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H. S. Schnyders, M.-L. Saboungi, and T. F. Rosenbaum

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Magnetoresistance in *n*- and *p*-type Ag_2Te: Mechanisms and applications

H. S. Schnyders[a] and M.-L. Saboungi
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

T. F. Rosenbaum[b]
The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637

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We compare the large magnetoresistive response of slightly nonstoichiometric $Ag_{2\pm\delta}Te$ for a wide range of hole ($p \leqslant 8\times10^{17}\,cm^{-3}$) and electron ($n \leqslant 4\times10^{18}\,cm^{-3}$) carrier densities. In the *p*-type material alone, a characteristic peak in the resistivity $\rho(T,H)$ is dramatically enhanced and moves to higher temperature with increasing magnetic field, resulting in a high field ($H\sim5\,T$) magnetoresistance that is sizeable even at room temperature. By contrast, *n*-type specimens are geared for low-field ($H<0.1\,T$) applications because of a striking linear field dependence of the magnetoresistance that appears to be restricted to the Ag-rich materials. © *2000 American Institute of Physics.* [S0003-6951(00)02013-1]

The semiconducting phases of the silver chalcogenides, Ag_2S, Ag_2Se, and Ag_2Te, historically have received less attention than other semiconductors with narrow band gaps and high carrier mobilities. Perfectly stoichiometric material has negligible magnetoresistance,[1] but recent experiments[2] have shown that small amounts of excess silver lead to large magnetoresistive effects on a scale comparable to the ''colossal'' magnetoresistance (CMR) compounds.[3] Elements of narrow gap semiconductor physics apply, but the size of the effects at room temperature, the absence of saturation at magnetic fields much larger than the cyclotron scale, and the linear field dependence down to a few Oersteds are surprising new features.[2] Technological prospects have been aided by the successful demonstration of a positive magnetoresistance of almost 400% at magnetic field $H=5\,T$ in thin films of Te-rich Ag_2Te.[4]

As with any new system, attempting to optimize the response of the silver chalcogenides involves the consideration of a large number of experimental parameters. The most important of these appear to be the effects of chemical composition, including the sign, number[2,5] and mobility[6] of the carriers, and the influences of modulated structure, including grain boundaries[7] and reduced dimensionality. In this letter, we systematically compare the magnetoresistance (MR) of Ag- and Te-rich samples of bulk Ag_2Te. Doping by holes and by electrons leads to very different magnetic field and temperature characteristics, with implications both for models of the underlying physics and for applications.

Appropriately weighted amounts of high purity Ag (99.999%, Alfa Aesar) and Te (99.9999% pure, metals basis, Alfa Aesar), sealed in quartz tubes under a vacuum better than 5 millitorr, were melted to create polycrystalline samples at desired stoichiometries, $-5\times10^{-4}<\delta<1.2\times10^{-3}$. The compound was rocked at 50 °C above the reported melting point to ensure complete mixing. Slowly cooled samples were cut perpendicular to the long axis of the cylindrical boule to avoid dopant variations due to small temperature gradients in the furnace. In addition, they were fashioned as long narrow pieces of typical dimensions ($5\times1\times1$)mm^3 to circumvent the geometrical effects that have been associated with high carrier mobility semiconductors.[8] We performed four-probe resistivity and five-probe Hall coefficient measurements in fields up to 5.5 T using a conventional ac bridge technique in the ohmic and frequency-independent limits. The relative error in the resistivity is less than 0.01%; there is an absolute uncertainty, however, of 20% because of the finite extent of multiple InBi solder contacts on samples of millimeter dimensions.

We contrast in Fig. 1 the temperature *T* dependence of the resistivity ρ at a series of magnetic fields *H* for representative *n*- and *p*-type polycrystalline material. Both Ag- and Te-rich samples exhibit a steep rise of the resistivity with decreasing temperature in the intrinsic regime, but differ

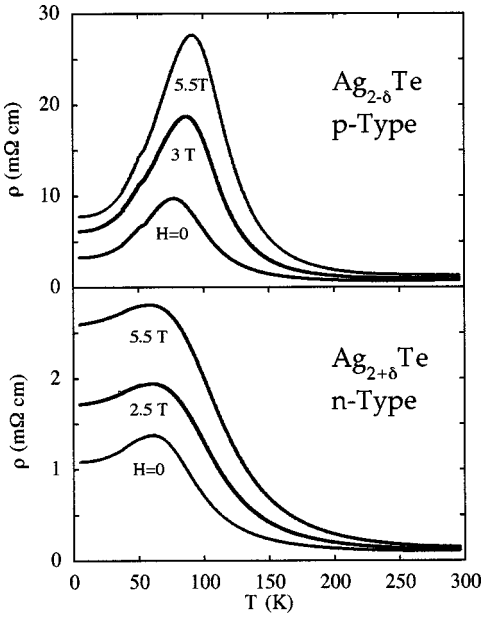

FIG. 1. Resistivity ρ vs temperature *T* at a series of magnetic fields *H* for representative hole and electron doped silver telluride. The *p*-type samples are marked by a resistivity maximum whose shape and position vary strongly with field.

