

Energy spectrum and transport properties of HgCr_2Se_4 single crystals

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Measurements of the thermoelectric coefficient and electrical conductivity are reported for the nondegenerate p -type magnetic semiconductor HgCr_2Se_4 in the temperature range 4.2–300 K. It is shown that at low temperatures the conductivity changes from p -type to n -type and becomes metallic. The band structure and its changes upon ferromagnetic ordering are discussed.

1. INTRODUCTION

Degenerate n -type single crystals of mercury selenium chromite exhibit¹ a strong increase in the electrical conductivity and electron Hall mobility upon cooling of the samples below the Curie point $T_c = 106$ K. The value of the mobility ($\sim 10^3$ $\text{cm}^2/\text{V}\cdot\text{sec}$) at $T = 4.2$ K is two orders of magnitude greater than the maximum electron mobility in the paramagnetic phase. Meanwhile, the electron density remains practically constant over the temperature range 4.2–300 K, amounting to 10^{17} – 10^{19} cm^{-3} for the samples studied in Ref. 1.

The strong effect of the magnetic ordering on the electronic properties of n - HgCr_2Se_4 is confirmed by optical measurements. In particular, plasmon-reflectivity studies² indicate that the electronic excitation spectrum changes at the transition to the ferromagnetic phase.

The transport properties of p -type HgCr_2Se_4 crystals have been studied less thoroughly, but the available experimental data point to the necessity of considering the role of magnetic ordering in hole conductivity processes in this magnetic semiconductor. In particular, a possible explanation for the change in sign of the normal Hall coefficient (from p -type to n -type) upon the magnetic ordering was discussed in Ref. 3.

As we know, the basic transport characteristics of undoped HgCr_2Se_4 single crystals are due more to the nonstoichiometry of the Hg and Se composition than to the presence of uncontrolled impurities.⁴ Thus, on the one hand, it is possible to vary the parameters of the crystals by means of judicious changes of the nonstoichiometry (this was the technique used in Ref. 1 to obtain n - HgCr_2Se_4 crystals with record high electron mobilities for magnetic semiconductors) and, on the other hand, it becomes problematical to compare the experimental data obtained on samples synthesized under different conditions. The latter circumstance is particularly important in the case of nondegenerate semiconductors with rather small deviations from stoichiometry, since chemical methods of composition analysis are too crude for quantitative comparison of the vacancy concentrations in different single crystals.

2. EXPERIMENTAL TECHNIQUES AND RESULTS

From the above considerations it is clear that in order to obtain useful data on transport phenomena in crystals of this class it is desirable to perform the various experimental procedures on the same samples. To this end we have measured

the resistivity ρ and the thermoelectric coefficient α as functions of temperature on the same HgCr_2Se_4 single crystal. A series of samples was prepared at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR. The samples were synthesized by the gas-transport method and were not given any special heat treatment. The changes in the Hall effect at the transition to the ferromagnetic phase displayed the same regularities as in Ref. 3. All the samples exhibited p -type conductivity at room temperature and n -type conductivity at liquid-helium temperature. The Hall density of holes at $T = 300$ K and of electrons at $T = 4.2$ K were $p \approx 4 \cdot 10^{17}$ cm^{-3} and $n \sim 8 \cdot 10^{14}$ cm^{-3} , respectively.

The resistivity ρ was measured in a direct current by the four-probe methods on samples in the shape of thin rectangular parallelepipeds with dimensions of $0.2 \times 0.5 \times 2$ mm. The current and potential contacts were fabricated by the technique described in Ref. 5. For the measurements of α we used samples and apparatus analogous to those described in Ref. 6. The only difference was that the temperature gradient was not stabilized automatically, as provided for in Ref. 6, but was measured continuously together with the thermoelectromotive force of the sample. For this purpose the output of a Cu–Cu:Fe differential thermocouple was connected to an F-30 digital voltmeter, and a computational complex based on an Elektronika-60 minicomputer⁷ provided synchronous recording of the data and automatic calculation of the value of α .

