Analysis of Electron Mobility in Some "Problematic Materials" from Magnetoresistance Effect at High Magnetic Fields

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Using examples of some perspective electronic materials ($HgSeS$, Fe_3O_4, InN, and others) it is shown that magnetoresistance data at high magnetic fields allow evaluating the true values of mobility of charge carriers in spite of any "adverse factors". Additional impacts involving high pressure and irradiation with high-energy particles (neutrons, electrons, ions) produce the enhancement of magnetoresistance technique of testing and allow to go into details of the type of electron structure and scattering mechanisms of charge carriers.

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1. Introduction

Precise values of charge carrier parameters of electronic materials, namely their mobility and concentration, present crucial factors for application at electronic devices [1–10]. Determination of concentration and mobility of charge carriers even in case of two-band conductivity requires measurements of at least four different experimental effects [2]. For inhomogeneous materials, the determination of electron mobility from the Hall effect presents a serious problem even in one-band case because of inclusions affecting the conductivity [4]. The magnetoresistance effect is known to carry the information on the conduction mechanism and mobilities of the most mobile charge carriers [11]. Values of mobility found from magnetoresistance (MR) effect in particular materials exceed those obtained from the Hall effect by $\approx 10^2$–10^4 times [3, 4] and the former seem to be close to *bona fide* values.

In the present work we examined the carrier mobility in some "problematic materials" with various kinds of adverse factors ($HgSeS$, Se, Fe_3O_4, Ti_2O_3 and InN) using magnetoresistance data.

2. Experiment

MR effect was measured in the static magnetic field B of up to ≈ 14 T and at temperatures of 4.2–370 K, using

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Oxford Instruments equipment [5, 6]. Measurements at the ambient pressure were performed by the conventional Montgomery method (a version of the Van der Pauw method), allowing anisotropy examination of galvanomagnetic properties [7]. For the investigations, we took single crystals ($HgSeS$, Fe_3O_4), amorphous samples (Se), polycrystalline bulk (Ti_2O_3), and thin film (InN) crystals. Compositions of the samples were determined by means of X-ray microprobe analysis using a Superprobe-JCXA-733 spectrometer (JEOL, Japan). The samples of magnetite (Fe_3O_4) were subjected to a fast neutron bombardment with a fluency of $\Phi = 2.2 \times 10^{20}$ cm^{-2} [8]. High hydrostatic pressure up to ≈ 2 GPa [9] as well as quasi-hydrostatic pressure up to ≈ 30 GPa [10] were used also as additional tuning parameters (for $HgSeS$ and Se).

3. Results

The collected results for all the materials are presented in Figs. 1–6. The obtained dependences of MR on magnetic field in most of the materials may be described by the following equation:

$$\frac{\Delta\rho}{\rho} = D\frac{(\mu B)^2}{1 + (\mu B)^2}, \tag{1}$$

where ρ is the electrical resistivity, B is the magnetic induction, μ is charge carriers mobility, coefficient D determines the sign and value of MR. Both positive ($D > 0$) and negative effects ($D < 0$) were found [1, 11]. The resultant sign of MR effect depends on contributions of both the negative and positive MR effects induced by the peculiarities of the electronic band structure as well as the mechanisms of charge carriers scattering [11].
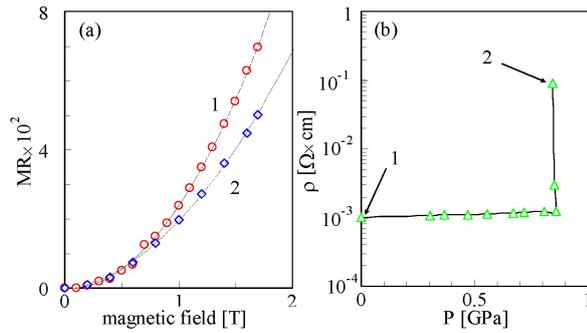
Fig. 1. (a) Dependences of magnetoresistance effects on magnetic field for $HgSe_{1-x}S_x$ with $x = 0.104$ at $T = 77$ K at $P = 0$ (1) and $P = 0.84$ GPa (2); (b) dependence of electrical resistivity on hydrostatic pressure for the same sample; the MR data (a) have been obtained at points 1 and 2 [13].
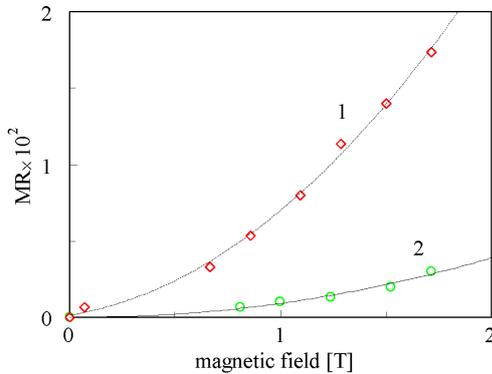