[a]Also at the James Franck Institute, University of Chicago.
[b]Electronic mail: t-rosenbaum@uchicago.edu

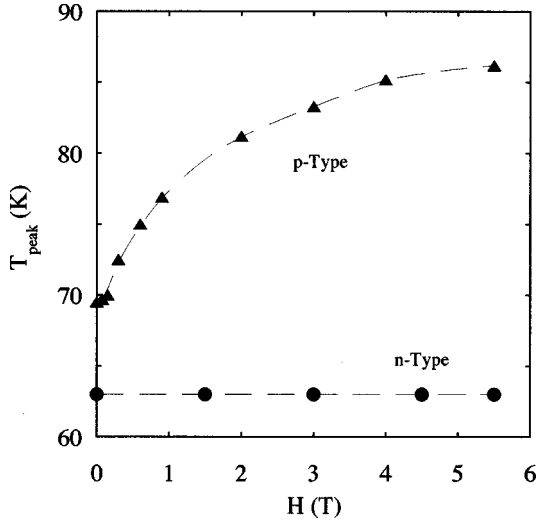

FIG. 2. Movement of the peak in the resistivity, T_{peak}, with applied field H.

markedly in the low temperature, extrinsic regime. Hole-doped polycrystals display a large peak in $\rho(T,H)$ that grows in size and moves to higher T with increasing H. For the sample shown here, the resistivity maximum at $H=5.5\,\mathrm{T}$ is 250% of its 5 K value; doping from $p=7.6\times10^{16}$ to $8\times10^{17}\,\mathrm{cm}^{-3}$ yields enhancements from 25% to 800%. By comparison, electron doping in the range 1.5×10^{17} to $4\times10^{18}\,\mathrm{cm}^{-3}$ produces a $\rho(T,H)$ characterized by a modest peak, barely amplified over its $T=5$ K value, with a fixed location in T and a shape that only evolves subtly with H.

We plot in Fig. 2 the movement of the peak in the resistivity, T_{peak}, with applied field. The pronounced peak in $\rho(T,H)$ for hole-doped samples moves quickly to higher T for $H>0.1\,\mathrm{T}$, saturating by $H\sim5\,\mathrm{T}$. By contrast, T_{peak} is independent of H for electron-doped material. The sensitivity of T_{peak} to H has important ramifications for the temperature dependence of the magnetoresistance. Huge enhancements in the magnetoresistance are found for temperatures just above T_{peak}, and extend to lesser degree all the way up to room temperature. We illustrate in Fig. 3 the temperature dependence of $\Delta\rho/\rho$ for bulk polycrystals at $H=5.5\,\mathrm{T}$ and note its consistency with the results on thin films of $Ag_{2-\delta}Te$.[4]

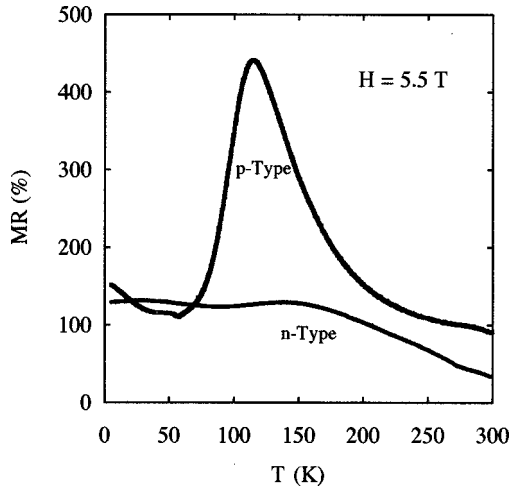

FIG. 3. Contrast of the temperature dependence of the magnetoresistance (MR) at high field for hole and electron doped samples.

