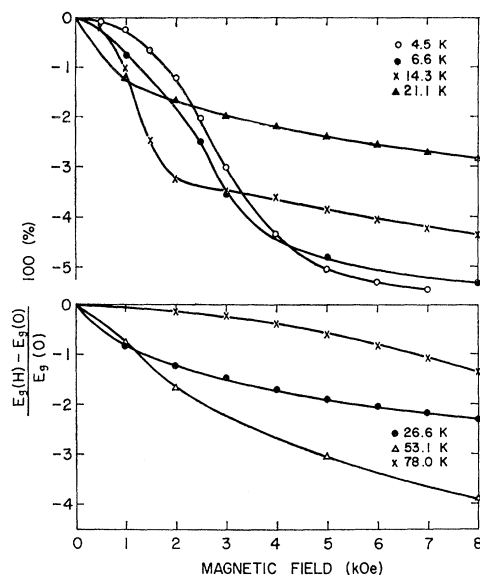


FIG. 5. Shift of energy gap as a function of applied magnetic field. Shift is given in percent of energy value in zero magnetic field.

netic field as a parameter between 4.5 and 78 K. Even in zero field, a very weak minimum can be seen at 21.5 K. For increasing fields, this minimum first gets more pronounced and shifts to lower temperatures. At larger fields, the increase of E_g on the low-temperature side of the minimum gets smaller and smaller and the minimum cannot be determined for fields greater than 4 kOe. For $H > 4$ kOe, the band edge is a monotonically increasing function of temperature. Figure 4 shows the temperatures of the minimum as a function of applied magnetic field.

Figures 5(a) and 5(b) show the magnetic field dependence of the band edge below and above 25 K, respectively. The S-shaped character of the curves is maintained up to 20 K. The inflection points of these curves move to lower fields when the temperature is raised. At temperatures above 25 K, the influence of the application of a magnetic field on the location of the band edge first decreases and then increases again (see also Fig. 8). At 78 K, the band edge varies approximately as the square of the magnetic field.

All the results reported so far have been taken in unpolarized light on the sample with the (111) faces parallel to the magnetic field. The crystal axes were not particularly oriented with respect to the magnetic field. This procedure is justified by the fact that the dependence on orientation is very small. We measured the change of the optical density as a function of the polarization angle of the incident light at 4.5 and 28 K. In one experiment the major faces of the sample were parallel to a (001) plane and its [110] direction was oriented parallel to the magnetic field. It was found that the optical density is largest when \mathbf{E} is parallel or perpendicular to [110]. It has a minimum at approximately

45° . The platelet was also turned by 45° in order to make \mathbf{H} parallel to [100]. Again, the optical density is smallest when \mathbf{E} makes an angle of 45° with \mathbf{H} . The changes of the optical density by varying the angle of polarization are never greater than 7%. This would correspond to a change of the band edge of about 0.2% equivalent to 2 meV. This effect is much smaller than all the effects which will be discussed below.

IV. DISCUSSION

The spin configuration of HgCr_2S_4 has been determined by neutron diffraction measurements.⁷ In zero field, a simple spiral was found at all temperatures up to 60 K with the propagation vector of the spiral directed along one of the cube edges within a given domain. The spins of the ions in a given (001) plane of the lattice are parallel and lie in the plane. The next (001) plane has its spins again aligned parallel in the plane but the direction of the spins is rotated with respect to the spins in the original plane by an angle φ . The wavelength of the spiral, which is inversely proportional to φ , increases from 42 Å ($\varphi = 22^\circ$) at 4.2 K to 90 Å ($\varphi = 10^\circ$) at 30 K. The projection of the spiral is schematically shown in Figs. 6(a) and 6(b). Between 30 and 60 K the wavelength of the spiral can no longer be exactly determined. Based on the appearance of satellites at some neutron diffraction lines at temperatures up to 60 K, Hastings and Corliss conclude that HgCr_2S_4 has a spiral structure over the whole range below its ordering temperature of 60 K. The situation changes drastically if external magnetic fields are applied. In low fields, the neutron diffraction intensity is very much enhanced by domain wall motion. At the same time, the flat spiral becomes a cone due to an additional spin component parallel to the magnetic field. With increasing field, the cone angle decreases and finally the spiral collapses into a ferromagnetic alignment, e.g., at 6.5 K by the application of a magnetic field of about 9 kOe. This transition is rather sharply