Figure 1 shows the temperature dependence of ρ . As can be seen from Fig. 1a, the conductivity above T_c is activation in character. At $T \lesssim T_c$ the dependence begins to deviate from the activation type; the resistivity reaches a

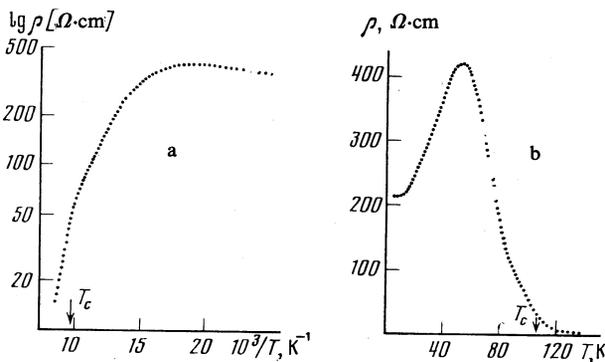


FIG. 1. Temperature dependence of the resistivity.

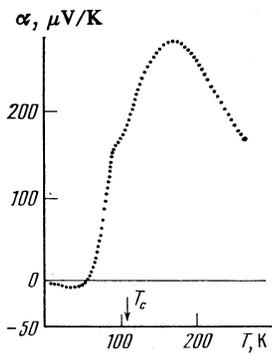


FIG. 2. Temperature dependence of the thermoelectric coefficient α .

maximum at $T \sim 50$ K, and at lower temperatures $\rho(T)$ becomes metallic in character (Fig. 1b).

Figure 2 shows $\alpha(T)$ for the same sample. It is seen that the temperature region 110–50 K corresponds to a sharp decrease in α , and at $T \sim 50$ K there is a change in the sign of α , corresponding to a transition to n -type conductivity. Thus the data on the thermoelectromotive force correlate with the Hall data, and, consequently, the change in sign of the Hall coefficient corresponds to a change in the type of conductivity and is not due to ferromagnetic anomalies in the Hall effect, as was assumed in Ref. 8.

3. THE BAND STRUCTURE PROBLEM

In order to interpret our data we must construct a model of the band structure of the magnetic semiconductor HgCr_2Se_4 . In the absence of a rigorous quantitative calculation, in constructing the model we shall be led by the most general considerations while striving to avoid contradiction with the known experimental results.

Figure 3 shows the proposed band diagram of HgCr_2Se_4 . A necessary feature of interpreting the experimental data is the presence of three bands of allowed states, denoted in Fig. 3 by the letter C (conduction), R (random), and V (valence). Bands C and V are the usual bands of Bloch states, while band R has a number of peculiar features. The states in band R are formed predominantly from the d_γ levels of the Cr^{3+} sublattice. These states are the most sensitive to lattice defects of the vacancy type. Evidence of this comes from the ferromagnetic-resonance data of Ref. 9, which implies that the anisotropy of HgCr_2Se_4 crystals is due to the presence of magnetic centers with “thawed out” orbital moments in the chromium sublattice. Moreover, it was shown

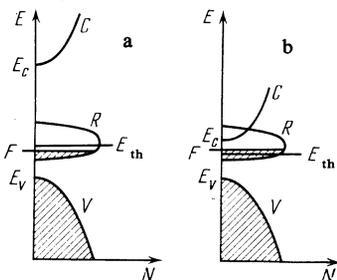


FIG. 3. Band-structure model for HgCr_2Se_4 : a) $T = 300$ K, $E_C - E_V = 0.8$ eV; b) $T = 4.2$ K, $E_C - E_V = 0.24$ eV.

in Ref. 9 that the magnetic anisotropy of HgCr_2Se_4 can be described quantitatively if it is assumed that these centers are Cr^{2+} and Cr^{4+} ions, which must coexist simultaneously. In the language of band structure the presence of the Cr^{2+} ion corresponds to the occurrence of an electron in the d_γ band, while a Cr^{4+} ion corresponds to the occurrence of a hole in the d_e band, which lies deep in the V band and is not shown in Fig. 3. Therefore, according to Ref. 9, we are forced to assume that electron-hole pairs with a negligibly small recombination probability are present in the crystal.

On the other hand, the “thawing” of the orbital moment can be explained without assuming a change in the valence of the chromium ions. In fact, the orbital singlet of the Cr^{3+} ions is due exclusively to the symmetry of the Coulomb potential of the nearest-neighbor anion environment. Since a lattice distortion of the vacancy type inevitably leads to a change in the local symmetry, as extremely likely candidate is the mechanism that was proposed in Ref. 10 for the analogous crystal CdCr_2Se_4 to explain the thawing of the orbital moment of the Cr^{3+} ions with no change in their valence.

