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Anomalous galvanomagnetic behavior of orthorhombic layered GeS single crystals

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Galvanomagnetic effects of orthorhombic layered GeS have been investigated in the temperature range 293–423 K. The results showed the existence of negative magnetoresistance and a kind of rapid oscillation of both the magnetoresistance and the Hall coefficient, depending on both the temperature and the magnetic field. To explain this peculiar behavior, the electronic structure of the material, which is a *p*-type semiconductor, was considered. The negative magnetoresistance was attributed to arise from localized moments located at impurity atoms, such as transition-metal atoms, which form antiferromagnetic clusters. Concerning the rapid oscillations of the magnetoresistance and the Hall coefficient, it was found that resonant defect states in the valence bands, probably from the same defects that give rise to the negative magnetoresistance, may be responsible for this behavior.

I. INTRODUCTION

Orthorhombic crystals are quite suitable for the study of the influence of a magnetic field on the electrical behavior of the crystalline materials, because of the zero-field-resistivity anisotropy that they exhibit along the three principal directions. Thus a comparison between the natural anisotropy and the imposed one by the magnetic field can be made.[1] On the other hand, the magnetic field is in general definitive for the value and the behavior of the magnetoresistance according to the weak- or strong-field conditions. Other factors affecting the electrical behavior of semiconductors are connected with the presence of point defects or extended defects, which introduce localized states or potential barriers, respectively.

Two very interesting semiconductors with a layered orthorhombic structure are GeS and GeSe. Most of the electrical, magnetic, and optical properties of these crystals have been studied in our laboratory.[2–11] Electrical and magnetic measurements on GeSe (Refs. 5, 6, and 11) showed an antiferromagnetic behavior connected with the negative magnetoresistance effect. From these measurements a Néel temperature at 381 K was determined. Also above this temperature a "metallic" behavior of the zero-field resistivity was materialized.

According to Toyozawa[12] the appearance of the negative magnetoresistance in semiconductors can be attributed to the presence of localized magnetic moments which are responsible for the increase of conductivity under the action of an external magnetic field. This scattering mechanism was used in the case of GeSe to explain the observed negative magnetoresistance in a direct connection with the antiferromagnetic behavior produced by a corresponding alignment of the spins of the magnetic moments up to Néel temperature. We should notice here that the magnetic moments were attributed to the existence of vacancies. Finally, according to Mott[6] the high-temperature behavior is probably due to a screening of localized levels rather than to a true metallic behavior.

Since, besides the scattering of the carriers by localized magnetic moments, there are also other scattering mechanisms, the total magnetoresistance $\Delta\rho/\rho$ can be given as a sum of two terms, one expressing the negative magnetoresistance and a second one corresponding to the usual positive magnetoresistance. Therefore, in such cases magnetoresistance measurements as a function of the field and the temperature can lead to the determination of the magnitude and the effective number of the magnetic moments, the magnetic susceptibility, and their variation with temperature.

The purpose of this work is to verify and further investigate the above-mentioned effects on GeS, in connection with the expected anisotropy, by measuring the zero-field resistivity, the magnetoresistance, and the Hall coefficient with temperature and for various values of the magnetic field under weak-field conditions. As we shall see the results were rather unusual and peculiar.

Monocrystalline GeS can be grown by two methods: sublimation of the material in a vertical furnace[13] or vapor transport in a horizontal furnace.[14] The obtained crystals have an orthorhombic structure of the space group D_{2h}^{16} (α=0.430, b=0.365, and c=1.044 nm) and exhibit an easy cleavage along the (001) plane containing the axes a and b. GeS is always found to be *p*-type and its direct band gap is equal to 2.04 eV (1.8 eV) for light polarization parallel to a (b) at room temperature. Finally GeS obeys Urbach's rule.[7]

Concerning the electrical behavior of GeS, its room-temperature resistivity is 3–6 orders of magnitude greater than the resistivity of GeSe.[15] Also impurity and trapping levels of a great variety have been found in the band gap.[16,17] Extended planar defects, mainly growth twins and twist low-angle grain boundaries producing typical dislocation networks,[18] affect the electrical properties of GeS at low temperatures.[10] A quite similar behavior has also been observed in GeSe.[8,9]

