

## The magnetoresistance of homogeneous and heterogeneous silver-rich silver selenide

G. Beck, C. Korte, and J. Janek<sup>a)</sup>

Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58,  
D-35392 Giessen, Germany

F. Gruhl and M. Kreutzbruck

Institut für Angewandte Physik, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16,  
D-35392 Giessen, Germany

The magnetoresistance (MR) effect of the low-temperature phase of silver selenide ( $\alpha$ -Ag<sub>2+ $\delta$</sub> Se) is measured as a function of composition. Very small composition variations in the order of  $\Delta\delta = 10^{-6}$  are achieved by coulometric titration and can be performed simultaneously during the MR measurement. A homogeneous Ag<sub>2+ $\delta$</sub> Se shows an ordinary magnetoresistance (OMR) effect, which can be well described by the two-band model. For silver selenide with a heterogeneous silver excess, we found quite a different MR behavior. Up to a minor silver excess of  $1 \times 10^{-4} < \delta < 1 \times 10^{-2}$ , a saturating negative MR effect, a linear positive MR effect, or a superposition of both can be measured. The microstructure of the silver-rich Ag<sub>2+ $\delta$</sub> Se determines its complicated MR behavior. A heterogeneous silver selenide with a larger silver excess ( $\delta > 10^{-2}$ ) shows again an OMR effect.

### I. INTRODUCTION

Due to strong technological interest (e.g., magnetic sensors and read heads in computers), the need for materials with a high magnetoresistance (MR) effect at ambient temperatures is growing. The common definition of the magnetoresistance effect is  $MR = [\rho(B) - \rho(B=0)] / \rho(B=0)$ , corresponding to the relative change of the specific electric resistivity in a homogeneous magnetic field. The ordinary MR effect (usually abbreviated as OMR) caused by the Lorentz force on drifting electronic charge carriers is generally too small for most applications. Thus, at present, the larger anisotropic MR (AMR) effect in ferromagnetic metals is used in technical applications. The discovery of an even larger MR effect in multilayer structures composed of a ferromagnetic and a nonmagnetic metal by Grünberg *et al.*<sup>1</sup> and Baibich *et al.*<sup>2</sup> promoted the interest and led to a steep rise of research activities in this field. The effect is called giant MR (GMR) effect and is already applied in read heads of hard disks. Strong efforts are now undertaken in order to understand and optimize the so-called colossal MR (CMR) effect, which is still larger than the GMR effect. It was first observed in perovskites containing magnetic transition-metal ions.<sup>3</sup> Unfortunately, the CMR effect occurs mainly at low temperatures, which currently prevents the use of the CMR effect. In any case, those MR effects that are relevant for technical applications of AMR, GMR, and CMR rely on the cooperative magnetism of the corresponding materials.

In this context, the recent observation of an unusually high MR effect in samples of the nonmagnetic silver-rich chalcogenide Ag<sub>2+ $\delta$</sub> Se by Xu *et al.*<sup>4</sup> is of appreciable interest. Xu *et al.* investigated the MR effect of bulk specimens of the

silver-rich Ag<sub>2+ $\delta$</sub> Se with the mean compositions between Ag<sub>2.01</sub>Se and Ag<sub>2.33</sub>Se. They found a large positive MR effect up to 120% at room temperature and magnetic fields of 5.5 T. Surprisingly, the magnetic-field dependence shows no evidence of saturation up to a magnetic field of 5.5 T and is linear down to 1 mT. This linear field dependence is of particular interest because the OMR effect is quadratic in B, and a linear behavior has so far only been found in polycrystalline metals in large magnetic fields. In the study by Manoharan *et al.*<sup>5</sup> and in an earlier work<sup>6</sup> by us, qualitatively comparable results for silver selenide with a linear field dependence were reported but with a smaller MR effect. The authors also proved that the size of the MR effect depends on the amount of the excess silver in the silver selenide. In a later work,<sup>7</sup> we found that the MR behavior of the silver selenide samples with a minor heterogeneous silver excess ( $1 \times 10^{-4} < \delta < 1 \times 10^{-2}$ ) strongly depends on the previous thermal treatment, and we discussed the influence of the thermal treatment on the microstructure of the system. We concluded that a silver excess in silver selenide, which is either incorporated as silver atoms on interstitial sites (undercooled solid solution) or as small silver clusters and precipitates (dispersion or colloid), is responsible for the MR behavior. These both types of supersaturation may coexist at room temperature. A material with silver atoms shows an anisotropic negative MR behavior and a system with small silver clusters shows a linear positive MR effect. For silver-rich silver telluride—a system with comparable thermodynamic, kinetic, and microstructural properties—Liang *et al.*<sup>8</sup> found also a negative MR effect.