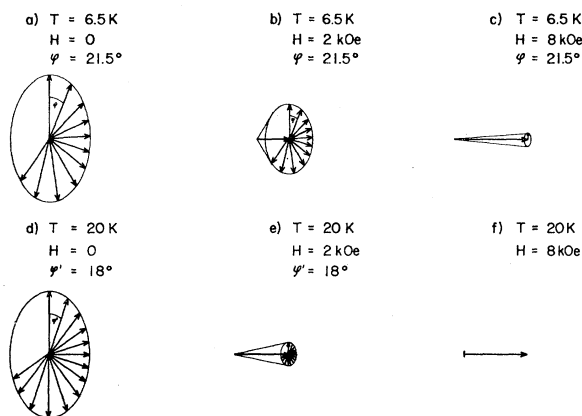


FIG. 6. Schematic spin configurations in HgCr_2S_4 at different fields and temperatures.

defined and has been observed up to temperatures of 27 K. The application of small magnetic fields at 27 K causes a rapid collapse of the cone angle, which means that the material is becoming ferromagnetic in very low fields. Measurements above 27 K have not been reported so far.

A. Ferromagnetic Case

We now turn to the discussion of our optical results in terms of the magnetic properties. The simplest case is that of the completely ferromagnetic alignment. This state is approximately represented by the curve for $H=8$ kOe in Fig. 2. The actual edge shift is obtained by subtraction of the measured curve from the extrapolated curve for a hypothetical paramagnetic state down to $T=0$. The most reasonable assumption for this curve is a linear extrapolation of the high-temperature part in combination with a quadratic dependence below the Debye temperature as it is usually found in paramagnetic semiconductors.¹⁰ This is shown as a broken line in Fig. 2, with an estimated Debye temperature of 150 K.¹¹ The extrapolation leads to a paramagnetic $E_g^{\text{para}}(T=0)$ of 1.534 eV.

In the case of ferromagnetic CdCr_2Se_4 , it has been shown by Callen¹² that the edge shift is qualitatively similar to the spin-spin correlation function $\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle / S^2$ for nn interaction with the appropriate parameters. The same correspondence has been found for EuS by Quattropani and Enz.¹³ The qualitative correspondence between the edge shift and the spin-correlation function is in agreement with both theoretical models which have been put forward to explain the anomalous band-edge variation in ferromagnetic semiconductors. Rys, Helman, and Baltensperger¹⁴ calculated the shift of the conduction band in the europium chalcogenides due to the exchange coupling to the 4f ions and obtained roughly the right numerical values based on the known intra-atomic s - f exchange coupling constant in Eu. Callen¹² considered the influence of the magneto-elastic volume strain which causes a band-edge shift via the deformation potential. Although for EuO this effect seems to contribute not more than one-tenth of the total shift observed, both contributions should be taken into account properly in each case.

One cannot expect such a good correspondence for metamagnetic HgCr_2S_4 , where a delicate balance between nn ferromagnetic and nnn antiferromagnetic exchange exists. For a detailed comparison one would also have to consider the nnn correlation function $\langle \mathbf{S}_1 \cdot \mathbf{S}_3 \rangle / S^2$ which is not known for HgCr_2S_4 . As shown in Fig. 7 the correspondence between the edge shift and

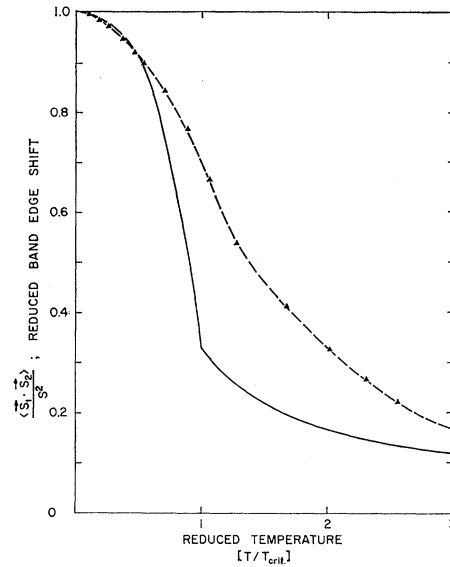


FIG. 7. Comparison of nn correlation function as calculated by Callen (Ref. 12) for CdCr_2Se_4 (solid line) and experimental band-edge shift in HgCr_2S_4 ($H=8$ kOe) (dashed line). The experimental data have been normalized to a critical temperature of 60 K and the value of the correlation function at $T=6.6$ K.