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II. EXPERIMENT AND RESULTS

The electrical measurements were performed using the Wasscher[19] method for anisotropic circular flat samples. In brief, the principle of the method is as follows. Four contacts, A,B,C,D, are taken along the circumference of the sample on two perpendicular diameters (Fig. 1). Thus the "resistances"

$$R_1=\frac{V_D-V_C}{I_{AB}},\quad R_2=\frac{V_A-V_D}{I_{BC}},\quad R_{12}=\frac{V_A-V_C}{I_{BD}} \tag{1}$$

are defined. The maximum value of the resistance ratio, $(R_1/R_2)_{\max}=(R_1)_{\max}/(R_2)_{\min}$, is obtained when the contacts are placed at an angle of 45° to the directions of the principal axes of resistivity x_1 and x_2 with resistivities ρ_1 and ρ_2, respectively ($\rho_1>\rho_2$). This ratio is related to the anisotropy ratio $\lambda=\rho_1/\rho_2$ by a conformal mapping of the shape of the sample in different complex planes. Thus the in-plane principal resistivities are determined by the following expression:[20]

$$\rho_1=\frac{\lambda^{1/2}\pi d(R_1)_{\max}}{\ln[2/(1-k)]}\,,\qquad \rho_2=\frac{\lambda^{-1/2}\pi d(R_2)_{\min}}{\ln[2/(1+k)]}\,, \tag{2}$$

where d is the thickness of the sample and k is the modulus of a complete elliptic integral, appearing during the conformal mapping. The Hall coefficient is calculated by the relation

$$R_H=\frac{d}{B}\Delta R_{12}\ . \tag{3}$$

ΔR_{12} is the change in the resistance R_{12} due to the presence of the field B, applied perpendicularly to the sample plane.

According to the above, a circular flat sample, of thickness $d=0.2$ mm and of diameter 6 mm, was prepared from a GeS single crystal grown from high-purity (99.999%) initial elements with the vapor-transport method.[14] The sample plane was the (001) cleavage plane and its principal crystallographic directions a and b were determined by a Laue diagram. Four Ohmic contacts were applied on it, as is indicated in Fig. 1. For the formation of the Ohmic contacts the procedure described by Wiley, Pennington, and Schonherr[15] was followed. Thus, aquadag graphite covered with a layer of conductive silver paste was used. The sample was mounted on a holder, which allowed measurements for two directions of the magnetic field, parallel or normal to the sample plane, at different temperatures. A coaxial heating cable was used to provide the uniform sample temperature. Finally all the measurements were taken under vacuum (about 10^{-4} mm Hg).

Ten sets of measurements were performed in the range of temperature 293–423 K, for various values of the magnetic field, from zero up to 1 T. The temperature of 423 K was a little lower than the upper limit of reproducible measurements. For the measurements the usual dc method was used with a current $I=400\ \mu$A. At each temperature the exact experimental procedure was as follows. At first the sample plane was oriented parallel to the direction of the field **B**, coinciding with the direction of the a axis. The results showed that this direction was the direction of the smaller resistivity ρ_2 (see Fig. 1). For this orientation, the zero-field resistivity along the two principal directions x_1,x_2 was measured. Also measurements of the magnetoresistivities $\rho_1(B),\rho_2(B)$ along the same directions were taken for several values of the magnetic field, as we have already mentioned above. Similar magnetoresistance measurements were also taken after a 90° rotation of the sample about the b axis. Thus its plane was oriented perpendicularly to the direction of the field **B** (**B**‖**c**). With the same arrangement the Hall coefficient for 0.5 and 1 T was measured. We should point out here, that when the field **B** is directed along a principal zero-field direction, as was done in the previous

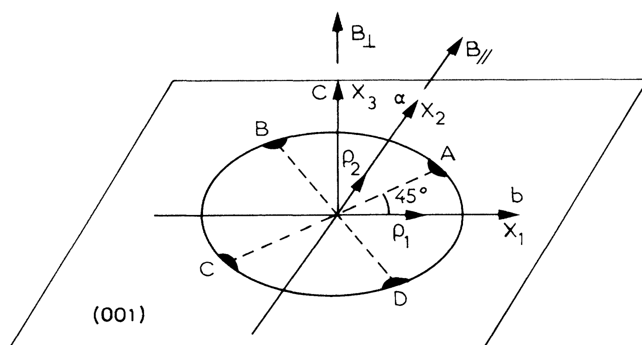

FIG. 1. Orientation of the used circular flat sample with respect to the crystallographic axes. The position of the four contacts and the two directions of the magnetic field are indicated.