Driven by the results by Xu *et al.*,<sup>4</sup> which cannot be explained by existing models, Abrikosov advanced a theoretical explanation for a linear MR effect.<sup>9</sup> He predicts a quantum magnetoresistance (QMR) effect for specific materials,

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: juergen.janek@phys.chemie.uni-giessen.de

which are inhomogeneous on an atomic scale, more precisely for a semiconducting matrix with dispersed metal clusters. His model further requires that the matrix is a gapless semiconductor with a linear energy spectrum. For such a hypothetical material, Abrikosov predicts a positive MR effect with a linear dependence on the magnetic field. So far, there is no experimental evidence for the existence of such a material. But Abrikosov suggests that the presence of small clusters of excess silver metal in  $\text{Ag}_{2+\delta}\text{Se}$  might cause a QMR effect.

It is the purpose of this paper to show that it is indeed a specific microstructure rather than simply the chemical composition that causes this unusual MR behavior of the silver selenide. Firstly, we prove by the MR measurements on the homogeneous single-phase  $\text{Ag}_{2+\delta}\text{Se}$  with electrochemically controlled composition (resolution better than  $\Delta\delta=10^{-6}$ ) that this material shows the OMR effect. The measured data can be described by the two-band model for the OMR effect, and the mobility of the electrons and holes in the silver selenide at 20 °C are evaluated. The results agree well with the existing data on the electronic transport properties of the material. Secondly, the silver content of  $\text{Ag}_{2+\delta}\text{Se}$  is increased electrochemically up to  $1 \times 10^{-4} < \delta < 1 \times 10^{-2}$  such that only a minor heterogeneous excess of the metal results (two-phase dispersion). This minor excess of the silver metal as a second phase already leads to a complete change of the MR behavior. In this composition regime, we found a linear positive MR effect and suprisingly a saturating negative MR effect. Thirdly, we prepared the  $\text{Ag}_{2+\delta}\text{Se}$  with a larger silver excess ( $\delta > 10^{-2}$ ) and measured the MR effect. These samples also represent the two-phase dispersions but show also an OMR effect.

Before going into detail, the phase diagram of  $\text{Ag}_{2+\delta}\text{Se}$  has to be discussed. The phase field of the binary phase  $\text{Ag}_{2+\delta}\text{Se}$  is well studied<sup>10</sup> between 75 °C and 190 °C, and the schematic phase diagram is depicted in Fig. 1. A phase transformation from the high-temperature  $\beta$  phase (Im3m) to the low-temperature  $\alpha$  phase (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) occurs at a temperature  $T$  of 133 °C. Since most potential applications of the MR effect work at room temperature, the  $\alpha$  phase is of primary interest. As it has been neglected in earlier works,<sup>4,5</sup> this phase exists only in a very small range of homogeneity under equilibrium conditions. With the decreasing temperature, the amount of silver metal, which can be solved homogeneously in silver selenide decreases even further. We determined the phase width of the low-temperature phase down to  $T=-100$  °C by means of a coulometric titration technique<sup>11</sup> and found a maximum silver (equilibrium) excess of  $\delta=0.79 \times 10^{-4}$  at  $T=20$  °C.<sup>12</sup> Thus, at room temperature, samples of the  $\alpha$  phase with a metal excess higher than  $0.79 \times 10^{-4}$  are either two-phase dispersions of Ag in the  $\text{Ag}_{2.000079}\text{Se}$  or supersaturated metastable solid solutions (in the following, a sample with a silver excess larger than the maximum equilibrium excess is named as “heterogeneous,” and we type the stoichiometric formula with quotation marks). Supersaturated silver-rich silver selenide, to be prepared by rapid quenching of Ag–Se melts, may result as a consequence of nucleation rates at low temperatures. During cooling from the melt, the  $\beta$  phase is crossed, which shows a very high diffusion coefficient for silver metal, e.g.,  $\tilde{D}_{\text{Ag}}$

