Cathode-absorption spectroscopy: application to $CdCr_2Se_4$

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The cathode-absorption technique, which has uncovered new opportunities in the spectroscopy of solids, is considered. The effect of pulsed electron excitation on the optical transmission of single crystals of the magnetic semiconductor $CdCr_2Se_4$, $\sim 30\,\mu$m thick, is investigated experimentally. The cathode-absorption spectra and relaxation curves are obtained in the spectral range 0.7–1.3 eV at temperatures between 80 and 300 K, using $100\,\mu$sec exciting pulses and 60 keV electrons. A "magnetic red shift" of cathode absorption is observed.

1. INTRODUCTION

Investigation of absorption spectra is the most direct method of studying the energy structure of electronic states in semiconductors. Various already developed optical-absorption modulation-spectroscopy methods are used at present to single out different features of the spectra.[1] Foremost among these methods are piezoabsorption,[2,3] electroabsorption,[4,5] and thermoabsorption.[6]

The most general expression for the absorption coefficient of photons of energy $\hbar\omega = \varepsilon' - \varepsilon$ is

$$\alpha = W(\varepsilon, \varepsilon')f(\varepsilon)(1-f(\varepsilon')), \qquad (1)$$

where $W(\varepsilon,\varepsilon')$ is the total probability of a transition from states with energy ε', and f is the Fermi probability of occupying the states.

The foregoing modulation methods are based on the action of external modulating factors (deformations of the crystal-lattice, electric field, temperature) on the function $W(\varepsilon,\varepsilon')$ without significant change of the equilibrium carrier thermal distribution function f. This makes possible measurements of the parameters of optical transitions between states whose occupation is determined by the equilibrium distribution function.

The method considered by us is based on modulation of the carrier distribution function by excitation of nonequilibrium carriers with the aid of a beam of accelerated electrons. The main advantage of this method is the possibility of studying the parameters (spectra and relaxation) of transitions between excited states, something impossible at equilibrium because there are no carriers.

2. PROCEDURE

A block diagram of the experimental apparatus is shown in Fig. 1. The apparatus consists of a controllable source of accelerated electrons (electron microscope), an electron-beam modulator, an optical channel, a cryogenic attachment, and an electronic signal recording system.

The sample, a $\sim 1 \times 1$ mm plate $\sim 30\,\mu$m thick, is placed inside the microscope column on the cryostat cold finger. The electron beam is focused on the sample with the electron-optics system of the microscope. Pulsed modulation at an excitation-pulse duration $\sim 10^{-4}$ sec and an off-duty cycle $\gtrsim 10$ prevents stationary heating of the sample at a current density $\sim 1\,\mu$A/cm^2 and a beam energy up to 60 keV. Incandescent-lamp stationary radiation, made monochro-

matic with a DMR-4 monochromator, is focused on the sample, and the light that has passed through the sample goes through a diaphragm and is focused by lenses on the photoreceiver. The photoreceiver is a dc-reverse-biased photodiode operating in the photocurrent-measuring mode. This ensures a constant rate of conversion of the changes of the light intensity at different levels of stationary illumination.

The pulsed electron beam modulates the optic transmission of the sample, whose amplitude is recorded by a stroboscopic system. To obtain the spectral dependence of the effect, the data are converted into a digital code with an F-30 voltmeter, and an "Elektronika-60" minicomputer is used to record the data and to control the monochromator.

The ~ 60 keV electrons incident on the sample excite secondary carriers. This avalanche process leads to formation of an excited state of a sample surface layer whose thickness depends on the atomic weight of the crystal elements.[8] Our estimates of this thickness for the $CdCr_2Se_4$ crystal, by the procedure indicated in Ref. 8, yield a value $d \sim 10\,\mu$m. Since the electrons are almost tangentially incident on the sample surface (see Fig. 1), the effective thickness of the excited layer may turn out to be somewhat smaller.