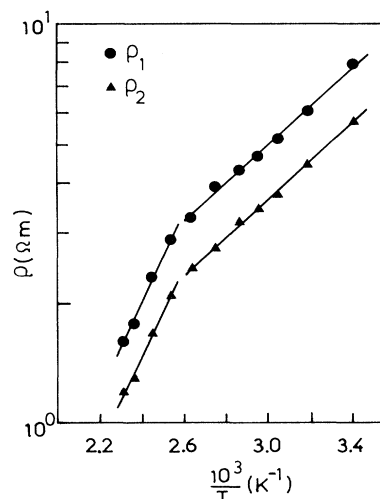

FIG. 2. The in-plane principal zero-field resistivities as a function of the reciprocal temperature, showing a typical semiconducting behavior. The straight lines represent the results of a least-squares fit of the data.

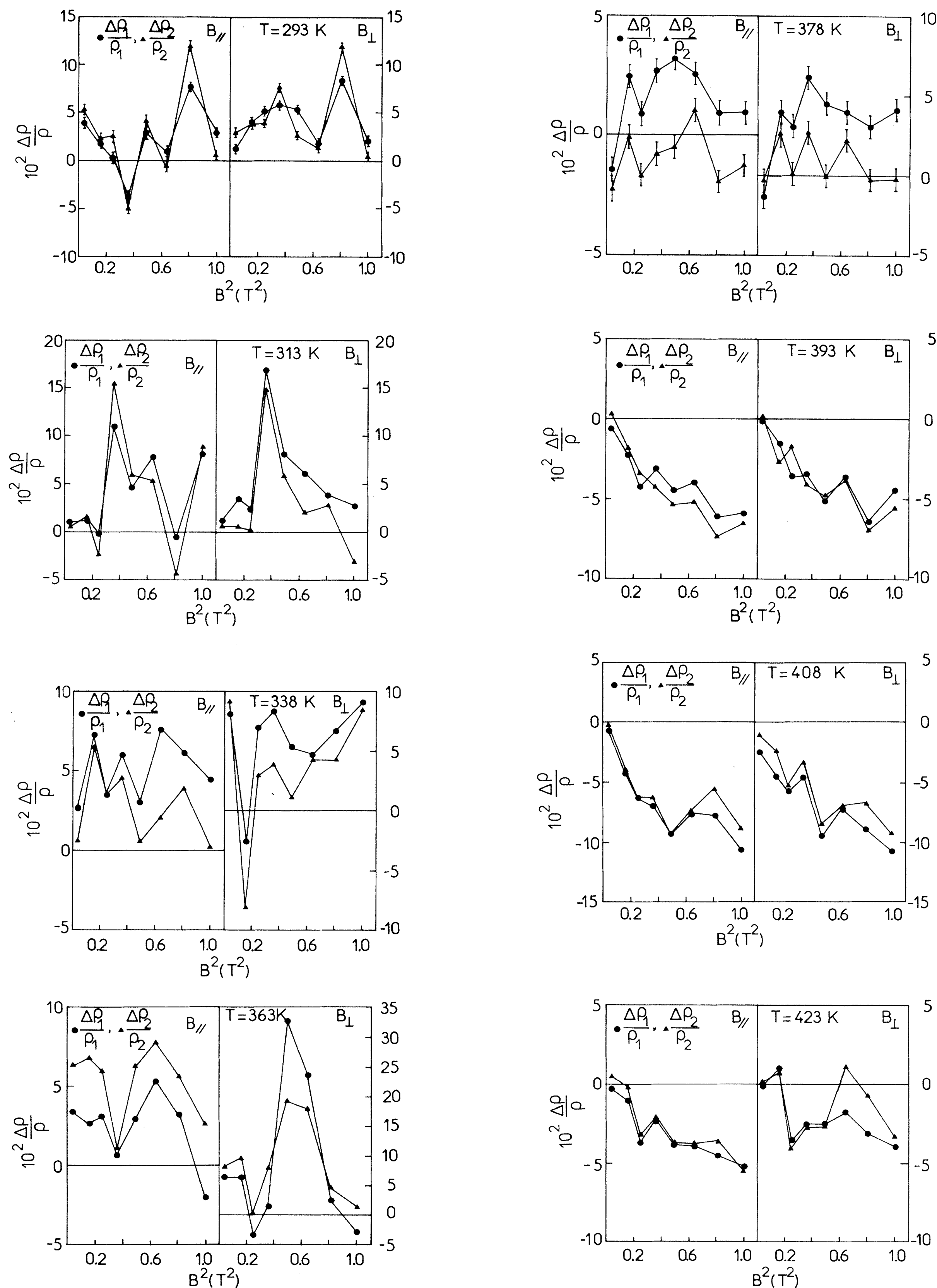

FIG. 3. Eight different magnetoresistance diagrams vs the square of the magnetic field for its two directions and at various temperatures. The effect of negative magnetoresistance and the rapid fluctuations are evident.

measurements, the directions of the principal resistivities remain constant.[1]

In Fig. 2 the results of the zero-field-resistivity measurements versus the reciprocal temperature are presented. As is evident, the material exhibits the expected semiconducting behavior in the whole temperature range. By a least-squares fit of the data, two activation energies were determined. Assuming extrinsic conduction,[15] the value of activation energy for both directions equals about 95 meV for the lower-temperature range and about 215 meV for higher temperatures.

On the other hand, the results of the magnetoresistance measurements are unusual and very interesting. Indeed, from the diagrams of Fig. 3 it is deduced that the reduced magnetoresistance does not obey the usual parabolic law as a function of the square of the magnetic induction. This is true for the two principal directions as well as for the two orientations of the magnetic field.