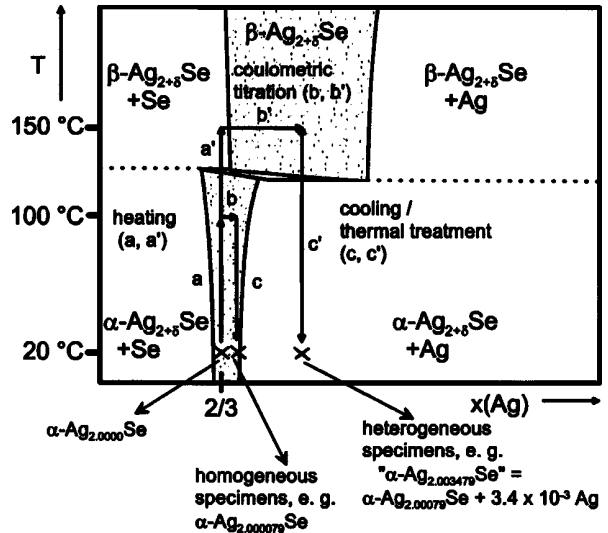


FIG. 1. Part of the phase diagram of the system silver selenide in the vicinity of the binary phase  $\text{Ag}_2\text{Se}$ . Route  $a-b-c$  indicates the synthesis of the homogeneous specimens: Heating up to  $T=100$  °C, changing the composition within the  $\alpha$  phase by coulometric titration, and cooling down again to  $T=20$  °C. Route  $a'-b'-c'$  indicates the synthesis of the heterogeneous specimens: Heating up to  $T=150$  °C, changing the composition within the  $\beta$  phase by coulometric titration, and cooling down again to  $T=20$  °C.

$=0.052 \text{ cm}^2 \text{ s}^{-1}$  at 200 °C in equilibrium with the silver.<sup>13</sup> Thus, silver diffusion is very fast, and a supersaturation can probably be created on the basis of the slow nucleation kinetics.

## II. SAMPLE PREPARATION AND MR MEASUREMENTS

In the present study, we prepared bulk  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  by a one-dimensional growth from the elements at  $T=240$  °C in a capillary.<sup>6</sup> By coulometric titration, we changed the silver excess  $\delta$  with high precision ( $\Delta\delta=10^{-6}$ ) within the magnetic field of a cryomagnet (field-variable Oxford Instruments magnet and maximal magnetic field  $B_{\text{max}}=8$  T), where we also measured the MR effect as a function of the composition using a four-probe dc technique. Figure 2 shows a micrograph of the constructed miniaturized solid-state galvanic cell combining the coulometric titration and MR measurement. By employing  $\text{Ag}_4\text{RbI}_5$  as a pure solid electrolyte, the time integral over the titration current directly corresponds (1:1) to the amount of silver metal being reversibly added to or removed from the selenide specimen. The silver electrode represents the reference electrode. All the titration and potential measurement steps are performed sequentially, thus, avoiding the use of a three-electrode cell. The procedure of changing the composition within the phase field of the  $\alpha$  phase at  $T=100$  °C is outlined in route  $a-b-c$  in Fig. 1. This treatment provides definitely homogeneous samples without silver precipitates. However, because the phase field becomes narrower with the decreasing temperature, samples with a small but well-defined heterogeneous silver excess can also be prepared. Accordingly, route  $a'-b'-c'$  in Fig. 1 denotes the procedure of changing the composition within the field of the  $\beta$  phase such as to obtain heterogeneous specimens of the  $\alpha$  phase with silver excess. Since the  $\beta$  phase field is wider than the field of the  $\alpha$  phase, the  $\beta$  phase

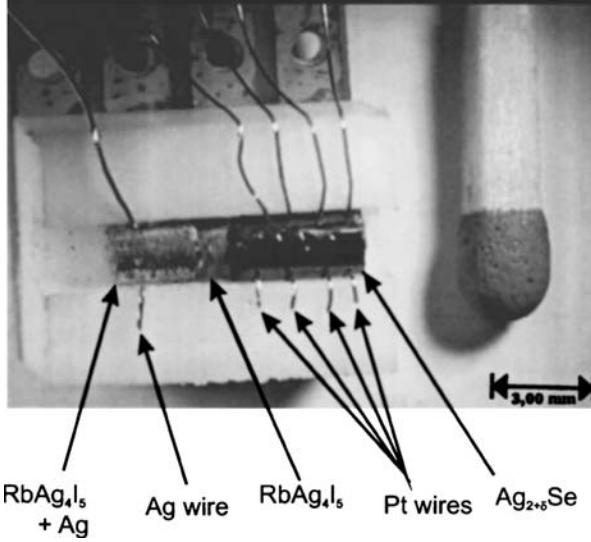


FIG. 2. Miniaturized solid-state galvanic cell for both the coulometric titration ( $\text{Ag}/\text{RbAg}_4\text{I}_5/\alpha\text{-Ag}_{2+\delta}\text{Se}/\text{Pt}$ ) and MR measurements (four Pt-probe dc arrangement is seen on the right side).

is still homogeneous with a maximum of  $\delta \cong 4 \times 10^{-3}$  at  $T = 190^\circ\text{C}$ .<sup>10</sup> By cooling a sample starting from this state below the transformation temperature, its composition runs out of the  $\alpha$  phase field, i.e., thermodynamically, the material should form a two-phase dispersion with a minor amount of the heterogeneous metal excess in the silver-saturated  $\alpha$ - $\text{Ag}_{2+\delta}\text{Se}$ . After each change of the composition, we measured the MR effect.

