ferring to terminate on the grid wires rather than pass close by them. Hence, it seems that those rings which disappear from the beam are destroyed by interacting strongly with a line, and the charge given up by the ring has good probability of being trapped by the line. It is worth noting that this is the first observation of significant trapping of positive charges by quantized vortex lines, an effect predicted to occur at low temperatures by Donnelly.[2]

The results described show that vortex-ring motion in rotating He II is a fascinating phenomenon: Indeed less has been done in the corresponding classical problem.[4] Taking a semiclassical approach to the theory, one finds that a quantitative treatment of the effect of a vortex-line velocity field on the motion of a ring is difficult. Qualitatively, one can see that a counterclockwise vortex line will deflect any approaching ring to the right, the effect being greater as the ring passes closer to the line. It appears that the large well-defined deflection of the beam which has been observed represents an average over a number of small deflections as the ring traverses the vortex-line array. If a ring passes through a region where the change in fluid velocity across the

ring is on the order of the ring velocity itself, it will be violently deformed and possibly destroyed. Since the velocity field of a line is $1.58 \times 10^{-4}/r$ cm/sec and typical values of v_0 for the rings are 10-100 cm/sec, our measured effective widths for removal of the rings from the beam are eminently reasonable from this point of view. A more detailed theoretical interpretation of the experimental results is being formulated.

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[1]B. E. Springett, D. J. Tanner, and R. J. Donnelly, Phys. Rev. Letters 14, 585 (1965).

[2]R. J. Donnelly, Phys. Rev. Letters 14, 39 (1965); also R. J. Donnelly and P. H. Roberts, to be published; P. E. Parks and R. J. Donnelly, Phys. Rev. Letters 16, 45 (1966); B. E. Springett and R. J. Donnelly, ibid. 17, 364 (1966).

[3]G. W. Rayfield and F. Reif, Phys. Rev. 136, A1194 (1964).

[4]G. I. Taylor, Proc. Roy. Soc. (London) A100, 114 (1921).

MAGNETOABSORPTION IN SINGLE-CRYSTAL SEMICONDUCTING FERROMAGNETIC SPINELS

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Chalcogenide spinels of the type ACr_2X_4, where A = Cd or Hg and X = S or Se, have been found to be both electrically semiconducting and ferromagnetic.[1-3] We report herein absorption-edge measurements and optical effects associated with both the spontaneous magnetization and an externally applied magnetic field in single crystal $CdCr_2Se_4$ and $CdCr_2S_4$. Somewhat similar effects have been observed before only in diffuse reflectance spectra of powered ferro- and antiferromagnetic europium chalcogenides[4] or by transmission measurements on single-crystal EuSe.[5]

Crystals of $CdCr_2S_4$ were grown by closed-tube vapor transport[6,7] with Cl_2 as the carrier

gas. Transport occurred across a gradient of about 50°C with the cooler growth end at temperatures of about 775°C. Numerous small (0.2-0.6 mm across) well-formed octahedra and plates normal to the (111) plane were obtained after 60-80 h. $CdCr_2Se_4$ crystals were grown by slow cooling (2-5°C/h) of a solution of $CdCr_2Se_4$ in anhydrous molten $CdCl_2$. The crystals were in the shape of rounded octahedra with an average diameter of about 1 mm. Powder x-ray diffractograms of selected crushed crystals showed that the material was single-phase cubic spinel with $a = 10.244$ Å for the sulfide and $a = 10.745$ Å for the selenide.[1] By chemical analysis of some of the $CdCr_2Se_4$ crystals

it was found that the chloride content was less than 0.02 wt%. Intensity measurements of the ferromagnetic resonance line performed on spheres prepared from single crystals of both materials[8] gave the same results for the magnetization as those of polycrystalline samples reported before.[1]

Plane-parallel samples of thicknesses d ranging from 15 to 50 μ have prepared for transmission measurements by conventional grinding and polishing techniques. Figure 1 shows the optical densities of a crystal of $CdCr_2S_4$ (d = 40 μ) at a number of fixed temperatures.[9] The room-temperature absorption edge (taken arbitrarily at $\ln(I_0/I) = 3$ equivalent to an absorption coefficient K of about 1500 cm^{-1}) is at 1.57 eV. Between 300 and 150°K the edge shifts to higher energies with a linear temperature coefficient of $-(3.8 \pm 0.5) \times 10^{-4}$ eV/°C. Below 150°K there is an anomalous change of the edge shape with a plateau between 1.6 and 1.7 eV developing most strongly around the Curie tem-

perature T_C = 84.5°K.[3] The upper part of the edge is displaced at low temperatures to higher energies by 0.1 to 0.12 eV compared with the position one would expect in the absence of the optical effects associated with the spontaneous magnetization. At energies below the absorption edge there are some weaker absorption bands between 1.0 and 1.5 eV which shift very little with temperature.

The absorption edge of $CdCr_2Se_4$ (taken at $K = 1500$ cm^{-1}) is at 1.32 eV at room temperature, does not show any pronounced structure, and is less steep than in $CdCr_2S_4$. The shape of the edge is unchanged in the ferromagnetic region below T_C = 129.5°K.[3] We can illustrate the temperature behavior in Fig. 2 by showing the position of the absorption edge versus temperature. We note that in this material the edge shifts to lower energies because of the internal magnetic field as is the case for EuO[4] and EuSe.[5] The dashed curve is an extrapolation based on a quadratic temperature dependence as found in most nonmagnetic semiconductors; e.g., CdTe.[10]