the nn correlation function for spin $S=\frac{3}{2}$ and number of nearest neighbor $Z=6$ is, in fact, not as good as for CdCr_2Se_4 , particularly for temperatures above 30 K. The agreement is, however, fairly good below 30 K. It is this temperature range below 30 K which is of greatest interest for the discussion of the results obtained in zero as well as in weak fields. The following discussion will therefore be based on the qualitative agreement between the edge shift and the nn correlation function below $T=30$ K.

The total measured edge shift of 0.43 eV between 260 and 5 K in the ferromagnetic state (8 kOe) of HgCr_2S_4 is the largest shift which has been observed so far. For a satisfactory explanation of this value as well as of its sign, a more intimate knowledge about the band structure and the different intra-atomic- and inter-atomic-exchange coupling constants would be required. Since, however, in the theories of Callen¹² as well as that of Rys *et al.*,¹⁴ the field and temperature dependence is mainly determined by the spin correlation, we note that our results obtained in the ferromagnetic state (8 kOe) are in qualitative agreement with present theoretical models. Considering the difficulties in the accurate calculation of the correlation function for such materials which cannot be treated in the framework of the molecular field theory, the measurement of the band-edge variation may be regarded as one of the best approaches to determine the spin correlation experimentally, as stated before by Quattropani and Enz.¹³

B. Field-Free Case

If we now turn to a discussion of the results of the field-free case depicted in Figs. 2 and 3, we have to take

¹⁰ See, e.g., H. Y. Fan, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1967), Vol. XXV/2a.

¹¹ E. F. Steigmeier, *Appl. Phys. Letters* **3**, 6 (1963).

¹² E. Callen, *Phys. Rev. Letters* **20**, 1045 (1968).

¹³ A. Quattropani and C. P. Enz, *Helv. Phys. Acta* **41**, 1109 (1968).

¹⁴ F. Rys, J. S. Helman, and W. Baltensperger, *Physik Kondensierten Materie* **6**, 105 (1967).

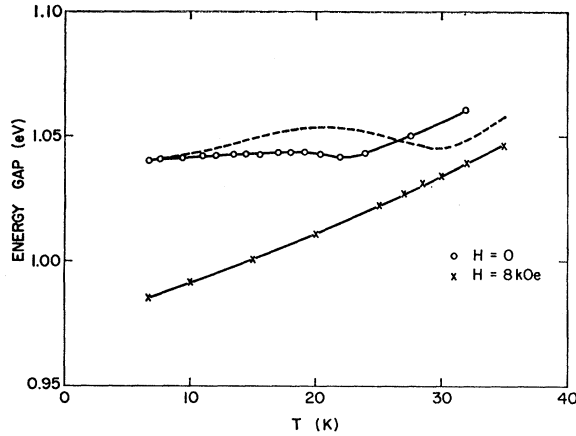


FIG. 8. Energy gap of HgCr_2S_4 . Broken line calculated for $H=0$, continuous lines measured, (O) $H=0$, (x) $H=8 \text{ kOe}$.