Samples with a silver excess larger than  $\delta \cong 4 \times 10^{-3}$  have been prepared by melting together silver and selenium in the required mass ratio in the evacuated silica ampoules. The ampoules were heated for 24 h at  $960^\circ\text{C}$  in a furnace and then cooled down to room temperature in about 2 h, as it was also done by Xu *et al.*<sup>4</sup> The MR effect of the as-prepared material was measured.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Homogeneous silver selenide

In Fig. 3, the results for the homogeneous  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  (compositions within the phase field) measured at  $T=20^\circ\text{C}$  are depicted. The MR effect is small and positive. With the increasing silver excess, the MR effect decreases. The dashed lines represent the data fit with the following equation, which is the general relationship ( $a$ ,  $b$ , and  $c$  constants) for the ordinary magnetoresistance:

$$\text{MR} = \frac{a \cdot B^2}{b + c \cdot B^2}. \quad (1)$$

The data for the samples with a metal excess of  $\delta=2 \times 10^{-6}$  and  $\delta=1.8 \times 10^{-5}$  are described perfectly by Eq. (1). The data for the samples with a metal excess of  $\delta=-6.5 \times 10^{-5}$  can also be described well by Eq. (1), but the regression coefficient (0.9929) is slightly worse. The fit can be improved by introducing a linear term ( $\text{MR}=d \cdot B + e \cdot B^2$ ) with a regression coefficient of 0.9997.

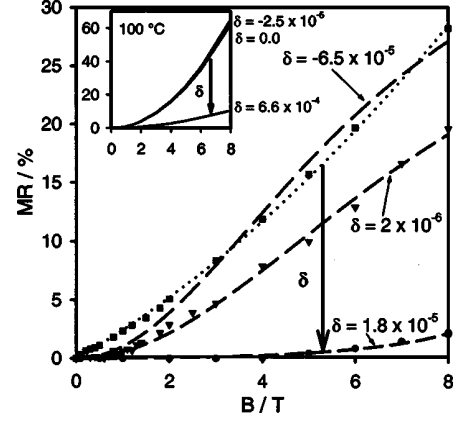


FIG. 3. MR effect of the homogeneous  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  measured at  $T=20^\circ\text{C}$  as a function of the  $B$  and  $\delta$ . Inset: OMR effect calculated via Eq. (2) for homogeneous  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  with different compositions at  $T=100^\circ\text{C}$ .

The two-band model of the OMR effect caused by the Lorentz force on the drifting charge carriers in a magnetic field always yields a positive effect with quadratic field dependence in low fields, which saturates in high fields for nonstoichiometric semiconductors.<sup>14</sup> In the most simple case of a nondegenerate semiconductor with a parabolic band structure and phonon scattering, one can calculate the OMR effect according to the following equation, which can formally be represented also by Eq. (1):

$$\text{MR} = \frac{\frac{\sigma_h \cdot \sigma_e}{e_0^2} \cdot \left( \frac{\sigma_h}{n_h} + \frac{\sigma_e}{n_e} \right)^2 \cdot B^2}{(\sigma_h + \sigma_e)^2 + \left( \frac{\sigma_h \cdot \sigma_e}{e_0} \right)^2 \cdot \left( \frac{1}{n_h} - \frac{1}{n_e} \right)^2 \cdot B^2} \cdot 100\%. \quad (2)$$

With the partial conductivities of the electrons  $\sigma_e$  and of holes  $\sigma_h$ ,

$$\sigma_e = -e_0 \cdot n_e \cdot u_e \quad (3)$$

$$\sigma_h = e_0 \cdot n_h \cdot u_h, \quad (4)$$

one only needs the mobilities of the electrons  $u_e$  and holes  $u_h$  and their densities  $n_e$  and  $n_h$  for calculating the OMR effect. The formal analysis of the coulometric titration provides the densities of the electrons and holes in the stoichiometric sample for  $\delta=0$  ( $n_e^\#$  and  $n_h^\#$ ).<sup>12</sup>

