THE INFLUENCE OF REDSHIFT OF THE OPTICAL ABSORPTION EDGE ON PHOTOELECTRIC EFFECTS IN FERROMAGNETIC HgCr₂Se₄ SEMICONDUCTOR

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In the ferromagnetic HgCr₂Se₄ semiconductor ($T_c \approx 108$ K), apart from the characteristic redshift of the edge of optical absorption, a redshift of photoconductivity and photo-emf spectra was also observed with decreasing temperature. The influence of magnetic ordering on the band structure also showed itself in the temperature and magnetic field dependences of these effects. Besides the peak near T_c , the dependences of the relative variation of photoelectric effects in the magnetic field on temperature exhibited an additional peak at $T > T_c$ for the light with an energy $h\nu$, which is close to the forbidden band width. This peak may be expected to appear in the paramagnetic region for other magnetic semiconductors, too.

The effect of the magnetic ordering on the optical and electrical properties of ferromagnetic semiconductors [1, 2] shows up most vividly in mercury chalcogenide spinel. This compound is characterized by a huge redshift of the edge of optical absorption which amounts to ~ 0.52 eV for the region from 300 to 4 K [3, 4]. The forbidden band width E_g is about 0.82 eV at room temperature. In an external magnetic field the absorption edge also shows a great redshift. Thus, according to [4], it attains ~ 0.04 eV in the field H = 4 kOe and T = 115 K. The anomalies in the optical and electrical properties of magnetic semiconductors are most appreciable in the region of the Curie temperature T_c (for HgCr₂Se₄, $T_c \approx 106$ -110 K).

The paper analyzed the influence of the redshift of the optical absorption edge on photoconductivity and photo-emf in high-resistance HgCr₂Se₄ single crystals ($\rho \approx 10^7$ ohm cm in the vicinity of T_c). The specimens were produced by the technique of gas-transport reactions and annealed in HgSe vapors to diminish the density of defects [5]. A modulated illumination (with a frequency of 80 Hz) of specimens with monochromatic light was employed to study the photoelectric effects. Use was made of a 500 W incandescent lamp, a DMR-4 double monochromator with an attachment for an automatic rotation of the prisms, a thermocell to control the light intensity, a selective V6-2 amplifier, and an EPP-09 automatic recorder of spectra. Photoconductivity was measured in the constant field regime that ensured the proportionality of the photoconductivity signal measured. The signal, which was proportional to the current dependent on the presence of photo-emf in the specimen, was measured from the load having a resistance R_H ($R_H \ll R_0$, where R_0 is the resistance of the specimen) in the absence of the electric field. The influence of the redshift of the absorption edge revealed itself in the spectral, temperature, and magnetic field dependences of photoconductivity and photo-emf.

The long-wave boundaries of photoconductivity and photo-emf spectra as well as the edge of absorption [3, 4] undergo a marked redshift as the temperature lowers. The position of the edge of absorption estimated from measurements of the spectral dependences of photoconductivity (from the energy for which the photoconductivity is half as little in relation to the maximum value) is consistent with the optical data, and this indicates that the carriers have been excited to the conduction band by the light with an energy corresponding to the absorption edge. The photo-emf spectra are shifted relative to the photoconductivity spectra toward the shorter-wave region, which can be regarded as evidence in favor of a diffusion nature of the effect. The results of the study of spectral dependences of photoconductivity in $HgCr_2Se_4$ agree with the data of [6, 7]. As far as we know, the photo-emf in this compound has not been investigated.

Temperature dependences of photoconductivity, $\Delta G(T)$, were measured at different values of the excitation energy $h\nu$ (from 1.6 eV to 0.6 eV), both considerably exceeding and close to the forbidden band

Moscow University Physics Bulletin

width. Figure 1 a shows the results for three $h\nu$ values. The photoconductivity data obtained for different $h\nu$ and light intensities are normalized to the photoconductivity value at T = 92 K. As is seen from the figure, the shape of the curves in the region of ferromagnetic ordering is independent of $h\nu$. In the paramagnetic region, however, the value and position of the peak on the curves depend on $h\nu$. The lower the value of the excitation energy, the lower the temperature at which the photoconductivity disappears.