The presence of an excited surface layer can change the optical density of the sample and lead thereby to cathode-absorption signals. A similar situation occurred in fact in experiments[9] on optical clearing of Te samples. The essential distinguishing feature of cathode absorption is the wide excitation-energy band, which is difficult to obtain by optical pumping.
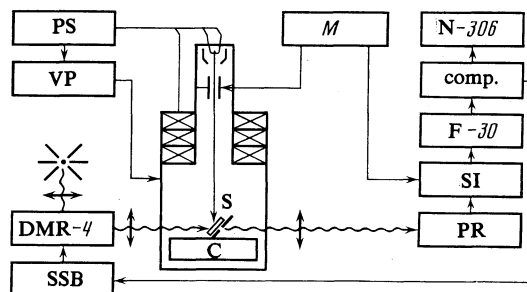

FIG. 1. Block diagram of setup: *PS*—power supply, *M*—modulator, *SI*—strobing integrator, *PR*—photoreceiver, *S*—sample, *C*—cryostat, *SSB*—step-scanning block, *VP*—vacuum post, N-306—automatic plotter, DMR-4—monochromator.

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3. MAIN FEATURES OF CATHODE ABSORPTION

We consider several mechanisms that can be responsible for the cathode-absorption signals.

1) The Burstein-Moss shift[10] of the intrinsic absorption edge, due to filling of the bands with injected carriers.

2) The appearance of new absorption bands, connected with transitions from states that are empty at equilibrium but become filled with carriers upon injection.

3) Modulation of the surface-barrier field by the injected carriers and the ensuing change of the optical density (the Keldysh-Franz effect).

Any of the foregoing mechanisms can predominate, depending on the properties of the investigated crystal and on the spectral range investigated. In the simplest uniform-excitation approximation, the relative change of the optical transmission T can be expressed in terms of the optical-transmission change $\Delta \alpha = \alpha^* - \alpha$ (α^* and α are the absorption coefficients with and without excitation)

$$\Delta T/T \approx -\Delta \alpha d, \qquad (2)$$

where the condition $\Delta \alpha d \ll 1$ is taken into account.

With allowance for (1) and under the assumption [verified by consideration of the mechanisms 1) and 2)] that the transition probability is constant, the relation (2) takes the form

$$\Delta T/T = -W(\varepsilon, \varepsilon') [\Delta f(\varepsilon) (1-f(\varepsilon')) - \Delta f(\varepsilon') f^*(\varepsilon)], \qquad (3)$$

where $\Delta f = f^* - f$.

Let us consider the consequences of relation (3) for mechanisms 1) and 2). In the case of mechanism 1), assuming $\varepsilon = \varepsilon_v$, $\varepsilon' = \varepsilon_c$ respectively to be the ceiling and bottom of the valence band and of the conduction band, we obtain $\Delta f(\varepsilon) < 0, \Delta f(\varepsilon') > 0$. Then, according to (3), the cathode absorption is positive, i.e., excitation decreases the optical density of the sample in the region of the intrinsic-absorption edge. In the case of mechanism 2) the initial and final states ε and ε' can be simultaneously either above for below the equilibrium Fermi-energy level ε_F:

a) $\varepsilon, \varepsilon' > \varepsilon_F$; $f(\varepsilon), f(\varepsilon') \ll 1$; $\Delta \alpha \sim \Delta f(\varepsilon)(1 - \Delta f(\varepsilon'))$,

b) $\varepsilon, \varepsilon' < \varepsilon_F$; $f(\varepsilon), f(\varepsilon') \sim 1$; $\Delta \alpha \sim -\Delta f(\varepsilon') f^*(\varepsilon)$.

The sign of the effect is determined either by $\Delta f(\varepsilon) > 0$ at $\varepsilon > \varepsilon_F$ or by $(-\Delta f(\varepsilon')) > 0$ at $\varepsilon' < \varepsilon_F$, i.e., an increase of the sample optical density is observed.

The two cathode absorption mechanisms considered above are the simplest ones. If the excitation leads to a substantial change of the function $W(\varepsilon, \varepsilon')$ [e.g., mechanism 3)], the analysis becomes more complicated. In fact, in the case of mechanism 3) the cathode-absorption signal is due to screening of the surface-barrier field by the injected carriers. By the same token, the absorption coefficient becomes strongly dependent on the electric field. Explanation of this dependence calls for additional information on the concrete features of the electron spectrum of the investigated crystal.