Assuming that a homogeneous metal excess of  $\delta$  in  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  dissociates completely to ions and electrons, we can also determine the charge-carrier densities for the nonstoichiometric compositions. The mobilities at  $T=100^\circ\text{C}$  have been determined by Junod.<sup>15</sup> He reports the values of  $|u_e| \cong 0.2 \text{ m}^2/\text{Vs}$  and  $u_h \cong 5 \times 10^{-2} \text{ m}^2/\text{Vs}$ . Inserting these mobility data and the charge carrier density data from Korte<sup>16</sup> in Eq. (2), we have calculated the OMR effect for  $T=100^\circ\text{C}$ , which is depicted in the inset of Fig. 3. Due to the different temperatures used in the calculation (corresponding mobility data are not available for lower temperatures) and in the experiment, we cannot directly compare the theory and the measurements. But the experimental results can be interpreted at least qualitatively. An increased silver

concentration should lead to a smaller MR effect and, indeed, we find this dependence for the compositions within the phase field (Fig. 2). Also, we find that the MR effect should not saturate up to a magnetic field of 8 T, as measured. As already mentioned previously, the measured data can be fitted satisfactorily by Eq. (1), whereas the data for the sample with the metal excess of  $\delta = -6.5 \times 10^{-5}$  are better fitted with an equation including a linear and a quadratic term. This small discrepancy might indicate that the structure of the energy spectrum of the electrons is more complicated and changes with the silver excess. Nevertheless, the comparison between the theory and the experimental results shows that the magnetoresistance of the homogeneous silver selenide can, without doubt, be interpreted as an ordinary magnetoresistance. It is worth noting that only coulometric titration offers the possibility of such a precise charge-carrier control *in situ*, i.e. within the magnetic field, using the same specimen for all the experiments but with different charge-carrier concentrations.

From the fitting parameters and by inserting the charge-carrier densities  $n_e$  and  $n_h$  from the coulometric titration,<sup>12</sup> we determined the mobility of the electrons and holes at  $T = 20^\circ\text{C}$  on the basis of Eq. (2). We find that  $|u_e| \cong 0.7 \text{ m}^2/\text{Vs}$  and  $u_h \cong 2 \times 10^{-2} \text{ m}^2/\text{Vs}$ . A comparison of these data with the data of Junod<sup>15</sup> shows that the mobility of the electrons increases and the mobility of the holes decreases with the decreasing temperature. The mobility of the delocalized electrons should indeed rise with the decreasing temperature because the phonon scattering is reduced upon the decreasing temperature ( $u_e \propto T^{-3/2}$ ). The much lower mobility of the holes indicates a polaron character. In this case,  $u_h$  should indeed fall with the decreasing temperature according to  $u_h \propto \exp^{-E_H/kT}$ , with  $E_H$  as the activation energy for hopping.

Comparing  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  and its OMR effect with other semiconductors—where the OMR effect equals usually only a few percent—the effect is relatively large as can be seen from Fig. 3. This is readily understood on the basis of Eq. (2), where the partial conductivities can be expressed by Eqs. (3) and (4). Introducing the dimensionless charge-carrier densities  $\alpha_e$  and  $\alpha_h$  (normalized by the charge-carrier concentrations of the intrinsic, stoichiometric material),

$$\alpha_e = \frac{n_e}{n_e^\#} \quad (5)$$

$$\alpha_h = \frac{n_h}{n_h^\#}, \quad (6)$$

and the mobility ratio  $\Psi_e$ ,

$$\Psi_e = -\frac{u_e}{u_h}, \quad (7)$$

Eq. (2) can be rewritten as

$$\text{MR} = \frac{-\Psi_e(\Psi_e + 1)^2 \alpha_e^2 \cdot B^2}{\frac{1}{u_h}(\Psi_e \alpha_e^2 + 1)^2 + \Psi_e^2(\alpha_e - 1)^2 \cdot B^2} \cdot 100\% . \quad (8)$$

TABLE I. OMR effect for systems with different mobilities and charge-carrier densities according to Eq. (8).

		$\Psi_e = 1$	$\Psi_e \gg 1$	$\Psi_e \ll 1$
$\alpha_e \gg 1$	$B$ small	$4u_h^2/\alpha_e^2 \cdot B^2$	$ u_e u_h/\alpha_e^2 \cdot B^2$	$ u_e u_h/\alpha_e^2 \cdot B^2$
	$B$ large	$4/\alpha_e^2$	$ u_e /u_h \alpha_e^2$	$u_h/ u_e  \alpha_e^2$
$\alpha_e = 1$		$u_h^2 \cdot B^2$	$ u_e u_h \cdot B^2$	$ u_e u_h \cdot B^2$
$\alpha_e \ll 1$	$B$ small	$4u_h^2 \alpha_e^2 \cdot B^2$	$ u_e ^3/u_h \alpha_e^2 \cdot B^2$	$ u_e u_h \alpha_e^2 \cdot B^2$
	$B$ large	$4\alpha_e^2$	$ u_e /u_h \alpha_e^2$	$u_h/ u_e  \alpha_e^2$

In Table I, the different limiting cases are considered. In most semiconductors—like silver selenide—the mobility of the electrons is larger than that of the holes and the middle row of the cases applies. And it is easily checked that in any case, the stoichiometric material provides the largest MR effect determined by the product of both mobilities. With both charge carriers, electrons and holes, being delocalized, the MR effect should always decrease with the increasing temperature. In the case of the silver selenide, the MR effect is less temperature dependent, as the hole mobility increases with the temperature.