into account the different spin order and its T dependence. From the spiral wavelength measured by Hastings and Corliss,⁷ we can determine the T -dependent turning angle $\varphi(T)$ between two adjacent (100) planes. The φ dependence of the edge shift can be written as

$$\begin{aligned} \Delta E_{g(H=0)}^{\text{calc}}(T) &= c f(\varphi) \Delta E_{g(H=8 \text{ kOe})} \\ &= c f(\varphi) [E_g^{\text{para}} - E_{g(H=8 \text{ kOe})}], \end{aligned} \quad (1)$$

where c is a correction factor to fit the experimental curve at one point. For the function $f(\varphi)$ we have to consider that four out of the six nearest neighbors are located in adjacent planes and their contribution to the nn correlation function amounts then only to the projection $\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle \cos \varphi(T)$. Summing up over these four nearest neighbors and the two in the plane of the central ion yields $f(\varphi) = \frac{1}{3}[1 + 2 \cos \varphi(T)]$. For the energy gap, we obtain

$$\begin{aligned} E_{g(H=0)}^{\text{calc}} &= E_g^{\text{para}} - \Delta E_{g(H=0)}^{\text{calc}} \\ &= E_g^{\text{para}} - \frac{1}{3}c[1 + 2 \cos \varphi(T)] \\ &\quad \times [E_g^{\text{para}} - E_{g(H=8 \text{ kOe})}]. \end{aligned} \quad (2)$$

The broken line in Fig. 8 has been calculated from Eq. (2) based on the experimental $E_{g(H=8 \text{ kOe})}$ curve and the extrapolated paramagnetic curve, both shown in Fig. 2. From the fit to the experimental $E_{g(H=0)}$ value at the lowest temperature $T=6.5 \text{ K}$, we obtain $c=0.945$. We see that the T dependence can well be explained by the variation of the spiral wavelength. The observed minimum is somewhat less pronounced than the calculated one and occurs at a slightly lower temperature around 22 K. In our simple model, the calculated minimum occurs at the temperature of the inflection point in the spiral-wavelength variation. This feature may be changed and better agreement might be obtained if in a more detailed treatment the antiferromagnetic exchange is also considered. The main point

at present, however, is that we can explain the occurrence of a minimum by the T dependence of the spiral wavelength.

C. Intermediate Field Case

Turning to the curves for intermediate field values in Fig. 3 we note, first, that with increasing field the band-edge curve is continuously shifted towards the curve for complete ferromagnetic alignment ($H=8 \text{ kOe}$) and, second, that the minimum in the edge shift becomes more and more pronounced and shifts towards lower temperatures with increasing field until it fades out at fields of about 4 kOe (see Fig. 4). These results have to be discussed in the light of the external-field data of Hastings and Corliss, who found that, with increasing field, all spins have an increasing component parallel to the field and a perpendicular spiral component with the same spiral wavelength as for zero field, until at sufficiently high fields this conical structure collapses into a completely parallel alignment. Obviously, the ratio between the spiral and the ferromagnetic component determines the actual shape of the band-edge curve and the position of the minimum. The variation of the ratio between ferromagnetic and spiral component with temperature and field is qualitatively sketched in Fig. 6.

It is worth noting that there is an advantage in the optical technique over neutron diffraction. Probing the spin structure with our optical method, we find that the build-up of the cone structure is not partly masked by domain repopulation effects which cause the initial increase of the characteristic satellite intensity in neutron diffraction. The electromagnetic radiation probes the spin correlation independent of the domain arrangement, provided the wavelength of the light is small compared to the domain dimensions. With the optical method, we therefore are able to see the influence of the ferromagnetic component at lower fields than in neutron diffraction. At 6.5 K, for example, the cone-structure effect is masked by domain repopulation up to fields of about 4.5 kOe in the diffraction experiment, whereas the 6.6 K curve in Fig. 5 shows the steepest decrease of the band gap due to the ferromagnetic component already between 2 and 3 kOe.

The variation of the relative strength of ferromagnetic and spiral component with temperature gives the explanation for the more pronounced minima in the weak-field curves in Fig. 3. At 1 kOe, for example, the ferromagnetic component is dominating down to 18.5 K, although the full magnetic moment is not reached at this field. Towards lower temperatures it decreases, thus, the spiral component gains more relative weight and brings the curve back almost to the $H=0$ curve. The field-free case is not completely recovered since, also at 4.2 K, there is a small net magnetic moment of $0.3\mu_B/\text{molecule}$ left for $H=1 \text{ kOe}$.⁶ From the shape of the 1-kOe curve we have to conclude that the ferro-