Fig. 2. Dependences of the magnetoresistance effects of amorphous Se on magnetic field at $T = 290$ K under pressure 23 GPa (1) and 12 GPa (2) [1].

3.1. High pressure phases and two-phase states

HgSe-based crystals undergo a phase transition from a semimetal cubic zinc-blende phase ($B3$) to a semiconducting hexagonal cinnabar ($B9$) one under pressure. The samples of HgSeS consisted of these two phases in an intermediate region of hydrostatic pressure (Fig. 1) [3, 12, 13]. The value of ρ of the samples in the two-phase state increased by 2–4 orders of magnitude (Fig. 1), but the positive sign of the temperature coefficient of ρ remained [3, 4], and the MR retained almost the same as for the initial phase (Fig. 1). The MR effect in the two-phase state was therefore affected by inclusions of the initial semimetal phase. At the completion of the phase transition to the hexagonal phase, the MR effect became negative (for all HgX, where X = Te, Se, S, O) [14, 15]. Under the pressure increase above ≈ 20 GPa, the phase transition to a metallic high-pressure phase happened. At this transition, the MR effect showed a tendency to change its sign to positive [15]. The decrease of pressure leads to the opposite variations of both the sign and the values of the MR effect [14].
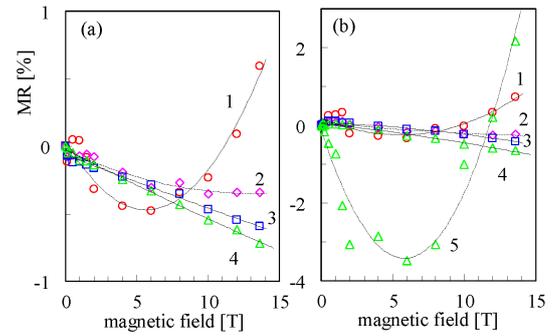

Fig. 3. Dependences of the magnetoresistance effects on magnetic field for as-grown (a) and fast-neutron-bombarded Fe_3O_4 (b) at $T = 140$ K (1), $T = 200$ K (2), $T = 305$ (3), $T = 370$ (4) and $T = 110$ K (5) [8].
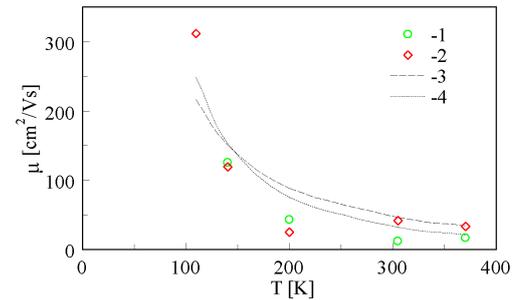

Fig. 4. Dependences of mobility values of Fe_3O_4 on temperature for: 1 — as-grown, and 2 — fast-neutron-bombarded samples; the points are data estimated from the MR effects (Fig. 3), and the lines are theoretical approximations: 3 — $\mu \sim T^{-3/2}$, 4 — $\mu \sim T^{-2}$.