## B. Heterogeneous silver/silver selenide

Firstly, we consider the results for the composition regime with a small silver excess ( $1 \times 10^{-4} < \delta < 1 \times 10^{-2}$ ). Figure 4 represents the MR effect for the composition of “ $\alpha\text{-Ag}_{2.000687}\text{Se}$ ” at  $T = 20^\circ\text{C}$ . The negative MR effect saturates with increasing magnetic field. Figure 5 shows the MR effect for a sample with the composition of “ $\alpha\text{-Ag}_{2.004}\text{Se}$ ” at  $T = 30^\circ\text{C}$ . Here, a linear positive MR effect has been found and in the inset in the figure, it can be seen that the linear field dependence is valid down to about 0.1 T. As we have shown elsewhere<sup>7</sup> in this composition regime, the linear positive MR effect can be transformed to a saturating negative MR effect or in reverse order by the thermal treatment, i.e., by changing the microstructure of the excluded silver excess.

For samples with a higher silver excess ( $\delta > 10^{-2}$ ), we found a different MR behavior. In Fig. 6, the results for the composition of “ $\alpha\text{-Ag}_{2.33}\text{Se}$ ,” (which corresponds to the material investigated by Xu *et al.*<sup>4</sup>) at  $T = -143^\circ\text{C}$  are shown. This sample shows an OMR effect. The size of this effect increases with the decreasing temperatures (Fig. 7). The MR

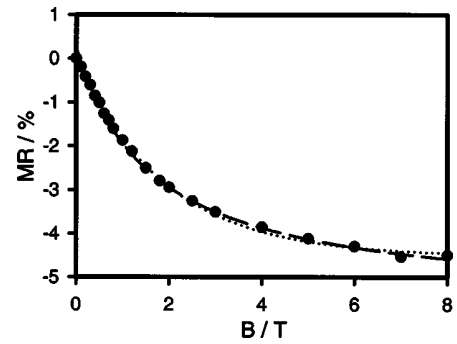


FIG. 4. Measured MR effect of the heterogeneous “ $\alpha\text{-Ag}_{2.000687}\text{Se}$ ” at  $T = 20^\circ\text{C}$  as a function of the magnetic field. The dotted lines show the results of the fit with a saturating negative function [ $f = y_0 + a \cdot \exp(-b \cdot x)$ ].



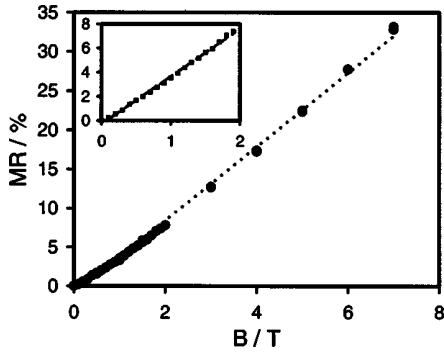


FIG. 5. Measured MR effect of the heterogeneous “ $\alpha\text{-Ag}_{2.004}\text{Se}$ ” at  $T = 30\text{ }^\circ\text{C}$  as a function of the magnetic field. The dotted line shows the results of the linear fit. Inset in Fig. 5: Magnified part of the graph.

effect of the samples with this high silver excess shows no sensitivity on the thermal treatment. In this composition regime, the silver excess always forms precipitates with a typical diameter of a few micrometers with the typical appearance of eutectic binary material (Fig. 8).

Based on our experimental results, we conclude that the MR behavior of  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  with different amounts of excess silver is by far more complicated than expected for a conventional nonmagnetic semiconductor. The homogeneous single-phase material shows the typical OMR effect of a diamagnetic semiconductor with near-intrinsic charge-carrier concentrations. The presence of both charge carriers, electrons and holes, prevents the establishment of the Hall field in the magnetic field. The homogeneity requires that all the excess metal atoms are built in as point defects. Adding silver to the stoichiometric material produces an  $n$ -doped semiconductor ( $\delta > 0$ ). This metal doping can be expressed as (building units)



Removing silver ( $\delta < 0$ ) produces a  $p$ -doped semiconductor. This can be expressed as



In an  $n$ -doped material, the excess silver ions form the interstitial defects  $\text{Ag}^*$ , and the electrons fill vacant states in the conducting band  $e'$ . In a  $p$ -doped material, the removal of the silver yields a vacancy in the regular silver lattice

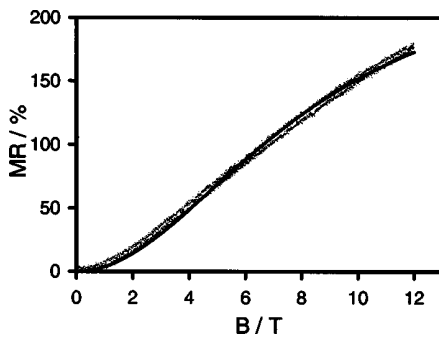


FIG. 6. Measured MR effect of the heterogeneous “ $\alpha\text{-Ag}_{2.33}\text{Se}$ ” at  $T = -143\text{ }^\circ\text{C}$  as a function of the magnetic field. The lines show the results of a fit with Eq. (1). The points represent the measurement.