In any of the mechanisms under consideration it is essential that the vacancies have a strong influence on the d_γ states forming the R band. Because the overlap integral between the d_γ states of the neighboring chromium ions is small, random perturbations of the periodic potential, even at moderate vacancy concentrations, can satisfy the Anderson localization criterion $W/U > K$, where W is the average value of the random potential, U is the energy overlap integral in the ideal d_γ band, and K is the critical percolation threshold, which depends on the symmetry of the crystal lattice.¹¹ One is thus justified in introducing a mobility threshold E_{th} such that states with $E > E_{\text{th}}$ are conducting and states with $E < E_{\text{th}}$ are localized and can only take part in a hopping conductivity.

The population of the R band is determined by the concentrations of donor and acceptor vacancies (N_d and N_a , respectively), and in the case $N_d > N_a$ the Fermi level F falls in the R band.

The model we have selected gives the following behavior of the transport characteristics of HgCr_2Se_4 as functions of temperature. In p -type samples the population of the R band is such that $F < E_{\text{th}}$. This means that in the paramagnetic phase the conductivity is due to holes of the V band and electrons of the R band that have been thermally activated to above the mobility threshold. Since the mobility of holes in the V band is much greater than the mobility of electrons in the R band, the crystal exhibits a p -type conductivity with an activation energy $F - E_V \sim 0.07$ eV. The transition to the ferromagnetic phase leads to an increase in the electron mobility. The principal role in this is apparently played by the following mechanism. The magnetic spin splitting of the C band leads to a lowering of the level E_C (see Fig. 3). The states of the R band fall into resonance with the states of the C band and become hybridized.¹² This increases the effective overlap integral U in the R band and thereby lowers the mobility threshold. If the hybridization of bands C and R is such that $E_{\text{th}} - F < 0$, then the conductivity becomes metallic all the way down to the lowest temperatures, since there are

delocalized electrons at the Fermi level. Thus, the degree of magnetic ordering governs the energy relationship of the C and R bands and thereby determines the degree of their hybridization. The temperature of the transition to the n -type mobility is determined by the relation $E_{th}(T) = F$ and depends on the defectiveness of the crystal. This temperature is lower in crystals with a lower concentration of donor vacancies, since the R band is less populated.

In using the data of optical measurements of the absorption coefficient¹³ it can be assumed that the fundamental absorption edge corresponds to V - C transitions whose energies $E_C - E_V$ decreases from 0.8 eV at $T = 300$ K to 0.24 eV at $T = 4.2$ K. At the same time, the long-wavelength wing, with a sharp red boundary at $E \sim 0.7$ eV, corresponds to V - R transitions.

Let us now consider the behavior of n -type crystals. Under the condition $N_d \gg N_a$ the inequality $E_{th} - F < 0$ can be satisfied even in the paramagnetic phase on account of an increase in the Fermi level in the R band as a result of its population by donor electrons. In this case the material is an n -type metal with a comparatively low mobility in the R band at $T > T_c$. The lowering of the bottom of the C band as a result of the magnetic ordering and the hybridization with the R band give rise to high-mobility electrons at the level F . These two factors increase the effective electron mobility, and one can now understand why the limiting mobility at low temperatures depends as it does on the donor concentration¹: The larger N_d , the higher the Fermi level and the greater the influence of the C band on the mobility.

4. CONCLUSIONS

The experimental results presented here show that, as in the case of n : HgCr_2Se_4 , the transport properties of p -type single crystals depend on the magnetic ordering. This justifies our discussion of a band-structure model which describes both the n -type and p -type conductivity from a unified point of view. The band structure of HgCr_2Se_4 discussed in Sec. 3 reduces to the three-band model which is usually used to describe the spectrum of compounds of the CdCr_2Se_4

type.¹⁴ However, the d band of Ref. 14 is in our case called the R band, since it is the presence of a random potential that enables us to introduce a mobility threshold E_{th} and thereby to stipulate localization of part of the band electrons.

It should be noted that a more detailed discussion of the properties of the R -band states must be based on quantitative calculations which have yet to be carried out.

In closing, we gratefully acknowledge our debt to V. V. Tugushev for an extremely fruitful discussion.

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