Surface and volume absorption of light in the magnetic semiconductor $CdCr_2Se_4$

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(Submitted 8 February 1983)
Zh. Eksp. Teor. Fiz. **85**, 967–973 (September 1983)

Absolute values of the absorption coefficient for single crystals of the magnetic semiconductor $CdCr_2Se_4$ in the energy and temperature ranges 1–1.5 eV and 77–300 K have been measured. It is found that there are two absorption mechanisms: a surface mechanism and a volume mechanism.

PACS numbers: 78.20.Dj, 78.40.Ha

1. INTRODUCTION

According to earlier studies,[1–4] the fundamental absorption edge in the magnetic semiconductor $CdCr_2Se_4$ lies at $E = 1.32$–1.34 eV at room temperature. This value is usually associated with the energy E_g of the band gap. However, most studies of the optical properties of $CdCr_2Se_4$ have been essentially qualitative, the absolute values of the absorption coefficient in the energy region 1–1.4 eV being given only in Refs. 1 and 2. This is apparently due to the fact that it is difficult to perform quantitative measurements on small (3–4 mm) single crystals, while the known methods of mechanical and chemical processing do not make it possible to produce the perfect plates necessary for quantitative absorption measurements.

Owing to the inadequacy of the experimental data on the absolute values of the absorption coefficient, the question of the nature of the optical transition responsible for the fundamental absorption edge of $CdCr_2Se_4$, which is important in connection with the physics of this material as well as for its applications, remains open. Detailed measurements of the absolute values and spectrum of the absorption coefficient of $CdCr_2Se_4$ are therefore to be desired.

2. SPECIMENS, EXPERIMENTAL TECHNIQUES, AND RESULTS

The optical measurements were made on $CdCr_2Se_4$ single crystals synthesized by spontaneous crystallization from the molten solution. Both pure crystals and crystals doped with various impurities were investigated. A detailed description of the preparation of the crystals and the experimental techniques will be found in Ref. 5.

To determine the absolute absorption coefficient α we measured transmission spectra of two specimens of different thicknesses and calculated α under conditions of low ($\lesssim 10\%$) transmissivity from the formula

$$\alpha=(d_2-d_1)^{-1}\ln(I_1/I_2), \qquad (1)$$

where I_1 and I_2 are the measured intensities of the light passing through specimens of thickness d_1 and d_2. The advantage of this method is that one can allow for the absorption in the surface layer of the specimen which, as will be shown below, distorts the absorption in the volume of the $CdCr_2Se_4$ single crystal. The thickness d_1 and d_2 of the specimens were in the range 20–30 and 90–100 μm, respectively.

Figure 1 shows the absorption spectrum (curve A) of a $CdCr_2Se_4$ specimen doped with Mg (0.5 at.%) at 77 K as calculated with Eq. (1). Similar spectra were obtained for other specimens doped with In and Cu, as well as for a pure (undoped) crystal. The difference between our spectrum A and the spectra presented in Refs. 1 and 2 is striking (the spectrum given in Ref. 2 for $T = 113$ K is shown by curve B in Fig. 1 for comparison). The authors of Refs. 1 and 2 unfortunately did not tell how they calculated the absolute values of α, but we were still able to reproduce their results (curve C in Fig. 1).

A spectrum of the form of curve C is obtained if the transmission of a single specimen is measured and α is calculated with the formula

$$\alpha=d^{-1}\ln[I_0/I(d)], \qquad (2)$$

where I_0 is the intensity of the light incident on the specimen and $I(d)$ is the intensity of the light after passing through a specimen of thickness d. This method is evidently the one chosen by the authors of Refs. 1 and 2 as the simplest and least laborious.

Thus, we must say that the absorption spectra depend strongly on the method used to normalize the initial spectra. Formula (2) is clearly less adequate for calculating α than formula (1) since it is based on the assumption that all the luminous energy is absorbed in the volume of the specimen. Moreover, formula (2) does not allow for possible reflections from the specimen nor for surface absorption.

As an additional test of the reliability of our results we successively measured the transmission $t = I(d)/I_0$ of the

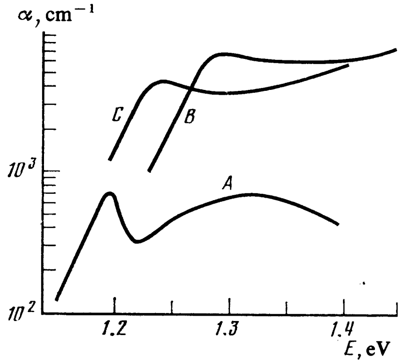

FIG. 1. Absorption spectra of pure and doped $CdCr_2Se_4$ crystals at 77 K: A—spectrum of a $CdCr_2Se_4$: Mg specimen calculated with Eq. (1), B—spectrum of an undoped $CdCr_2Se_4$ specimen according to the data of Ref. 2 (at 113 K), C—spectrum of the $CdCr_2Se_4$: Mg specimen calculated with Eq. (2).