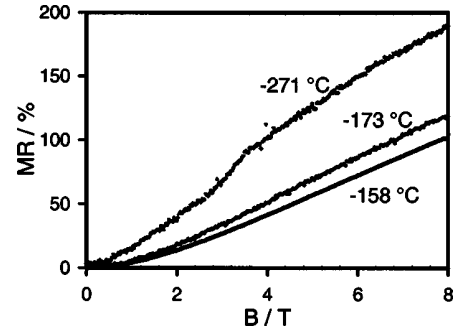


FIG. 7. Measured MR effect of the heterogeneous “ $\alpha\text{-Ag}_{2.33}\text{Se}$ ” at the different temperatures as a function of the magnetic field.

$|\text{Ag}'|$  and a hole in the valence band  $h^*$ . An experimental work by Korte and Janek<sup>17</sup> proves that Eq. (9) is indeed valid for the high silver activities and Eq. (10) is valid for the low silver activities in the homogeneous  $\alpha\text{-Ag}_{2+\delta}\text{Se}$ , i.e., the donor or acceptor is completely ionized. The electronic conductivity is almost independent from the silver excess due to the small band gap and the high intrinsic electronic charge-carrier concentration. In the silver-rich  $n$ -doped material, the OMR effect is reduced (Fig. 3) as described by Eq. (8). So far, homogeneous  $\alpha\text{-Ag}_{2+\delta}\text{Se}$  behaves completely like a typical semiconductor, however, with a reasonably high OMR effect, due to the unusually large product of the  $u_e$  and  $u_h$ .

The MR behavior deviates from the OMR effect for specimens with a metal excess being larger than the maximum equilibrium excess. Samples with a minor heterogeneous silver excess up to  $\delta < 10^{-2}$  show an unusual MR behavior. We found a saturating negative and a linear positive MR effect. In our previous work,<sup>7</sup> we discuss the possible microstructures of the heterogeneous silver excess, which can be expected in this composition regime. We speculate that nanoscale silver clusters, originating from the nucleation at extended lattice defects in the semiconductor matrix, might be responsible for the unusual positive and linear MR effect (Figs. 4 and 5). In this case, the linear contribution to the MR effect might be explained theoretically by the QMR model of Abrikosov.<sup>9</sup>

As also discussed in our previous work,<sup>7</sup> the negative MR effect is found in samples where the excess silver probable exists in the form of silver atoms on interstitial sites as a supercooled solid solution. These isolated silver atoms

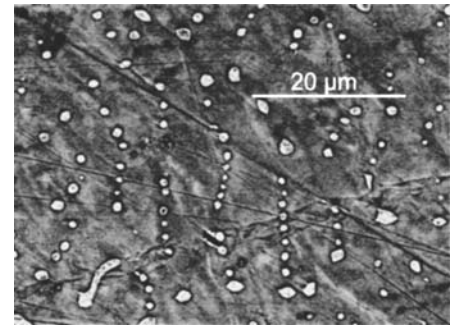


FIG. 8. HSEM image of a cross section of “ $\alpha\text{-Ag}_{2.33}\text{Se}$ .” Excess silver forms precipitates of a few micrometers size. This silver precipitates are arranged chainlike in the silver selenide matrix.

should have magnetic moments ( $4s^1$ ), and thus, the negative MR effect might be explained by a combination of the model for an AMR effect and the model of Toyozawa.<sup>18</sup> Both forms of the silver distribution may coexist in the metastable material<sup>23</sup> and lead to a superposition of both MR effects.

Figure 6 shows that in samples with a larger silver excess ( $\delta > 10^{-2}$ ), again, an OMR effect is measured. In this case, the metal/semiconductor dispersion behaves like a conventional semiconductor, but the observed OMR effect can of course not be explained with the ordinary two-band model, as the material is not homogeneous.

In conclusion, only the silver-rich  $\alpha$ -Ag<sub>2+ $\delta$</sub> Se with a small heterogeneous silver excess ( $1 \times 10^{-4} < \delta < 1 \times 10^{-2}$ ) shows an unusual MR behavior. The homogeneous silver selenide can be regarded as a typical semiconductor with an OMR effect being large due to the advantageous combination of the mobilities. Also a silver selenide with a large heterogeneous silver excess ( $\delta > 10^{-2}$ ) shows an OMR effect.