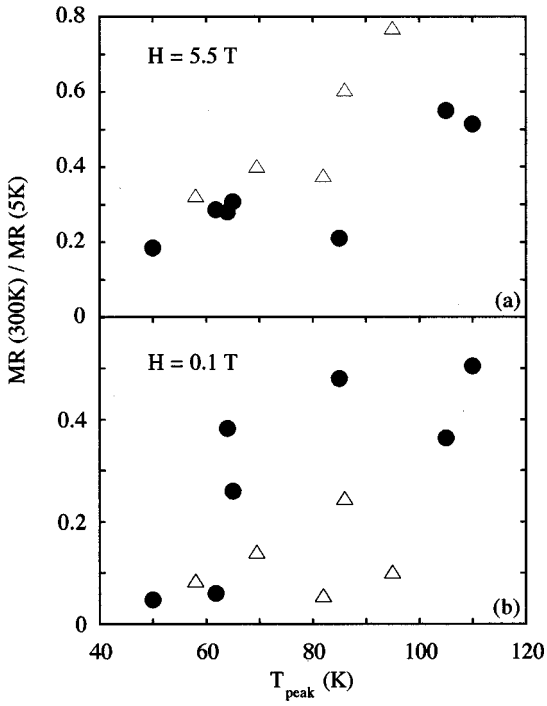

FIG. 4. The ''retention ratio'' of the magnetoresistance between room and liquid helium temperatures at (a) high field and (b) low field. Open triangles are *p*-type samples; filled circles are *n*-type samples. The sensitivity of the resistivity maximum to H makes *p*-type samples most suitable for high-field applications.

These general tendencies in MR(T) are not observed for $Ag_{2+\delta}Te$, although the small variations in T seen in Fig. 3 for an *n*-type sample also can be linked to (slight) modifications with H of the high temperature side of the resistivity maximum.

The persistence to room temperature of a sizeable magnetoresistance depends crucially on the presence of a peak in MR(T). In this context it is important to note that the behavior of $\rho(T,H)$ with increased Te doping mirrors the effects of increasing induction.[9] The enhancement of the resistivity maximum and its movement to higher temperature with H and p makes hole doping the preferred strategy for creating materials suitable for high field applications. We parameterize in Fig. 4(a) the salient high field characteristics by plotting the ''retention ratio,'' MR($T=300\,\mathrm{K}$)/MR($T=5\,\mathrm{K}$) at $H=5.5\,\mathrm{T}$, as a function of T_{peak} for both *n*- and *p*-type samples. As T_{peak} increases steadily with increasing δ (up to 110 and 95 K for electrons and holes, respectively), the retention ratio continues to improve. The effect is most marked for hole-doped material, where T_{peak} is most sensitive to H.

At $H=0.1\,\mathrm{T}$, however, the story is different. In this lower field regime, *n*-type material is the material of choice, with a considerably larger retention ratio [Fig. 4(b)]. The reasons are twofold: (i) as shown in Fig. 2, T_{peak} does not move to higher T for $H\leqslant0.1\,\mathrm{T}$ in either $Ag_{2-\delta}Te$ or $Ag_{2+\delta}Te$; and (ii) the magnetoresistance falls off more slowly with decreasing field in the case of $Ag_{2+\delta}Te$. With the enhancement and movement of T_{peak} with H mitigated in the small field regime, the functional form of $\rho(H)$ becomes the determining factor. As seen in Fig. 5, the *n*-type samples maintain a linear behavior down to surprisingly small fields; *p*-type samples are subquadratic, but still nonlinear in H be-

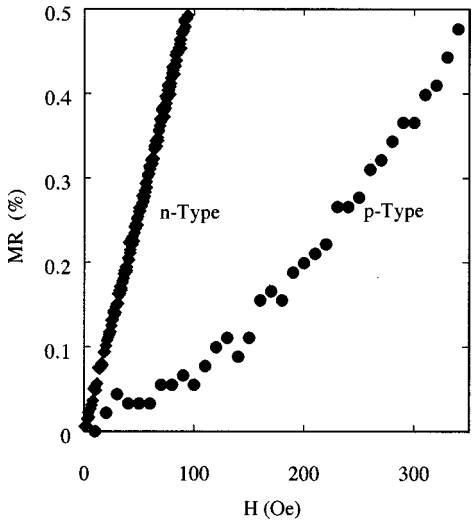

FIG. 5. The magnetoresistance vs H at small fields. The unusual linear dependence found in $Ag_{2+\delta}Te$ makes n-type samples most suitable for low-field applications [Fig. 4(b)].

low 0.1 T even at $T=5$ K. By room temperature, p-type samples approach the usual quadratic field dependence. The two samples shown in Fig. 5 ultimately reach the same $\mathrm{MR}(H=5.5\,\mathrm{T})=350\%$, but the early effects of linearity give a clear advantage to n-type samples as low field sensors.

A multiband model can be used to heuristically describe the magnetoresistance.[10] A hole to electron mobility ratio that varies with either carrier concentration or magnetic field can account for a shift in T_{peak}, and may play a role in systems ranging from traditional narrow gap semiconductors like InSb[11] to semimetallic Bi nanowires.[12] In the latter example, quantum confinement effects appear to be important. It is not clear to what extent quantum effects,[13] perhaps involving mesoscopic regions of excess Ag or Te, bear on the unusual field and temperature dependence of the magnetoresistance in the silver chalcogenides.

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