Notice that in wide-gap semiconductors, such as GaP, ZnSe, ZnS, CdS, CdSe, and CdTe, the resistivity decreases at phase transitions into a rock-salt lattice by $\approx 6-7$ orders of magnitude, and the magnetoresistance was found to be negative with a nearly parabolic dependence on B [1, 14, 15]. Classical positive MR has to be small in these metal phases due to factor of $D = (k_B T/\eta)^2 \ll 1$ [11, 1] (η is the chemical potential, $\eta \gg k_B T$, k_B is the Boltzmann constant, T — temperature), so the negative MR dominated. The dependence of the negative MR-effect on magnetic field and its rising with lowering in temperature suggested that it may be due to one of the following reasons: (i) the "hot" or "warm" electrons, which are "cooled" by the magnetic field [11], (ii) interference quantum additions to the conductivity [14], or (iii) by impurity levels splitting in the magnetic field [16]. We can conclude that the MR data showed the charge carrier dominating scattering mechanisms at various high-pressure phases.

3.2. Inhomogeneous semiconductors

In trigonal Se, the Hall effect data showed low mobility values of holes, $\mu \approx 0.01$ cm^2/(V s), while direct MR measurements gave much higher values of $\mu \approx$
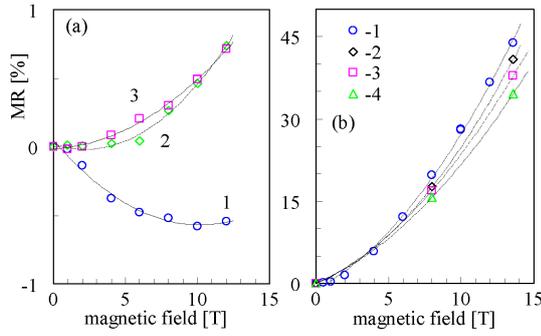
Fig. 5. Dependences of the magnetoresistance effects on magnetic field for the gold phase of Ti_2O_3 (a): at $T = 247.2$ K (1), $T = 296.5$ K (2), $T = 346$ K (3) and for InN thin film (b) at $T = 4.2$ K (1), $T = 107$ K (2), $T = 206$ K (3), at 286 K (4). The points are experimental data and the lines are fits by polynomial (a) and quadratic (b) approximations.
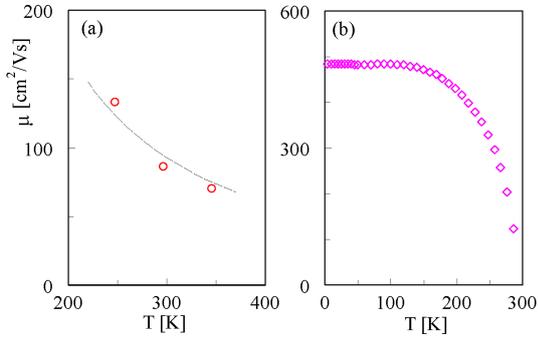

Fig. 6. Dependences of mobility values on temperature for Ti_2O_3 (a) and InN (b). The points are data estimated from Fig. 5, the line shows a fit by the function $\mu \sim T^{-3/2}$.

30–50 $cm^2/(V\,s)$ [4]. This divergence is related to the worsening of the electrical resistivity due to intrinsic potential barriers in the material [4]. In our measurement, the mobility values ($\mu \approx 68$ $cm^2/(V\,s)$ at $P = 23$ GPa and ≈ 32 $cm^2/(V\,s)$ at $P = 12$ GPa) estimated from the MR data (Fig. 2) increased under pressure, suggesting a closing of direct energy gap at $P \approx 25$ GPa [10]. For direct-energy-gap semiconductor Se (its gap is at H-point of the Brillouin zone) $\mu \sim 1/m \sim 1/E_g$, where m is the effective mass of charge carriers and E_g is the semiconductor gap [17, 18]. The exponential increase of the MR effect under pressure is related to the decrease of E_g and m (Fig. 2). Thus, the positive MR effect characterizes the mobility $\mu(P)$ of the light carriers [11], and hence it gives information about the type of semiconductor gap E_g (direct gap at high pressures) [17, 18]. Similar results have been obtained for other direct-gap semiconductors Te [14], and PbTe, PbSe [19, 20]. For sulphur, the gap at $P \approx 40$ GPa was found from the MR measurements to be indirect [21].