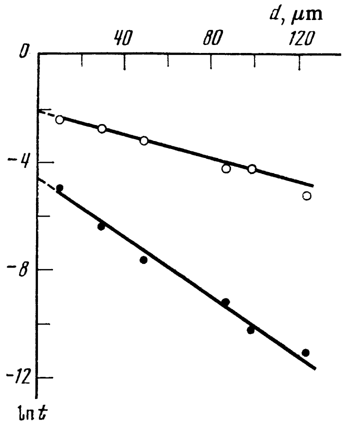

FIG. 2. Transmission vs thickness of the specimen for two photon energies: ○—$E = 1.32$ eV, ●—$E = 1.35$ eV.

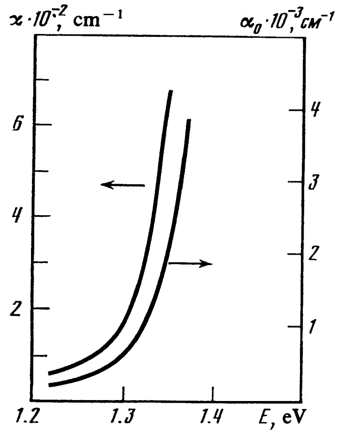

FIG. 3. Absorption spectrum of the surface layer (α_0) and of the volume (α) of the specimen at 300 K.

same specimen at room temperature, decreasing the thickness of the specimen between each measurement. Figure 2 shows plots of ln t vs d for two incident-photon energies E. As should be expected, each plot is a straight line whose slope gives the value of the corresponding volume absorption coefficient and whose (extrapolated) intercept with the ln t axis gives the fraction of the luminous power that passes through the volume of the specimen. The value of α calculated from the lower line on Fig. 2 (for $E = 1.35$ eV) is 580 cm^{-1}, which is in good agreement with the value of α at that same energy on spectrum A of Fig. 1 and is much smaller than the absorption coefficients obtained from spectra B and C on Fig. 1.

The values of α calculated with Eq. (1) characterize the uniform absorption of $CdCr_2Se_4$ single crystals that is additive with respect to the thickness of the crystal, whereas the larger absorption coefficients given in Refs. 1 and 2 were apparently obtained by neglecting the luminous energy that was not absorbed in the volume of the specimen.

Let us estimate the fraction of the incident luminous intensity that penetrates into the volume of the specimen. As Fig. 2 shows, when $E = 1.34$ eV only about 1% of the incident luminous intensity I_0 penetrates into the volume of the specimen, most of the incident luminous energy being either reflected or absorbed at the two opposite faces of the crystal. Measurements of the reflection coefficient R in the wavelength range of interest to us at an angle of incidence close to normal ($\sim 10°$) gave values in the range $R = 0.31$–0.355, in agreement with the results of Ref. 7. Such reflection could reduce the transmission by perhaps a factor of two, but not by a factor of 100.

The large difference between spectrum A and spectra B and C in Fig. 1 must therefore be attributed to the effect of surface absorption, which was not taken into account in Refs. 1 and 2. In that case the intensity of the light transmitted by a specimen of thickness d can be expressed in the form

$$I(d) = I_0(1-R)^2 e^{-2\alpha_0 d_0} e^{-\alpha d}. \quad (3)$$

Here α_0 is the absorption coefficient for a surface layer of thickness d_0 and α is the volume absorption coefficient.

Obtaining the spectrum of R by measuring α and using formula (1), and calculating the transmission $I(d)/I_0$ of a thin specimen at $T = 300$ K, we can obtain the spectrum of the intrinsic surface absorption, which is shown in Fig. 3. Figure 3 also shows the spectrum of the volume absorption α as calculated with Eq. (1). In calculating α_0, the thickness d_0 of the surface layer was assumed to be 5 μm; this value will be discussed below.

