Anomalies of impurity absorption in the magnetic semiconductor $CdCr_2Se_4$

A. A. Samokhvalov, N. N. Loshkareva, Yu. P. Sukhorukov, T. I. Arbuzova, and M. I. Auslender

Institute of Metal Physics, Ural Scientific Center of the Academy of Sciences of the USSR

(Submitted 20 December 1985)
Zh. Eksp. Teor. Fiz. **91**, 621–625 (August 1986)

An absorption band at 0.41 eV was found in the absorption spectra of the magnetic semiconductor $CdCr_2Se_4$, and is ascribed to a transition from a state of the "selenium vacancy-Cr^{2+}" complex into a narrow peak of the conduction band. The temperature dependence of the absorption at the peak of this absorption band has an anomaly in the form of an increase in absorption on cooling near 230 K. The application of an external magnetic field up to 700 Oe leads to a reduction in the anomaly. Annealing of $CdCr_2Se_4$ single crystals in vacuum or in Se vapor suppresses the anomaly in ordinary light, and it is only observed in linearly polarized light. The temperature of the anomaly is close to the paramagnetic Curie temperature $\Theta = 230$ K and falls within the temperature range 195–310 K, in which a field dependence of the magnetic susceptibility is observed. The results point to a magnetic nature for the observed impurity absorption anomaly. The sharp increase in light depolarization at the ferromagnetic Curie temperature $T_C = 130$ K is ascribed to the formation of magnetic domains.

INTRODUCTION

There have been several papers devoted to studying the absorption spectra of $CdCr_2Se_4$ in the impurity absorption region. Their results are contradictory, possibly because of the high level of uncontrolled impurities in the specimens. The values of the absorption coefficient indicated in the articles amount to 13–50 cm^{-1}. We have studied $CdCr_2Se_4$ single crystals, the phonon absorption in which was at the 1–3 cm^{-1} level. The thickness of the crystals was 1.5–4.8 mm. This enabled weak absorption lines to be resolved. We interpreted the absorption bands[5] by comparing them for specimens which has been heat treated in vacuo (in evacuated sealed ampules), in Se and Cd vapors, with the addition of results on photoconductivity.[6] In the present work we discuss features of the temperature and magnetic-field dependences of one of the absorption bands, attributed to a transition from the donor level of the "selenium vacancy-chromium ion" complex (V_{Se}–Cr^{2+}) into the conduction band.

METHOD OF INVESTIGATION AND RESULTS

The spectral characteristics of $CdCr_2Se_4$ single crystals were studied with the help of a modernized IKS-21 spectrometer. The updating consisted in replacing the spectrometer amplifier by a high-sensitivity amplifier and in providing an additional thermostating system for the monochromator. The spectral width of the slit at 0.41 eV was 0.01 eV. The specimens, in the form of cylinders, were housed in a sleeve on the cryostat cold finger. Uniform cooling of the specimen was thereby achieved. Temperature measurements by paramagnetic susceptibility were carried out on a Faraday magnetic balance.

Among the observed impurity absorption bands of $CdCr_2Se_4$ single crystals,[5] only one absorption band at 0.41 eV (3.0 μm is subject to a strong influence of temperature and magnetic field. An increase in the absorption coefficient at the peak of the band on reducing the temperature to 80 K is common to unannealed $CdCr_2Se_4$ specimens and to specimens annealed in vacuo and in Se vapor (inset in Fig. 1). No appreciable shift in the position of the absorption peak with temperature is then noticed, nor a change in shape of the absorption line (for unannealed specimens).

The temperature dependence of the absorption coefficient at the peak has an anomaly; a sharp rise in absorption on cooling below 230 K (Fig. 1). The intensity of the absorption of light changes sixfold, compared with room temperature. The temperature range in which the sharp change in absorption takes place is narrow (2 K).

The anomaly was observed in all unannealed specimens and varied in magnitude on annealing (Fig. 1). The peak grows after annealing in vacuo, compared with unannealed specimens (Fig. 1, b). The peak at 0.41 eV is not observed at room temperature for specimens annealed in Se vapor (Fig 1, c), but it appears on lowering the temperature and grows monotonically. The anomaly at 230 K is only observed in polarized light for specimens annealed in vacuo and in Se vapor.

The application of an external magnetic field between 50 and 700 Oe along the propagation direction of the light, in the temperature range 230–195 K leads to a reduction in the absorption (Fig. 2). At temperatures below 195 K, a magnetic field slightly increases the absorption. A magnetic field does not produce a shift or change in shape of the absorption band. A long term relaxation (about a day) of the step at $\approx$230 K is noticed after the action of a magnetic field.