Examining these diagrams we can see that the magnetoresistance exhibits at each temperature an irregular behavior. Sometimes an exchange between the maximum and minimum values of the two directions is observed. Also, below 373 K the magnetoresistance is mainly positive and some negative values it takes are due to its irregular behavior. Increasing the temperature above 373 K a total displacement to the zero line appears and after a further increase of the temperature the magnetoresistance becomes negative. The last diagram at 423 K shows a displacement of the magnetoresistance again to the zero line, so that a transition to positive values is possible at a little higher temperature.

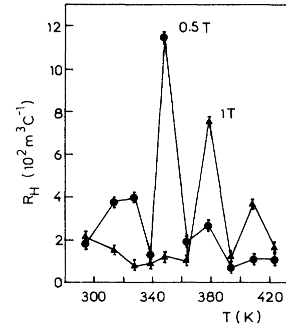

FIG. 5. The Hall coefficient diagram vs the temperature for two values of the magnetic field. The existence of rapid oscillations depending on the magnetic field and the temperature is confirmed.

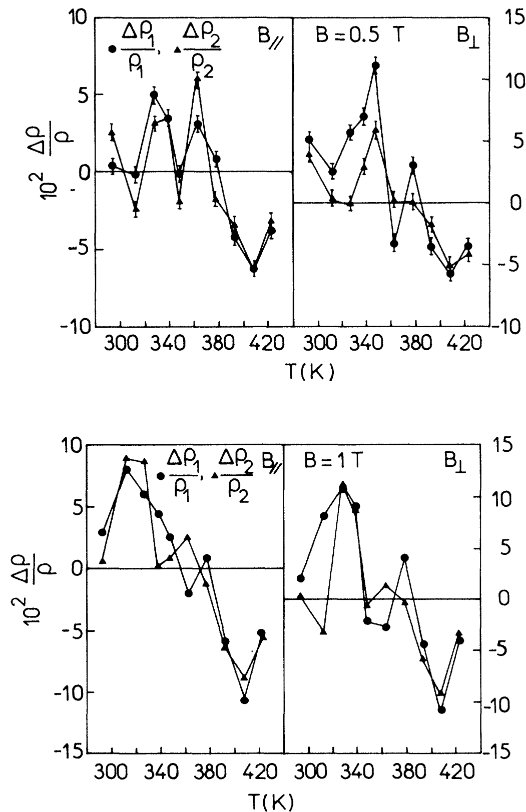

FIG. 4. The two principal magnetoresistances for 0.5 and 1 T as a function of the temperature for the two orientations of the magnetic field. Magnetoresistance oscillations are again observed.