As Fig. 3 shows, the surface absorption spectrum has an edge at $E \approx 1.34$ eV. A comparison of the spectra presented in Fig. 3 with the published data[1–4,8,9] on the absorption and photoconductivity spectra provides grounds for asserting that the absorption edge obtained in those studies at $E = 1.32$–1.34 eV is actually the surface-absorption edge. The photoconductivity is also a surface phenomenon, and this must be taken into account in analyzing its spectra and kinetics.

3. DISCUSSION

Thus, on the basis of Sec. 2 we may conclude that there are two light-absorption mechanisms effective in $CdCr_2Se_4$ single crystals: a surface mechanism characterized by the absorption coefficient α_0, and a volume absorption mechanism characterized by α. Moreover, since $\alpha_0 \gg \alpha$, certain methodological difficulties are encountered in measuring the optical parameters of the single crystals in the shortwave region of the spectrum, owing to the necessity of distinguishing the weak volume absorption against the background of the strong surface absorption. We feel that the study of the spectral features of the volume adsorption is an independent problem, so here we shall consider the possible reasons for the substantial difference between the optical properties of the volume of the crystal and those of its surface.

The main difference between the surface- and volume-absorption spectra is the appearance at the surface of an optical transition which, because of its shape (an absorption edge at 1.34 eV at room temperature) and the characteristic values of the absorption coefficient ($\alpha_0 \approx 5 \times 10^3$–$10^4$ cm^{-1}) may be attributed to an interband transition. There are two possible reasons for the change in the absorption coefficient at the surface: 1) an increase in the density $N(\epsilon)$ of states taking part in the transition, and 2) the probabilities W for the optical transition at the surface and in the volume of the specimen may be different. An increase of $N(\epsilon)$ at the surface might be due to a change in the chemical composition of the surface layer of the $CdCr_2Se_4$ specimens, the possibilities ranging, for example, all the way from an increase in the number of impurity vacancies to the appearance of a new chemical compound at the surface. It is known[10] that $CdCr_2Se_4$ is a thermally unstable compound in which the number of Se vacancies increases sharply even at temperatures of 150–300 °C. According to the results of Ref. 10, a new chemical compound, $CdCr_2O_4$ may appear if the specimen is heated to 540–710 °C in air. It may therefore be supposed that the mechanical processing of the crystals may have altered the chemical composition of the surface layer.

We have investigated the chemical composition of $CdCr_2Se_4$ specimens by the methods of Auger spectroscopy (electron penetration depth, ~ 50 Å) and scanning electron microscopy (to a depth of 2–3 μm). Specimens with natural faces and with mechanically polished surfaces were analyzed. Before the measurements, the surfaces of the specimens were subjected to ionic cleaning in an Ar atmosphere for one hour. The Auger spectra of two surfaces showed that the natural face of a single crystal does not differ from the polished surface as regards the presence of chemical elements. A quantitative analysis of the same $CdCr_2Se_4$ specimens was carried through using the scanning electron microscope. Table I shows the percentages of Cd, Cr, and Se in the specimens together with their stoichiometric values; it follows from the tabulated data that, within the $\lesssim 1\%$ measurement errors, the specimens with natural and polished faces do not differ in chemical composition at a depth of 2–3 μm below the surface from the stoichiometric composition. On the basis of this analysis of the composition of the specimens we may conclude that the mechanical processing, and in particular, grinding and polishing with diamond paste, does not alter the chemical composition of the surface layer of the specimens.

The appearance of a surface absorption could evidently be due to structural changes in the surface layer of the specimens. According to the calculated[11] band structure of $CdCr_2Se_4$ shown in Fig. 4, the fundamental absorption edge corresponds to transitions from the valence band to free d_γ states of the trivalent ions. The energy of this transition decreases from 1.35 eV at room temperature to 1.1 eV at 77 K (the so-called magnetic red shift). It is this transition "with a change in the valence of the chromium ion" that is responsible for the photoferromagnetic effect in $CdCr_2Se_4$.[12] A comparison of the surface- and volume-absorption spectra (Fig. 3) shows that the absorption of light is due to the same transition in both cases, but the probability for this transition in the volume of the crystal differs substantially from its value at the surface, as is illustrated by the $W(x)$ curve on Fig. 4. This difference is essentially due to a structural (but not a chemical) change in the symmetry of the immediate surroundings of the Cr^{3+} ions at the surface. In our opinion these structural changes are not due to the manner in which the single crystals were prepared, but rather to a specific feature of the crystals. This also follows from the fact that the transmission of specimens of the same thickness depends only weakly on the manner in which the surfaces were prepared. The transmissions of specimens with natural, polished, and etched surfaces were compared.

TABLE I. Results of the chemical analysis of the surface of $CdCr_2Se_4$ specimens.