In the temperature region in which the impurity absorption anomaly is observed, a singularity is also found in the behavior of the paramagnetic susceptibility χ. At high temperatures ($T > 310$ K) the susceptibility follows the Curie-Weiss law with a paramagnetic Curie temperature $\Theta = 203$ K and an effective magnetic moment per $CdCr_2Se_4$

0038-5646/86/080366-03$04.00

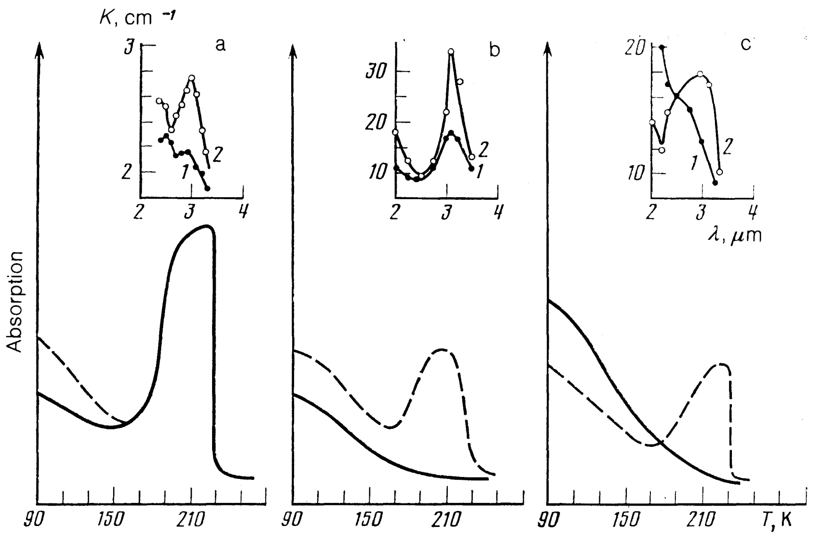

FIG. 1. The temperature dependence of the light absorption in the peak at 0.41 eV (3.0 μm) for different $CdCr_2Se_4$ single crystals. Full lines—in natural light, dashed lines—in polarized light (**E**⊥**k**): a) annealed specimen; b) after annealing in vacuum; c) after annealing in Se. The insets show the dispersion of the absorption 1) 293 K; 2) 80 K.

molecule $\mu_{\text{eff}} = 5.25\mu_B$, close to the theoretical value $\mu_{\text{eff}} = 5.48\mu_B$. A field dependence of the susceptibility is observed in the temperature range 190–310 K. An increase in the external magnetic field to $H_e = 3500$ Oe leads to a small increase in the susceptibility. A further increase in H_e has hardly any influence on the value of χ in this temperature range. The behavior of the paramagnetic susceptibility of $CdCr_2Se_4$ can be compared with the analogous $\chi^{-1}(T)$ relation for non-stoichiometric and alloyed EuO specimens. The susceptibility anomaly in $CdCr_2Se_4$ appears in smaller magnetic fields than in EuO. In addition, the susceptibility of the chalcogenated chromium spinel is independent of the external magnetic field both far from the paramagnetic region ($T > 310$ K) and in the range $T_C < T < 195$ K).

In the region of the ferromagnetic Curie temperature (130 K), no anomalies are observed in the temperature dependence of light absorption at the peak. A depolarization of the light is observed in this region for unannealed and annealed specimens, i.e., there is some light intensity transmitted through the specimen placed between crossed polarizers (see Fig. 2). On cooling the specimen, depolarization starts at 190 K and grows sharply at the Curie temperature. As distinct from the anomaly at 230 K, the depolarization does not have a selective nature, and its dispersion is similar to the dispersion of the absorption. The depolarization of a 4.8 mm long specimen of unannealed $CdCr_2Se_4$ is shown in Fig. 2. The maximum value of the depolarization is 0.75 of the light transmission of the specimen for parallel polarizers. The magnitude of the depolarization is proportional to the length of the specimen. The temperature dependence of the depolarization can be used to determine the ferromagnetic Curie temperature.