3.3. Material with magnetic ordering

The high degree of magnetization and resultant large anomalous Hall effect in magnetite are serious obstacles for the examination of ordinary MR effect [8]. At high magnetic fields above $B > 3$ T, the correct measurements of MR effects become available (Fig. 3). In the temperature range 100–300 K there are both positive and negative contributions to the MR effects of magnetite. The negative MR effect may be attributed to the suppression of scattering of electrons with spin flip [22]. The equation for the negative MR effect for this case is the following:

$$\frac{\Delta\rho}{\rho_0} \approx -\left(\frac{gS\beta B}{Tk_B}\right)^2, \qquad (2)$$

where $g \approx 2$, $\beta = 9.27 \times 10^{-24}$ J/T is the Bohr magneton, S is the value of spin [23]. The increase of the degree of magnetic ordering with increasing B is known to reduce electron scattering (and, hence — the electrical resistivity). Below the Verwey temperature, an absolute value of the positive magnetoresistance effect increases in accordance with the higher mobility of holes in the low-temperature phase [8]. A temperature dependence of the mobility obtained from the positive MR effect of magnetite can be described by a function of $\mu \sim T^{-3/2}$ (Fig. 4), which corresponds to the scattering of charge carriers by acoustic phonons [11]. The hole mobility value decreased after neutron irradiation, but its value still remained rather high (as in trigonal Se). This result confirmed the Peierls model of the Verwey transition in Fe_3O_4, but did not support the charge-ordering model of this transition [8].

3.4. Two-band conductivity

A localized donor state, resonant with the conduction band, influences electrical conductivity in InN samples [23, 24]. Above ≈ 140 K, the mobility value estimated from the MR effect (Fig. 5) in the thin films studied (of ≈ 1 μm thickness) decreases, suggesting a dominant acoustic phonon scattering at high temperatures [25], while at low temperatures the mobility was independent of temperature (Fig. 6).

The Hall effect data of Ti_2O_3 (in so-called "golden" phase synthesized at high pressure–high temperature (HP–HT) conditions) in magnetic fields up to 14 T indicated a two-band model of electrical conductivity [26]. In weak-magnetic-field approximation ($\mu B < 1$) the magnetoresistance effect ($\Delta\rho/\rho$) for two-band semiconductor comes as follows [11]:

$$\frac{\Delta\rho}{\rho} = B^2 b_r \left[\left(\frac{\sigma_n}{\sigma}\mu_n^2 + \frac{\sigma_p}{\sigma}\mu_p^2\right) - \left(\frac{\sigma_n}{\sigma}\mu_n - \frac{\sigma_p}{\sigma}\mu_p\right)^2 \frac{a_r^2}{b_r}\right], \qquad (3)$$

where σ_n and σ_p are the electron and hole partial contributions, respectively to the total electrical conductivity σ; a_r and b_r are the constants, depending on scattering parameter r defining the dependence of relaxation time τ on electron energy ε: $\tau(\varepsilon) \sim \varepsilon^r$. For semimetals, the MR effect may be considered by analogy with simple

one-band case as follows [11, 19]: MR $\sim (\mu_{\text{eff}} B)^2$, where $\mu_{\text{eff}} = (\mu_n \mu_p)^{1/2}$ is an "effective" mobility that accounts contributions from electron and holes bands (Fig. 5). The carrier mobility values in Ti_2O_3 samples rapidly decreased with increasing temperature (Fig. 6), which is characteristic for the intrinsic conductivity with phonon scattering mechanism of charge carriers ($\mu \sim T^{-3/2}$) [11].

4. Conclusions

The MR effect depends strongly on both the magnetic field and the mobility value of the most mobile carriers (MR $\sim (\mu B)^2$) and therefore it allows a direct determination of μ in "problematic materials", that include (but are not limited to) inhomogeneous semiconductors, mixture of phases, materials with magnetic ordering, two-band conductivity, and others. Thus, MR data allow to reveal the electron structure (direct or indirect semiconductor gap) and charge carriers scattering mechanisms. The influences tending to the negative contribution to MR effect usually have a weaker dependence on B and may be ruled out at high fields (e.g., saturation of magnetization at Fe_3O_4). Additional impacts like high-energy particles bombardment and high pressure enhance the power of the MR method of testing.

Acknowledgments

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