	Relative content, %		
	Cd	Cr	Se
Natural face	21.35	19.30	60.5
Polished surface	21.74	19.55	60.2
Element content, %	21.12	19.54	59.34

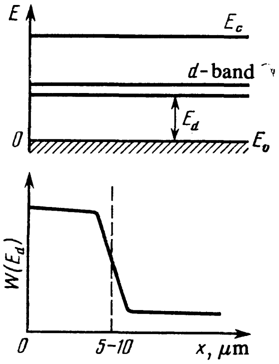

FIG. 4. Band structure and the probability W for the 1.3-eV optical transition in the volume of the specimen and at the surface.

The assumption that there are structural changes in the surface layer of the $CdCr_2Se_4$ specimens is confirmed by studies of the domain structure (DS) of the specimens used for the optical measurements. The domain structures of the $CdCr_2Se_4$ specimens were examined using the Faraday effect method[13] in the near infrared (1–1.2 μm) where the Faraday rotation amounts to 10^4 deg/cm. Domain structures of two types were found to exist simultaneously in specimens thicker than 30 μm: a band structure in the volume of the specimen and a labyrinth structure at the surface (Fig. 5).

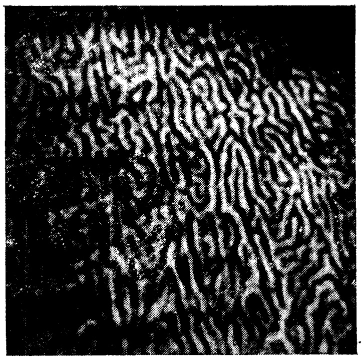

FIG. 5. Domain structure of $CdCr_2Se_4$.

The width of the internal domains was 30–100 μm, while that of the surface domains was 7–10 μm. The thickness of the surface domains could be estimated from the Faraday rotation; it amounted to 5–10 μm.

It should be noted that the band DS, unlike the labyrinth DS, is very sensitive to defects in the specimen and to the manner in which the specimen is clamped in the cryostat. The labyrinth DS, on the other hand, is found even in specimens containing many cracks and other defects. The presence of a labyrinth DS at the surface cannot be attributed to the manner in which the surface was prepared, since it is also found in $CdCr_2Se_4$ specimens with a natural face, which were grown by the gas transport method as plates $\sim 150\,\mu$m thick.

The domain structures observed in $CdCr_2Se_4$ can be explained under the assumption that there is a surface layer 5–10 μm thick with uniaxial anisotropy of the easy-axis type of magnitude $\sim 10^5$ erg/cm^3, i.e., that considerably exceeds the cubic crystallographic anisotropy. It is known[14] that the low magnetic anisotropy of the trivalent chromium ions in $CdCr_2Se_4$ is due to the fact that the orbita angular momentum is frozen in the octahedral surroundings of the Cr^{3+} ion with the average value $\langle L \rangle = 0$ in the ground state of the Cr^{3+} ion. The symmetry is broken in the surface layer, and this releases the orbital angular momentum and leads to a strong uniaxial anisotropy of the trivalent chromium ions.[15]

Thus, observations of the DS confirm the presence of structural nonuniformities in $CdCr_2Se_4$ associated with the thickness of the specimen. The presence of a labyrinth DS may also speak in favor of a disordered surface of $CdCr_2Se_4$, since such a DS is found in amorphous magnetic films.[16] However, a crystallographic study of the surface structure will be required to clarify this point.

4. CONCLUSIONS

The results of our experiments show that the energy $E = 1.32$–1.34 eV corresponds to the long-wave edge of the strong surface absorption of $CdCr_2Se_4$ crystals at 300 K, but not to the volume-absorption edge.

Analysis of the actual surfaces of the investigated specimens show that there are no substantial changes in the chemical composition of the surfaces due to the mechanical treatment.

Study of the DS of the specimens indicates that there are macroscopic (5–10 μm) changes in the anisotropy of the magnetic ions and that these changes are not due to the mechanical treatment of the surfaces.

The experimental data can be explained under the assumption that there is a strong change in the crystallographic symmetry of the immediate surroundings of the ions at the surface of the single crystals.

In conclusion the authors thank V. I. Tarasov for assistance with the measurements, I. M. Yurin for processing the data on the computer, A. V. Shirkov for making it possible to use the Auger spectrometer, T. Yu. Kuleshova for making the Auger measurements, and V. A. Myzina for the scanning electron microscope studies.

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Translated by E. Brunner