magnetic component decreases steeply on the low-temperature side of the minimum. It should be noted that in weak fields, the location of the minimum in E_g is determined by the temperature variation of both the spiral wavelength and the ratio of ferromagnetic to spiral component. We saw in Sec. IV B that the variation of the spiral wavelength even in the absence of a ferromagnetic component produces a very shallow minimum. This weak influence is still present in intermediate fields since the function $\varphi(T)$ is not changed by external fields but already, for $H=1$ kOe, the effect of the T dependence of the ratio of ferromagnetic to spiral component is by far the strongest one. If φ were temperature-independent, there would be no minimum in the $H=0$ curve, but the location of the minimum for $H>0$ would only be slightly different from the actual position. If we disregard the weak influence of $\varphi(T)$, we can say that the minima in the E_g -versus- T curves occur at the temperature where the ferromagnetic component of the cone has its maximum. Below this temperature, the component in the direction of the external field decreases due to the increasing antiferromagnetic interactions which are responsible for the formation of the spin spiral. Above the temperature of the minimum, the ferromagnetic component decreases as in a normal ferromagnet due to thermal fluctuations.

The band-edge minima shift to lower temperatures with increasing field (see Fig. 4) since the balance between the two types of interactions in HgCr_2S_4 is such that, with decreasing temperature, the spiral structure is more and more favored and it requires higher and higher fields to increase the cone angle and to eventually enforce ferromagnetic alignment. In fields greater than 4 kOe, we do no longer observe a minimum in the E_g -versus- T curve. This indicates to us that in fields greater than 4 kOe, the ferromagnetic component has its maximum at 0 K and decreases steadily with increasing temperature.

D. Field Dependence

The field dependence of the edge shift shown in the upper half of Fig. 5 can, of course, be interpreted in an analogous way since these curves are identical to vertical sections through the set of curves in Fig. 3. The steepest decrease at low fields occurs at such temperatures where the minima in Fig. 3 are most pronounced. The field dependence at higher temperatures depicted on the lower half of Fig. 5 can be discussed solely in terms of the ferromagnetic correlation function. At 53 K the total shift for 8 kOe is much larger than at 78 or 26 K since close to the critical temperature the increase of the correlation function by an external field is larger than far from the critical temperature. The difference between the correlation functions calculated in the two-cluster theory with and without field, respectively, is actually largest at the critical temperature

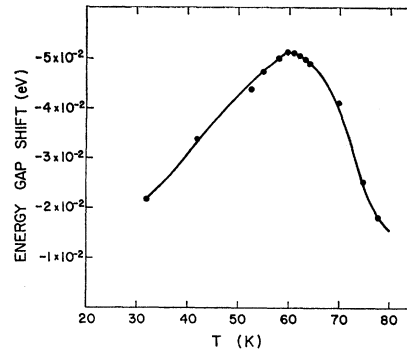


FIG. 9. Field-induced energy-gap shift versus temperature, $H=8$ kOe.

itself.¹² If one plots the measured field-induced edge shift for a field of 8 kOe in the temperature range from 30 to 80 K in Fig. 9 one finds a maximum at (60.0 ± 1) K. This constitutes a completely independent determination of the critical temperature with somewhat higher accuracy but in excellent agreement with the neutron scattering data. According to our measurements this is the only well-defined critical temperature in HgCr_2S_4 .

The physical significance of this critical temperature is still somewhat controversial. Baltzer *et al.*⁶ did not find any anomaly at this temperature. These findings were supported in a recent paper by Srivastava¹⁵ who measured the pressure dependence of the ferromagnetic transition temperature of chromium-chalcogenide spinels. He did not find any anomalies in mutual inductance measurements in small ac fields (~ 5 Oe) around 58 K. On the other hand, Hastings and Corliss⁷ define the temperature of 60 K as the Néel temperature in HgCr_2S_4 . This is the temperature below which they start to observe satellites at some of the neutron diffraction lines. Our observation of a well-pronounced maximum in the $(E_{g(H=0)} - E_{g(H=8 \text{ kOe})})$ -versus- T curve at 60 K (see Fig. 9) might at first glance be taken for evidence that this temperature constitutes a Curie temperature.¹² This is a consequence of the fact that in this region the edge shift is almost entirely determined by the *ferromagnetic* spin-correlation function. It is to be noted that even at low temperatures where the turning angle φ assumes its highest values, the effect due to the spin spiral (difference from a purely ferromagnetic alignment) amounts to only 10% of the total shift. From optical measurements in the temperature range above 30 K alone one would thus not be able to conclude whether HgCr_2S_4 has a ferromagnetic or a metamagnetic-spiral spin structure. The point is that both the neutron diffraction and the optical technique respond sensitively to the onset of long-range order at 60 K. A corresponding response at 60 K could not be found in magnetization measurements. Baltzer *et al.*⁶