4. INVESTIGATION OF THE CdCr₂Se₄ CRYSTAL

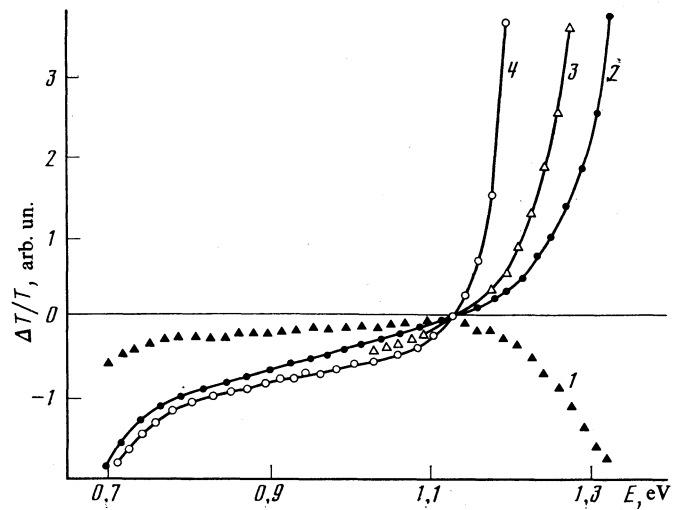Some capabilities of the cathode-absorption method are illustrated by the data obtained by us for single crystals of

FIG. 2. Cathode absorption spectra at various temperatures: $1 - T = 300$ K, $2 - T = 244$ K. $3 - T = 133$ K, $4 - T = 97$ K.

the magnetic semiconductor $CdCr_2Se_4$. This semiconductor becomes ferromagnetic at temperatures below $T_c = 130$ K and reveals a strong dependence of the energy spectrum on the degree of the magnetic order (see, e.g., Ref. 11). In addition, the defects in $CdCr_2Se_4$, which are due to inevitable deviation of the composition from stoichiometry, lead to the presence, in the forbidden band, of various electronic states that take part in the light absorption.[12] The details of the band structure of this semiconductor remain unclear to this day.

Figure 2 shows the $CdCr_2Se_4$ cathode-absorption spectra corresponding to different sample temperatures. It can be seen that in the energy band 0.7–1.1 eV the samples show an absorption increase due to electron excitation in the entire working temperature interval. At energies above 1.1 eV optical clearing is observed, except at near-room temperature (curve 1). At $E > 1.1$ eV the cathode-absorption spectra (curves 2–4) correspond apparently to interband transitions. It can be seen from the figure that the cathode-absorption edge undergoes a "red shift" with decreasing temperature, in agreement with the data on absorption in $CdCr_2Se_4$ (Ref. 11).

The long-wave wing of the cathode-absorption spectrum can be connected with intraband transitions, or with transitions in which impurity states take part. Attention is called to the great difference between the spectra at $T = 300$ K and $T = 244$ K (curves 1 and 2). This seems to correlate somehow with the fact that this is precisely the temperature region where the "magnetic red shift" of $CdCr_2Se_4$ sets in.

Further evidence of the difference between the types of transitions at $E > 1.1$ eV and $E < 1.1$ eV is provided by the cathode-absorption relaxation curves plotted at different spectral points (Fig. 3). The time is reckoned from the instant when the electronic excitation ceases. It follows from Fig. 3 that the relaxation of the cathode absorption near the absorption edge differs substantially from the relaxation in the long-wave region of the spectrum. Curve 2 shows clearly the reversal of the sign at ~ 200 μsec after the end of the excitation.

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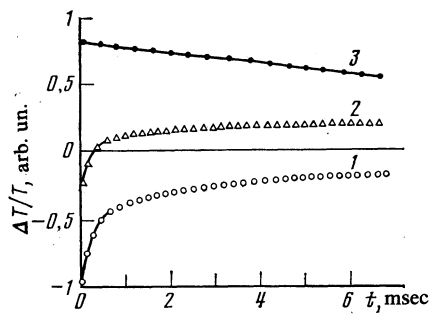
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FIG. 3. Relaxation of cathode absorption, $T = 133$ K: $1 - E = 0.8$ eV, $2 - E = 1.1$ eV, $3 - E = 1.2$ eV.

5. CONCLUSION

Summarizing, we can state that the cathode-absorption method uncovers new possibilities in spectroscopy of solids. These capabilities include primarily the study of the characteristics of optical transitions in systems that are not in equilibrium. The main advantage of the method is the wide excitation-energy band, which is difficult to realize by optical-pumping methods. Another advantage over the known cathode-reflection method[13] is the possibility of investigating impurity transitions in semiconductors and dielectrics, transitions usually occurring in the crystal transparency region.

The fact that no contacts need be attached to the sample and the insensitivity of the photoreceiver to the electronic pump pulses compensate for some complications, caused by the use of an electron microscope, in the realization of the method.

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