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MAGNETORESISTANCE AND ELECTRICAL NOISE IN THE SILVER CHALCOGENIDE Ag_2Te

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The relatively large and linear magnetoresistance found in nonstoichiometric silver chalcogenides makes them attractive candidates for studying the mechanisms of linear magnetoresistance and for field sensing applications. After a brief review of the magnetoresistive properties of these materials, we report on the intrinsic electrical noise in bulk, polycrystalline $Ag_{2+\delta}Te$. Low-frequency noise is due to resistance fluctuations having a 1/*f*-like power spectrum. The temperature dependence of the noise magnitude and its spectral slope indicate thermally activated kinetics which we attribute to some form of charge trapping-detrapping process occurring in or near the intergranular regions. The effective magnetic field noise in $Ag_{2+\delta}Te$ is also compared to other materials systems used in field sensing applications.

Keywords: Magnetoresistance semiconductor 1/*f* noise charge trapping.

1. Introduction

Narrow-gap semiconductors are generally considered to be the weaker sibling in the family of semiconducting materials, ranking behind ‘normal’ semiconductors such as silicon and gallium arsenide. The most renowned narrow-gap semiconductors are from the II-VI compounds such as mercury-cadmium-telluride (HgCdTe) which has found applications in a variety of fields, including: medicine and astronomy. Less celebrated are the class of I-VI semiconductors of which the silver chalcogenides are an example. The scientific and technological interest in these materials stems from the extremely high sensitivity of their band structure to external effects such as magnetic field, light, temperature, pressure, impurities, etc.

Silver telluride is a member of the silver chalcogenide family of non-magnetic, self-doped, degenerate, narrow band gap semiconductors. Although the stoichiometric material (β-Ag_2Te) exhibits no appreciable magnetoresistance [1,2], large magnetoresistive effects have been reported for small deviations from stoichiometry [3]. These effects include resistance increases of up to 200% at room temperature and in a magnetic field of ~

50 kOe. The magnetic response found in Ag-rich material is surprisingly linear, down to a few Oersteds, making it an attractive candidate for low field applications. Te-rich material seems most suitable for high-field applications, maintaining a high-field magnetoresistance that is sizeable even at room temperature and does not saturate at magnetic fields much larger than the cyclotron scale [4]. Recent pressure-dependence studies have highlighted the importance of carrier density to the magnetoresistance (MR); maximal MR and minimal onset field for linearity were observed at perfect compensation [5].

Conventional theory is incapable of explaining these observations. Based on the quasiclassical treatment of electrons and the Boltzman transport equation [6], the orbital magnetoresistance of a metal is controlled by the ratio of the cyclotron frequency to the scattering rate, $\omega_c\tau = eH\tau/m^*c$. Explicitly, $\Delta\rho \propto \rho_0(\omega_c\tau)^2$ for $\omega_c\tau \ll 1$, and $\Delta\rho \propto \rho_0$ for $\omega_c\tau \gg 1$, where τ is the collision time, ρ_0 is the resistivity in zero field, and e is the electron charge. Doped narrow-gap semiconductors have small effective electron masses, $m^* \approx 0.02m_e$, which gives a large magnetoresistance. Hence, one expects a positive magnetoresistance, scaling as H^2 at low field, and saturating for $\omega_c\tau > 1$.

One possible explanation is based on the assumption that doping results in samples that are highly *inhomogeneous*, so that they contain small regions (clusters) with a large concentration of excess silver atoms that are doping the rest of the material with a low concentration of electrons. Under these conditions, Abrikosov has proposed that an essential ingredient for linear magnetoresistance in both small and large field limits is a semiconducting gap that approaches zero with a linear energy spectrum [7].

In this paper, electrical noise is employed to probe and to illuminate further the nature of conduction in these materials. For technological prospects the detection sensitivity to resistance changes will be limited by the intrinsic noise of the material. Characterizing this noise and identifying its origin is then particularly relevant to making materials with optimal properties for magnetic field sensing applications.

2. Experimental

Bulk, polycrystalline samples of silver rich (*n*-type) and silver deficient (*p*-type) β-$Ag_{2+\delta}Te$ material were made by a melt-doping process whereby appropriately weighed quantities of high purity Ag and Te were sealed in quartz tubes under vacuum better than 5 millitorr and then melted to create polycrystalline samples [4]. 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. The stoichiometric index, δ, of these samples ranged from approximately –0.0005 to 0.0009.

We cut specimens with typical dimensions of 1 mm wide and 3 mm long and then mechanically polished them to a thickness of approximately 0.2 mm. Wire leads were ultrasonically soldered to each corner of the specimen. A low melting point Indium alloy solder was used to prevent heating the specimen above 400 K and transforming it into its high temperature (α) phase [2]. Four-probe resistance and noise measurements were performed in applied magnetic fields up to 90 kOe, oriented perpendicular to the direction of the current. Due to the finite extent of the In pads there can be up to 50% error in the absolute value of the resistance. Noise measurements were performed under constant current conditions by using a battery and a ballast resistor.

3. Results and Discussion

3.1. *Resistivity*

The temperature dependence of the resistivity, $\rho(T)$, is plotted in Fig. 1 for a series of dopings. $\rho(T)$ reflects the behavior of a narrow-gap semiconductor. In the extrinsic regime ($T < 60$ K for these samples), the resistivity is nearly independent of temperature because effective carrier density is constant [3]. At higher T, the carrier density becomes activated and the resistivity decreases with increasing T as expected in the intrinsic regime.