Recent work by other groups emphasizes both the practical and theoretical relevance of the unusual MR effect in the silver-rich silver selenide. In a theoretical work, Parish and Littlewood attempt to explain the linear MR effect in the silver chalcogenides by a simulation of a random network of the microscopic (four terminal) resistors.<sup>19,20</sup> For such a heterogeneous conductivity distribution, they obtain a linear positive and nonsaturating MR effect, which however, still appears at the much higher critical fields than the linear MR effect in the  $\alpha$ -Ag<sub>2+ $\delta$</sub> Se. Von Kreutzbruck *et al.* interpret conductivity data for silver selenide over a very wide range of composition by a percolation model, assuming a nanoscale network of silver precipitates in the grain boundaries and the bulk.<sup>21</sup> Husmann *et al.*<sup>22</sup> successfully used the  $\alpha$ -Ag<sub>2+ $\delta$</sub> Se as a high-field sensing material as it did not show saturation up to pulsed fields of 55 T.

## ACKNOWLEDGMENTS

The authors thank Professor P. Heitjans and Dr. S. Indris for their technical support. Financial support by the FCI (Fonds der Chemischen Industrie) and the DFG is gratefully acknowledged.

- <sup>1</sup>P. Grünberg, R. Schreiber, Y. Pang, M. B. Brodsky, and H. Sowers, *Phys. Rev. Lett.* **57**, 2442 (1986).
- <sup>2</sup>M. N. Baibich *et al.*, *Phys. Rev. Lett.* **61**, 2472 (1988).
- <sup>3</sup>K. Chahara, T. Ohno, M. Kasai, Y. Kanke, and Y. Kozono, *Appl. Phys. Lett.* **62**, 780 (1993).
- <sup>4</sup>R. Xu, A. Husmann, T. F. Rosenbaum, M. L. Saboungi, and B. P. Littlewood, *Nature (London)* **390**, 57 (1997).
- <sup>5</sup>S. S. Manoharan, S. J. Prasanna, D. E. Kiwitz, and C. M. Schneider, *Phys. Rev. B* **63**, 212405 (2001).
- <sup>6</sup>G. Beck and J. Janek, *Physica B* **308–310**, 1086 (2001).
- <sup>7</sup>G. Beck and J. Janek, *Phys. Rev. B* (submitted).
- <sup>8</sup>B. Q. Liang, X. Chen, Y. J. Wang, and Y. J. Tang, *Phys. Status Solidi B* **215**, 1145 (1999); *Phys. Rev. B* **61**, 3239 (2000).
- <sup>9</sup>A. A. Abrikosov, *Phys. Rev. B* **58**, 2788 (1998); *Europhys. Lett.* **49**, 789 (2000).
- <sup>10</sup>U. von Oehsen and H. Schmalzried, *Ber. Bunsenges. Phys. Chem.* **85**, 7 (1981).
- <sup>11</sup>C. Wagner, *J. Chem. Phys.* **21**, 1816 (1953).
- <sup>12</sup>G. Beck and J. Janek, *Solid State Ionics* **170**, 129 (2004).
- <sup>13</sup>B. Hartmann, H. Rickert, and W. Schendler, *Electrochim. Acta* **21**, 319 (1976).
- <sup>14</sup>A. I. Anselm, in *Einführung in die Halbleitertheorie* (Akademie, Berlin, 1962).
- <sup>15</sup>P. Junod, *Helv. Phys. Acta* **32**, 567 (1959).
- <sup>16</sup>C. Korte, Ph.D. thesis, Universität Hannover, 1997.
- <sup>17</sup>C. Korte and J. Janek, *Z. Phys. Chem. (Munich)* **206**, 129 (1998).
- <sup>18</sup>Y. Toyozawa, *J. Phys. Soc. Jpn.* **17**, 579 (1962).
- <sup>19</sup>M. M. Parish and P. B. Littlewood, *Nature (London)* **426**, 162 (2003).
- <sup>20</sup>T. F. Rosenbaum, *Nature (London)* **426** (6963), 135 (2003).
- <sup>21</sup>M. von Kreutzbruck, B. Mogwitz, F. Gruhl, C. Korte, and J. Janek, *Appl. Phys. Lett.* (submitted).
- <sup>22</sup>A. Husmann, J. B. Betts, G. S. Boebinger, A. Migliori, T. F. Rosenbaum, and M. L. Saboungi, *Nature (London)* **417**, 421 (2002).
- <sup>23</sup>Y. Kumashiro, T. Chachi, and I. Taniguchi, *Solid State Ionics* **86–88**, 761 (1996).