The described behavior of the magnetoresistance with temperature is also obvious from the diagrams of Fig. 4, where the dependence of the magnetoresistance on temperature for fields 0.5 and 1 T is presented. These last results support our opinion that the transition temperature from negative to positive values might be around 455 K. But the main characteristic of the diagrams is again the observed fluctuations in the magnetoresistance values. Therefore, from the results of Figs. 3 and 4 we may conclude that a kind of oscillation of the magnetoresistance, which depends on both the magnetic field and the temperature, exists. Of course, periodicity is not observed and this could be rather expected since weak-field conditions are valid.

Oscillations are also observed in the Hall measurements. The results of the Hall coefficient measurements for $B=0.5$ and 1 T as a function of temperature are shown in Fig. 5. From this diagram it is deduced that the sharp variations of the magnetoresistance with the magnetic field and the temperature, might be mainly caused by a corresponding variation of the free carrier concentration. If we take the mean value of the zero-field resistivity at room temperature equal to 7 Ω m and the value of the Hall coefficient about 0.02 $m^3 C^{-1}$, then the Hall mobility $\mu_H = R_H/\rho$ is equal to about 3×10^{-3} $m^2 V^{-1} s^{-1} = 30$ $cm^2 V^{-1} s^{-1}$. It should be noticed here that the lines in Figs. 3–5 have been drawn to guide the eye and they do not represent the actual variation of the corresponding quantities. Also in some diagrams of the same figures, typical error bars have been drawn.

III. DISCUSSION

As we have seen, the magnetoresistance and the Hall coefficient vary in a complex way when the temperature or the magnetic field are varied. To explain this behavior

we can analyze the present results with the help of the similarities which GeS and GeSe have. Specifically both materials have very similar orthorhombic structure, similar electronic structure, and are *p*-type semiconductors. If one ignores the wild variations of the magnetoresistance and of the Hall coefficient that GeS has, the overall behavior of the two materials is very similar. Therefore we will analyze the present experimental results in two steps. First, the negative magnetoresistance will be considered and second, the rapid variation of the measured properties.

It is well known that negative magnetoresistance is associated with the existence of localized moments. If the local moments are ordered then no spin-flip scattering of the carriers occurs and the resistance is lower compared to the state of disordered moments. The problem is to find the origin of the localized moments. Toyozawa[12] has considered the case of a semiconductor in the metallic impurity band conduction and found that magnetic states appear embedded in the metallic impurity band. Application of this theory to semiconductors has shown that the coupling between the localized spins is weak and antiferromagnetic. Also negative magnetoresistance increases as the magnetic field increases and as the temperature decreases, as for example, it has been observed for the case of Te-doped GaSb.[21]

Although the above theory can account for the negative magnetoresistance observed in some semiconductors, in our case there are some points which do not comply with the basic assumptions of this theory. First of all, the conduction in GeSe and GeS is not carried by states lying in an impurity band. Both materials, like most other IV-VI compounds, are *p*-type because the main defects are anion vacancies. These defects introduce holes in the valence band and resonant levels deep in the valence bands, as will be discussed later in detail. Therefore, the carriers are free to move and their wave function is delocalized. On the other hand, GeSe has been found to be antiferromagnetic with very large T_Θ (333 K),[6] where T_Θ is a corrective temperature for the Curie law of the paramagnetic branch of the magnetic susceptibility. This large value means that the interaction of the localized spins is very high, and that the localized spins should interact via direct interactions. Therefore, we may suggest that the negative magnetoresistance observed in GeSe and GeS, is induced from localized moments located at impurity atoms, such as transition-metal atoms, which form antiferromagnetic clusters either at planar defects or at twin boundaries or between the double layers of their characteristic structure. We remember that defects of this kind have been verified in both crystals.[18]