DISCUSSION OF THE RESULTS

It follows from our results that the absorption band in $CdCr_2Se_4$ has of impurity origin. It can be assumed that it is associated with a transition from deep states of the V_{Se}–Cr^{2+} defect complex into a narrow peak in the density of states in the conduction band. It is known[8] that such transitions are possible if the impurity levels are deep, while the final band states are grouped near fixed wave vectors. There is also evidence in favor of this in the existence of a photoconductivity peak at 0.38 eV,[6,9] near the absorption peak at 0.41 eV. Electrons are not induced at the donor levels by light. Measurements of the dispersion of the absorption with a Ge filter, which cuts off the wave length region below 2.0 μm, provide evidence for this: no change in the magnitude of the absorption maximum at 0.41 eV takes place. According to the band calculations of Oguchi *et al.*,[10] the empty $d\gamma$ band with an overall width of 1 eV, lies close to the bottom of the conduction band at the point Γ_1. The width of the observed band is 0.3 eV, which is less than calculated. This discrepancy can be explained in that transitions which lie below some closeness to the peak in the density of states from some broad background, due to the presence of the conduction band, in which the $d\gamma$ peak is immersed, or by insufficient accuracy in the calculations.[10] It is known that a "red shift" of the absorption edge in $CdCr_2Se_4$ starts at high temperatures.[11] The absence of a red shift in the impurity ab-

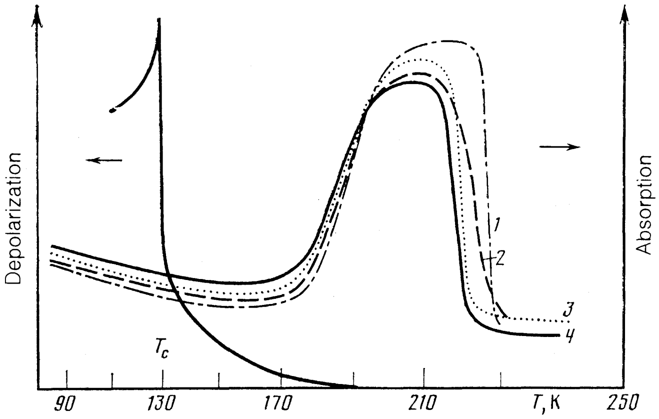

FIG. 2. The temperature dependence of the depolarization and absorption of light in the peak at 0.41 eV for a $CdCr_2Se_4$ single crystal for different magnetic fields: 1) 0; 2) 50 Oe; 3) 350 Oe; 4) 700 Oe.

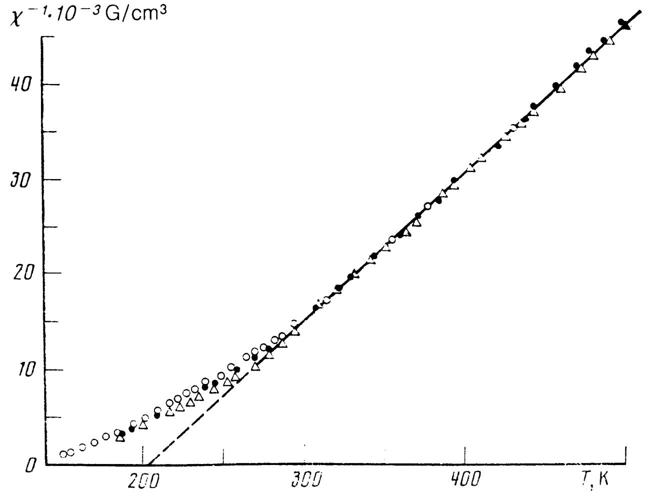

FIG. 3. The temperature dependence of the paramagnetic susceptibility of $CdCr_2Se_4$ for different magnetic fields: ○ 880 Oe, ● 2640 Oe, △ 3500 Oe.

sorption peak observed by us is evidently due either to the impurity level of the V_{Se}-Cr^{2+} complex and the narrow conduction d-band not undergoing a red shift, or to an equal red shift within the measuring accuracy, ±0.01 eV. The contraction of the absorption band and the growth in its intensity on cooling the specimen are probably associated with a reduction in the electron-phonon interaction. However, the anomalously sharp change in the absorption in the peak at 230 K does not have an analog in usual semiconductors. The influence of a magnetic field on the impurity absorption anomaly and on the magnetic susceptibility is evidence of a magnetic nature for the observed absorption peak. It is probable that states analogous to the magnetic impurity states in EuO (impurity ferrons)[12,13] are formed in the vicinity of the V_{Se}-Cr^{2+} defect complex. The binding energy at high temperatures, $T > 310$ K, is mainly produced by the interaction between an electron and the vacancy. The role of exchange interaction between an electron and the magnetic ions surrounding the vacancy is magnified on reducing the temperature, which gives an additional contribution to the paramagnetic susceptibility.