Fig. 1

Temperature dependences of the photoconductivity ΔG (a) and the photomagnetic conductivity (b) in a high-resistance HgCr₂Se₄ single crystal for $h\nu = 1.18$ eV (1), 0.72 eV (2), and 0.60 eV (3).

As to the photo-emf, its temperature dependence in the high-resistivity specimens under consideration is similar to that of the photoconductivity. Thus, a minimum of photo-emf is observed in the vicinity of T_c and a maximum in the paramagnetic region. The position and value of this maximum depend on $h\nu$ as in the case of photoconductivity. It is reasonable to relate the influence of the excitation energy on temperature dependences of the photoconductivity and photo-emf to the redshift of the optical absorption edge. Comparison of the results of the spectral and temperature studies with the literature data on the absorption coefficient supports this interpretation.

Earlier we have revealed a powerful influence of an external magnetic field on the photoelectric effects in HgCr₂Se₄ [8, 9]. Thus, around T_c the relative change of the photoconductivity in the field H = 6 kOe was about 600% and that of the photo-emf-dependent current reached about 1600%. (The values of $(J_H - J_0)/J_0$ were calculated, where J_H and J_0 are the photoconductivity or photo-emf in the field and in the absence of the field, respectively.) In the vicinity of T_e the influence of the field was also observed in the ferromagnetic region. We considered the anomalous photoelectric effects to be due to the interaction of charge carriers with magnetization fluctuations and defects. The radiation with an energy $h\nu > E_{\sigma}$ was used in those experiments. In the present study, the temperature dependences of the relative change of photoconductivity and photo-emf in the magnetic field exhibited additional peaks at $T > T_c$ as a result of using the light with an energy close to $E_g(T)$. Figure 1 b illustrates the dependences of the photomagnetic conductivity $(\Delta G_H - \Delta G_0)/\Delta G_H$ on T for three values of the excitation energy $h\nu$ (ΔG_H and ΔG_0 are, respectively, the photoconductivity in the field and in the absence of the field). For $h\nu = 1.18$ eV a single maximum is observed at a temperature close to T_c , while for the other two values of $h\nu$, there are two maxima: near T_c and at $T > T_c$. The magnitude of the additional maximum at $T > T_c$ and its position on the temperature scale depend on the excitation energy and the field H. When one chooses an energy $h\nu$ close to $E_g(T)$ in the vicinity of T_c , the photomagnetic conductivity increases at $T > T_c$. It also grows with increasing strength of the field H, and the peak of the effect shifts toward higher temperatures.

The magnetic field also affects the photo-emf in the paramagnetic region when an appropriate radiation energy is used. For instance, the temperature dependence of $(J_H^{\rm ph} - J_0^{\rm ph})/J_H^{\rm ph}$, where $J_H^{\rm ph}$ and $J_0^{\rm ph}$ are respectively the photo-emf current in the field and in the absence of the field, showed an additional peak

Moscow University Physics Bulletin

for $h\nu = 0.6$ eV at $T \approx 137$ K whose magnitude reached about 50% in the 6 kOe field. The changes of the photoelectric effects observed in the magnetic field can be explained by a direct influence of the field on the optical absorption edge. According to [4], the forbidden band width E_g in HgCr₂Se₄ substantially depends on the field H in the paramagnetic region. However, the principal maximum close to T_c may, apparently, be due to the effect of the magnetic field H first and foremost on the current carrier parameters determining the magnitude of photoconductivity and of photo-emf. The fact that measurements of the variation of dark conduction in the magnetic field revealed a single peak in the vicinity of T_c also supports the above interpretation.

The appearance of an additional maximum on the curves of the relative change of the photoelectric effects in the field can also be expected for other magnetic semiconductors in which the field strongly affects the edge of absorption.

Thus, it has been established that photoelectric effects in $HgCr_2Se_4$ are remarkably sensitive to the influence the magnetic ordering exerts on the kinetic properties of current carriers and on their energy spectrum, and this shows itself in spectral, temperature, and magnetic field dependences of the photoconductivity and photo-emf. Hence, the photoelectric effects, as well as optical measurements, can be used to study the influence of the magnetic ordering on the band structure. Owing to the extremely strong dependence of the photoelectric effects in $HgCr_2Se_4$ on H, it is possible to design $HgCr_2Se_4$ -based photoelectric devices, which can be controlled by means of an external magnetic field.

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