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ELECTRONIC PROPERTIES OF HgCr$_2$S$_4$ IN CONNECTION WITH DEPARTURE FROM STOICHIOMETRY.

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Résumé.— Des monocristaux du semiconducteur ferromagnétique HgCr$_2$Se$_4$. on été élaborés par transport en phase vapeur. Les monocristaux ainsi obtenus, ou recuits sous Se sont de type p à 300K. Un recuit sous atmosphère de mercure change de manière drastique les propriétés de transport, les échantillons deviennent de type n, le nombre de porteurs et la mobilité augmentent avec la pression de Hg lors du recuit. Ces résultats s'interprètent en admettant que les lacunes de sélénium et de mercure agissent comme donneurs et accepteurs respectivement.

Abstract.— Single crystals of the ferromagnetic semiconductor HgCr$_2$Se$_4$. were grown from the vapor. As grown and Se annealed crystals are p type at 300K. A drastic change of the transport properties appears after Hg annealing, the samples become n type, the number of carriers and the mobility increase with increasing pressure of Hg annealing. The results are understood assuming that Se vacancies act as two charged donors, whereas Hg vacancies act as acceptors.

Introduction.— HgCr$_2$Se$_4$. is a ferromagnetic semiconductor (T$_c$ ≈ 110 K). The magnetic order arises from the localized 3d$^3$ electrons of Cr$^{3+}$.

Most of the interest in the chalcogenide spinels centers on typical properties arising from the existence in the same sample of localized and conduction electrons. This gives a strong dependence of the transport properties on the magnetic order giant magnetoresistance, spontaneous Hall effect, anisotropic resistivity.

Most of the theoretical models derived so far consider the exchange interaction between carriers and localized 3d electrons.

This interaction results in a splitting of the conduction band (Haas /1/ and /2/, in ref. /2/ correction to the man field theory have been brought).

In classical semiconductors, usually charged impurities give localized states whose binding energy result from the Coulomb field interaction whereas in magnetic semiconductors additional exchange interaction may occur.

This give two types of localized states depending wheter an impurity makes a deep donor level (Magnetic Impurity State MIS /3/ or a shallow donor (Bound Magnetic Polaron BMP /4/).

Recently Heritier /5/ discussed a model in which conduction occurs in a correlated d-band.

The doping concentration usually used in magnetic spinel semiconductor is muchmore higher than in semiconductor physics. Spinel semiconductors are usually grown from the vapor or in fluxes. As grown samples exhibit a large concentration of defects. Ag doping in spinel chalcogénide give p-type samples whereas In doping give n-type samples. HgCr$_2$Se$_4$. samples reported here were not intentionally doped, these samples offer the unique opportunity to have two volatile elements Hg and Se so that annealing either on Hg or Se atmosphere can change the nature and number of carriers. Furthermore HgCr$_2$Se$_4$. presents among all chalcogenide magnetic semiconductors the largest red shift decreasing from 0.84 eV at 300 K to 0.26 eV at 4.2 K.

Experimental.— HgCr$_2$Se$_4$. samples were grown by chemical transport using Al + Cl$_3$ (or Ga + Cl$_3$) as transport components /6/. As grown samples are p-type at room temperature. n and p - type were obtained by heating respectively under vapor pressure of Hg and Se.

Data on two type samples are given in table I.
Se annealed samples are p-type at room temperature. This was checked by Seebeck measurements. No marked anomaly was observed at $T_C$. At $T<60K$ Hall voltage shows that the sample becomes n-type.

A drastic change of the transport properties appears after Hg annealing. All the samples become n-type. The number of the carriers and the mobility increase with increasing pressure of Hg annealing as shown in Table I. The temperature dependence of the mobility is given in figure 1: the mobility decreases monotonically down to a low value for $T>T_C$. A jump in the resistivity curve as a function of temperature appears at $T_C$. This jump is higher the lower the number of carriers as expected from theories of critical behavior of the resistivity in magnetic semiconductors.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\eta(4.2K)\ cm^{-3}$</th>
<th>$\mu(4.2K)\ cm^2/\ V\ s$</th>
<th>$T_C(\ K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm</td>
<td>$10^{17}$</td>
<td>300</td>
<td>107</td>
</tr>
<tr>
<td>3 atm</td>
<td>$10^{18}$</td>
<td>900</td>
<td>109.5</td>
</tr>
<tr>
<td>8 atm</td>
<td>$6\times10^{18}$</td>
<td>1 200</td>
<td>114.5</td>
</tr>
<tr>
<td>Se</td>
<td>$1.6\times10^{14}$</td>
<td>185</td>
<td>106</td>
</tr>
</tbody>
</table>

Discussion.— In HgCr$_2$Se$_4$, the nature and the concentration of carriers can be easily changed by heat treatment. Donors and acceptors are obviously related to Se and Hg vacancies. The results are understood assuming that Se vacancies act as two charged donors (the activation energy of Se vacancies was found to be 0.1 eV in CdCr$_2$Se$_4$ /7/). Hg vacancies act as shallow acceptors (0.02 eV). Hg annealing decreases the number of Hg vacancies, thus increasing the number of donors. The samples contain about 80 p.p.m Al as a result of the crystal growth process (Al$^+$ Cl is used as transport component). But about 5 p.p.m Ga using Ga$^+$ Cl. If we supposed that all Al appear in A site and is fully ionized, the number of carriers should be of the order of $10^{19}\ cm^{-3}$ which is not the case. It is assumed either that Al acts as a deep donor or gives with Hg vacancies $\text{Hg-Al}$ complexes (like Ge in GaAs). Hg annealing results in destroying these complexes enhancing the donors behaviour of Al. In other words, Hg annealing produce a modification of the crystal self-compensation. Systematic studies of HgCr$_2$Se$_4$ prepared from Ga+Cl and careful determination of Ga content are carried out in order to check the proposed assumption. It can be concluded that Hg vacancies act as acceptor whereas Se vacancies as donors and possibly Al and Ga as donors.

These vacancies are charge compensated by either Cr$^{2+}$ or Cr$^{4+}$ which changes the magnetocrystalline anisotropy of the sample. Recent data on the magnetocrystalline anisotropy $K_1$ measurements on these HgCr$_2$Se$_4$ are consistent with the above hypothesis.
about the nature of acceptors and donor levels /8/.

The temperature dependence of n, p can be understood from the large variation of the band gap, the well-known redshift effect in magnetic semiconductors at low temperature, the n-type samples are degenerate; the Fermi level is located in the conduction band which overlaps donor levels. At higher temperature, up to 200K, the gap increases, donor levels become localized.

A plausible explanation of the red shift and mobility variations was given by Heritier: for chalcogenide spinels the d-band broadening due the magnetic order causes the red shift and enhances the mobility for \( T < T_c \). The conduction occurs in a d-band (Cr\(^{2+}\)) when \( T > 200 \) K, due to the short range order the bottom of the band starts to move towards lower energies, at lower temperature the d-band reaches the Se vacancy level, its width increases with the magnetic order so that the mobility increases by several order of magnitude when \( T = T_c \).

Although this model seems plausible, the high values of the mobility are not completely consistent in the framework of a correlated d-band. A model of conduction in large band is more related to our data. Recent optical measurement of reflectivity confirms this hypothesis /8/.

References

/8/ Unpublished results.