¹⁵ V. C. Srivastava, J. Appl. Phys. **40**, 1017 (1969).

reported a Curie temperature of 36 K and a transition to metamagnetism at 25 K. Since our critical temperature is in excellent agreement with the Néel temperature reported by Hastings and Corliss and since the optical properties clearly reflect the spiral-spin structure, we also have to conclude that in zero field HgCr_2S_4 is antiferromagnetic at all temperatures below 60 K and that our critical temperature therefore is a Néel temperature.

It is not yet understood why this discrepancy between magnetic measurements on one side and neutron and optical measurements on the other side exists. One could imagine that the purity and the stoichiometry of the material plays a very important role in HgCr_2S_4 where such a delicate balance between nn ferromagnetic and nnn antiferromagnetic interactions exists. Magnetic measurements which have only been reported for powders are now in progress on single crystals.¹⁶

The field dependence at temperatures above T_N is quadratic (see 78 K curve in Fig. 5) since, in this range, the increase of the correlation function is proportional to the square of the magnetization.¹ Below T_N , the curve is initially linear (53.1 K) and then superlinear (50 K > T > 20 K). This indicates that practically in the entire temperature range below T_N there are already strong changes in the spin order occurring in fields below 1 kOe.

The origin of the small polarization effect is as yet not understood. It is worth noting that there is clearly no effect of the orientation of the electric light vector (or magnetic field) relative to the crystal axes. The light transmission is only sensitive to the configuration of electric vector and magnetic field. The independence on the crystallographic orientation proves again that the electromagnetic radiation probes a volume property, namely, the spin correlation, independent of internal interfaces as domain walls, although the existence of domains is known from the neutron scattering measurements. The conclusion is that the domain dimensions are large compared to the wavelength of the light. This is also confirmed by the fact that we did not observe any light scattering beyond our error limit in measuring the transmission. This is in contrast to the situation in

EuS , where the domain size has been found to be smaller than the wavelength of light in the visible.¹⁷

V. SUMMARY

It has been shown that the anomalous shift of the absorption edge in HgCr_2S_4 depends on the spin-spin correlation function, the temperature dependence of the spiral wavelength, and the magnetic field dependence of the ferromagnetic component parallel to the applied field. There exists very good agreement between the neutron diffraction study by Hastings and Corliss and our optical work. A comparison of the additional shift of the band edge in a magnetic field in HgCr_2S_4 with the results obtained on other magnetic semiconductors reveals that HgCr_2S_4 has only one critical temperature, namely, 60 K. At this temperature, it changes in zero field from a paramagnetic to an antiferromagnetic state with helical spin order. The present paper gives another example of the close relation between optical properties and the nature of the spin system (spin-spin correlation function, spiral wavelength, spin-cone structure) of magnetic semiconductors.

Note added in proof. It should be stressed that the well-pronounced maximum in the $[E_g(H=0) - E_g(H=8 \text{ kOe})]$ -versus- T curve occurs at 60 K in a field of 8 kOe. As can already be seen from Fig. 3, this maximum is at lower temperatures for smaller magnetic fields but approaches the Néel temperature $T_N=60$ K asymptotically with increasing fields. Additional measurements on a new batch of crystals have again shown how critical the dependence of the physical properties on the exact stoichiometry is. The general features are again the same, but the observed minima in the E_g -versus- T curve at various magnetic fields can shift by as much as 4 K.

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¹⁶ P. K. Baltzer (private communication).

¹⁷ F. Rys and P. Wachter, *Solid State Commun.* **6**, 805 (1968).