Application of an external magnetic field shifts

FIG. 1. Optical density of single-crystal sample of $CdCr_2S_4$ versus photon energy. Thickness d = 40 μ.
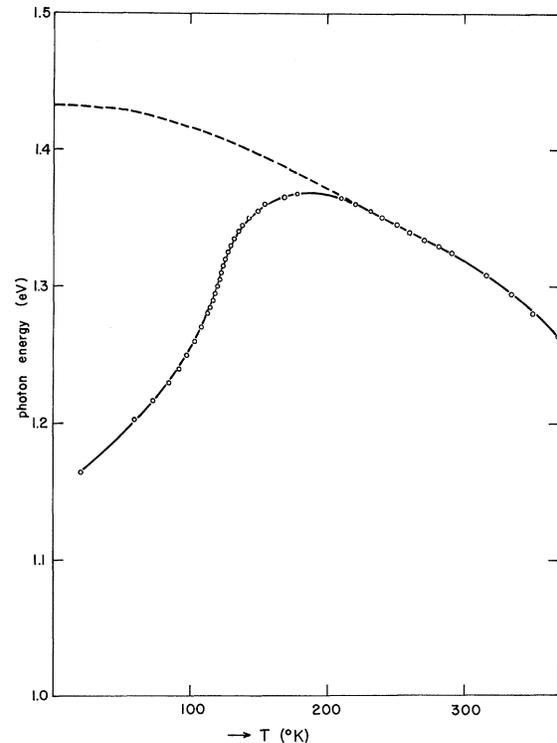
FIG. 2. Energy gap of $CdCr_2Se_4$ versus temperature. Dashed line: assumed extrapolation for paramagnetic state.

the edge further to lower energies. This shift exhibits a magnetic linear dichroism, i.e., it depends on the relative orientation of the electric light vector and the direction of the magnetic field. The field shift is strongest right at the Curie temperature with values of 0.007 eV for $E \parallel H$ and 0.004 eV for $E \perp H$ for an applied field of 8500 Oe. It is lower by a factor of 2 to 3 at temperatures 20 deg below or above T_C, respectively.

In $CdCr_2S_4$ the absorption edge is further shifted to higher energies by the application of an external magnetic field. The field shift thus goes in the same direction as the shift due to the spontaneous magnetization in both materials. Also we find a similar temperature dependence of the additional magnetic field shift in $CdCr_2S_4$ with a maximum at T_C.

It is obvious that all the observed anomalous optical properties are closely related to the magnetic ordering. The total edge shift in $CdCr_2Se_4$ in an external magnetic field shows roughly the same temperature behavior as the magnetization.[1] One could then expect that the edge shift in the absence of a magnetic field is related to the spontaneous magnetization. However, we observe edge shifts at temperatures above the Curie temperature where the spontaneous magnetization is zero. The fact that the shift is observed up to the Curie-Weiss temperature (204°K for $CdCr_2Se_4$)[3] indicates that in this region it is due to short-range magnetic order. We conclude, therefore, that the edge shift in the absence of a magnetic field is given by the total magnetic energy consisting of both long- and short-range order.

The edge shift in $CdCr_2Se_4$ is of the same size and has the same temperature and magnetic field dependence as in the europium chalcogenides. Argyle, Suits, and Freiser[5] proposed that in the Eu salts the optical transition involved is a $4f$-$5d$ charge-transfer transition and explained the edge shift in terms of an intra-atomic f-d exchange. Rys, Helman, and Baltensperger[11] invoked a model based on a ferromagnetic coupling term and the exchange interaction between localized f electrons and conduction electrons in a band of s-like symmetry. The conduction band containing the final state of the optical transition moves to lower energies because of this interaction, thus yielding a smaller energy gap. The present

results give evidence that similar effects arise from the presence of unfilled $3d$ shells and the d-s interaction.

As one notes from Fig. 1, $CdCr_2S_4$ shows a magneto-optical behavior different from $CdCr_2Se_4$ in many respects. Only the upper part of the absorption edge has an unusually strong shift to higher energies due to magnetic ordering. We believe that the lower part of the edge coincides with absorption bands due to transitions between the chromium d bands. Such transitions also have been found in this energy range in the chromium trihalides.[12] If a conduction band of, say, s character is situated slightly above an empty d band, it would be pushed to higher energies by the s-d interaction. This results in a shift to higher energies of the corresponding part of the edge, leaving behind the band due to d transitions.

[1]P. K. Baltzer, H. W. Lehmann, and M. Robbins, Phys. Rev. Letters 11, 493 (1965); N. Menyuk, K. Dwight, R. J. Arnott, and A. Wold, J. Appl. Phys. 37, 1387 (1966).

[2]H. W. Lehmann and M. Robbins, J. Appl. Phys. 37, 1389 (1966).

[3]P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, Phys. Rev. 151, 367 (1966).

[4]G. Busch, P. Junod, and P. Wachter, Phys. Letters 12, 11 (1964); G. Busch and P. Wachter, Phys. Condensed Matter 5, 232 (1966).

[5]B. E. Argyle, J. C. Suits, and M. J. Freiser, Phys. Rev. Letters 15, 882 (1965).

[6]H. Schäfer, Chemische Transportreaktionen (Verlag Chemie, Berlin, Germany, 1962).

[7]R. Nitsche, J. Phys. Chem. Solids 17, 163 (1960).

[8]We are indebted to S. B. Berger for performing these measurements.

[9]We have been informed by G. Busch, B. Magyar, and P. Wachter, Laboratorium für Festkörperphysik, Eidgenossische Technische Hochschule, Zurich, that they have performed diffuse reflectance measurements on both $CdCr_2S_4$ and $CdCr_2Se_4$.

[10]G. D. Mahan, J. Phys. Chem. Solids 25, 751 (1965).

[11]F. Rys. W. Baltensperger, and J. Helman, Helv. Phys. Acta 39, 197 (1966).

[12]J. F. Dillon, Jr., 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, 1965).