The observed temperature anomaly of the absorption peak is evidently associated with the fact that as the temperature approaches Θ the fluctuations in the local magnetic moments in the immediate neighborhood of the complex grow sharply. It is therefore advantageous, from the free energy point of view, for the impurity state to reduce its radius, to maintain the stability of the spin polarization of the immediate surroundings. As a result, the probability of a transition between the deep, narrow impurity level and the narrow d-band should increase,[8] and this leads to a sharp increase in the absorption peak at 0.41 eV. The immediate neighborhood becomes ordered below Θ (short range order is established) the radius of the impurity state increases again, and the intensity of the absorption peak decreases. The slight change in magnetic susceptibility with field (see Fig. 3) can be explained by the magnetic moment of the impurity state in $CdCr_2Se_4$ being far from saturation, unlike the case of EuO. There is as yet no explanation for the existence of an anomaly in impurity absorption at 230 K for annealed specimens only in polarized light ($\mathbf{E} \perp \mathbf{k}$).

The depolarization of light starts at $T < 190$ K. It is just at these temperatures that the field dependence of the magnetic susceptibility disappears and the character of the temperature dependence of the light absorption at the peak changes with external magnetic field (see Fig. 2). This fact indicates that at such temperatures an external magnetic field has more influence on the magnetic moment of the matrix (Cr^{3+} ions) than on the moment of the impurity state. The sharp growth in depolarization near T_C, as for EuO,[14] takes place because of Faraday rotation of the plane of polarization in domains with different directions of the spontaneous magnetization.

In the magnetic semiconductor $CdCr_2Se_4$ the temperature anomaly polarization in domains with different directions of the spontaneous magnetization.

In the magnetic semiconductor $CdCr_2Se_4$ the temperature anomaly found in the impurity absorption thus has a magnetic nature, and is probably associated with the formation of impurity states near the magnetic defects.

The authors are grateful to T. G. Aminov for providing the $CdCr_2Se_4$ single crystals and to M. I. Simonova for carrying out the anneals.

[1] P. F. Bongers and G. Zanmarchi, Solid State Commun. **6**, 291 (1968).
[2] K. Myatani, F. Okamoto, P. K. Baltzer *et al.*, Proc. 17th AIP Conf. on Magnetism and Magnetic Materials, Chicago, 1971, N.Y. (1972), part 1, p. 285.
[3] V. Prosser, P. Hlidek, P. Hischl *et al.*, Czech. J. Phys. **B24**, 1168 (1974).
[4] P. Hlidek, M. Zvara, V. Prosser, and S. Unterricker, J. Phys. (Paris) **41**, Colloq. **5**, C5-335 (1980).
[5] N. N. Loshkareva, Yu. P. Sukhorukov, B. A. Gizhevskii, M. I. Simonova, T. G. Aminov, and A. A. Samokhvalov, Fiz. Tved. Tela (Leningrad) **27**, 3462 (1985) [Sov. Phys. Solid State **27**, 2087 (1985)].
[6] L. N. Novikov, L. L. Golik, T. G. Aminov, and V. A. Zhegalina, Fiz. Tverd. Tela (Leningrad) **22**, 3032 (1980) [Sov. Phys. Solid State **22**, 1771 (1980)].
[7] A. A. Samokhvalov, T. I. Arbuzova, M. I. Simonova, and L. D. Fal'kovskaya Fiz. Tverd. Tela (Leningrad) **15**, 3690 (1973) [Sov. Phys. Solid State **15**, 2459 (1973)].
[8] F. Bassani and P. Parraviccini, Electronic States and Optical Transitions in Solids, [Russian Translation] Nauka, Moscow (1982).
[9] L. Treitlinger and H. Brendecke, Mater. Res. Bull. **12**, 1021 (1977).
[10] T. Oguchi, T. Kambara, and K. I. Gondaira, Phys. Rev. **B22**, 872 (1980).
[11] G. Harbeke and H. Pinch, Phys. Rev. Lett. **17**, 1090 (1966).
[12] T. Kasuya, Proc. 10th Int. Conf. on Semiconductors, Cambridge, Mass (S. P. Keller, J. C. Hensel, and F. Stern, eds) (1970), p. 243.
[13] E. L. Nagaev, Fizika Magnetnykh Poluprovodnikov [The Physics of Magnetic Semiconductors], Nauka, Moscow (1979).
[14] P. Wachter, Phys. Kondens. Mater. **7**, 1 (1968).

Translated by R. Berman