For a given magnetic field the magnetoresistance of GeSe exhibits the following behavior. At temperatures around room temperature it is almost zero. As the temperature increases it takes positive values; it forms a cusp and then goes down taking negative values. At still higher temperatures it rises up and takes again positive values. To explain this variation we must take into account the antiferromagnetic ordering of the spins. At low temperatures the spins are ordered and a weak external field is not going to change their state. As a result the resistance is going to be independent of the magnetic field and of the temperature. As temperature rises, some spins disorder and they have a positive contribution to the resistance. The application of the magnetic field helps the antiferromagnetically ordered spins to disorder and therefore a positive magnetoresistance is observed. At temperatures close to the Curie temperature of the antiferromagnetic phase, spins can be ordered by the external magnetic field and the magnetoresistance becomes negative. At still higher temperatures the magnetic field cannot order the spins any more and the magnetoresistance becomes again positive. Apart from the rapid variations of the magnetoresistance found in the present results, we can say that GeS and GeSe exhibit similar behavior and therefore we can infer that it is possible for GeS to be antiferromagnetic with a Néel temperature around 455 K.

Now we turn to examine the rapid variations of the galvanomagnetic coefficients. Transport properties are known to be very sensitive to the band structure and defect levels. The band structure calculations[22,23] show that GeS is a direct gap semiconductor. Little is known about the defects levels in the orthorhombic IV-VI compounds. To gain some understanding for the defects levels it is useful to know the relation between the band structure and the bonds. A discussion for such a relation has been given in a previous paper.[24] The central result is that the bonds are mainly formed from *p* orbitals as in the case of the cubic and rhombohedral IV-VI materials. The only difference being that the bonds are not resonating any more and as result they are more localized. The *s* orbitals form σ bonds with energies lower than the *p* bonds. If we allow the interaction between the *s* and *p* orbitals then the states at the top of the valence bands will be antibonding. This is similar to the electronic structure of the cubic and the rhombohedral IV-VI materials, but quite different from the electronic structure of the tetrahedrally bonded semiconductors.[25] The above picture will be extended to describe the defect levels in the orthorhombic IV-VI materials. The first thing to consider is the cation and anion dangling-bond energies. Are they in resonance with the conduction of the valence bands? It can be shown[26] that for the case of orthorhombic phosphorus (ortho-P or black-P) the dangling-bond energy is deep in the valence bands and that P vacancies will introduce holes in the top of the valence bands. This result is in contrast to what has been found for Si, where the dangling-bond energy is well inside the fundamental gap. It can also be shown that, for the ionic orthorhombic compounds, the cation dangling-bond energy is deep in the valence bands. This picture is also in variance with what has been found for the materials with tetrahedral bonds, but similar with what was found for the cubic IV-VI compounds.[27] Therefore, we can expect similar results concerning the effects of the defects on the electronic structure. Namely, an anion vacancy induces electrons in the conduction bands and a cation vacancy induces holes in the valence bands. Since the states at the top of the valence bands are antibonding the anion vacancies are more probable and a *p*-type material is expected, in accordance with the experimental findings. Also many substitutional defects will lead to states in resonance with the conduction or the

valence bands.

Under the above considerations, the rapid variation of the Hall coefficient and of the magnetoresistance can be explained. These variations can be due to a corresponding variation of the number of carriers and/or to the variation of the mobility as the temperature or the magnetic field varies. The reason for such a variation can be ascribed to the existence of resonant defect states in the valence bands. Some of these defect states may be induced by the impurities which are responsible for the magnetic properties of GeS. Such states are localized around the defects and as the temperature rises they can be emptied. The magnetic field can also influence these states by splitting them. In any case some localized states will have energies close to the energies of the carriers and they can influence their number and/or their lifetime by scattering or trapping them. As a result the Hall constant will increase as is indeed the case.

In conclusion, we may say that the described electronic structure in connection with the existence of possible transition-metal impurities are responsible for the two observed effects, that is, the negative magnetoresistance and the rapid fluctuations of the magnetoresistance and the Hall coefficient with the temperature and the magnetic field. These effects normally appear at low temperatures. In addition, to observe oscillations of the magnetoresistance the strong-magnetic-field condition must be satisfied. Therefore, the present results seem to suggest that it would be interesting, for a future work, to study GeS samples doped with specific transition-metal impurities.

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