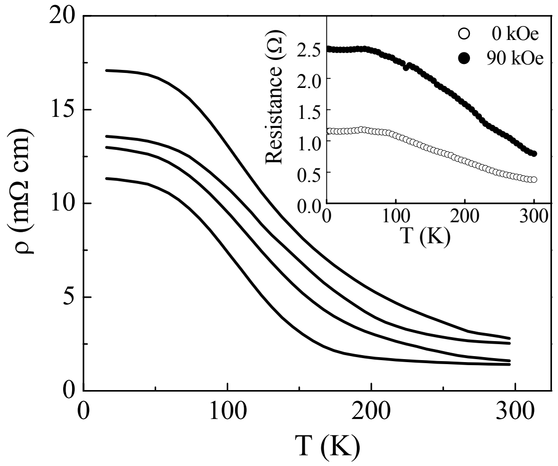

Fig. 1. Resistivity of $Ag_{2+\delta}Te$ as a function of temperature for a series of dopings: from top to bottom $\delta \approx -0.0005$, 0, 0.0005, and 0.0009. The inset shows the effect of a 90 kOe magnetic field on the resistance and its temperature dependence for an *n*-type sample.

In the inset to Fig. 1 we contrast the temperature dependence of the resistance of a representative *n*-type sample measured in zero and a 90 kOe magnetic field. A magnetic field increases the material's resistivity but leaves the general form of its temperature dependence largely unchanged. The large size and magnetic field dependence of the normalized magnetoresistance, $\Delta\rho(T,H)/\rho(T,0)$, can be seen explicitly in Fig. 2 for the same *n*-type sample. There is no evidence of saturation up to at least 90 kOe over the entire temperature range. $\Delta\rho/\rho$ increases linearly with increasing H above a few kOe at 150 K. The linear dependence of $\Delta\rho/\rho$ on H is most pronounced at temperatures for which the MR is maximal, with a tendency towards slightly superlinear dependence below tens of kOe at other temperatures. The inset shows that $\Delta\rho_{H=90kOe}/\rho \approx 110\%$ at room temperature and varies weakly with temperature, peaking at 135% around 200 K. Since our samples are close to stoichiometry, the observed magnetoresistance is smaller and the onset of linearity is at higher fields compared to previous reports [3] on samples with $\delta \sim 0.01$.

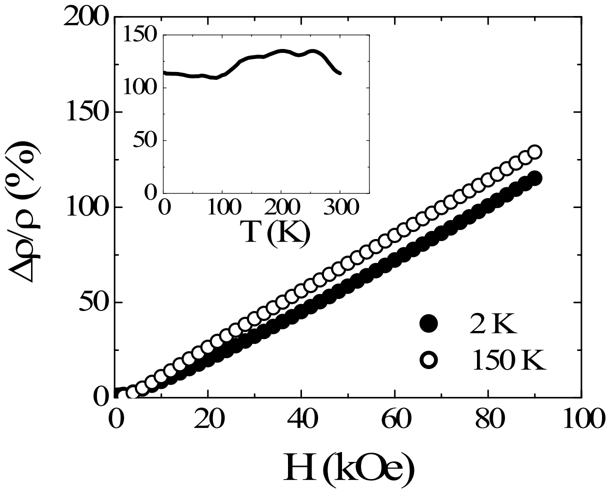

Fig. 2. The normalized magnetoresistance $\Delta\rho(T,H)/\rho(T,0)$ for a representative *n*-type sample as a function of magnetic field *H*. The magnetoresistance increases linearly with H at high fields and with no sign of saturation. Inset, the temperature dependence of $\Delta\rho/\rho$ measured at $H = 90$ kOe.

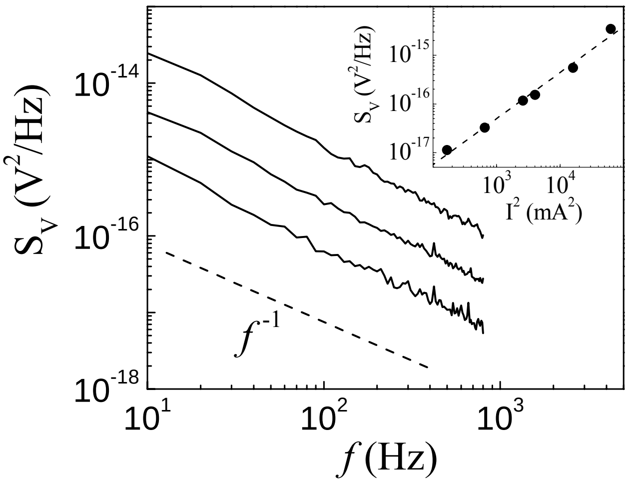

Fig. 3. Noise power spectral density S_V plotted as a function of frequency f for dc currents of 250, 125, and 60 mA, from top to bottom. Dashed lines are guides to the eye. Low frequency 1/*f*-like noise is observed over the entire range of temperatures studied; $T = 300$ K data is shown. Inset, current dependence of S_V at $f = 40$ Hz. The noise power at a particular frequency scales as the square of the dc current.

3.2. *Noise*

The power spectral density, S_V, of the voltage fluctuations across the sample is shown in Fig. 3 at a series of dc currents. At low frequencies, the noise magnitude scales approximately as I^2/f^β, where I is the dc current and f is frequency. The scaling with the square of the current is consistent with resistance fluctuations. The spectral slope, β, ranges between 0.6 and 1.4 and is temperature dependent. Measurements of a sample's intrinsic noise were generally restricted to frequencies less than a few kiloHertz due to a combination of factors including: large sample volumes, self-heating due to contact resistance, and amplifier noise. We expect the noise spectrum to crossover from 1/*f*-like to frequency-independent behavior at higher frequencies due to either Johnson noise or carrier recombination noise [8].

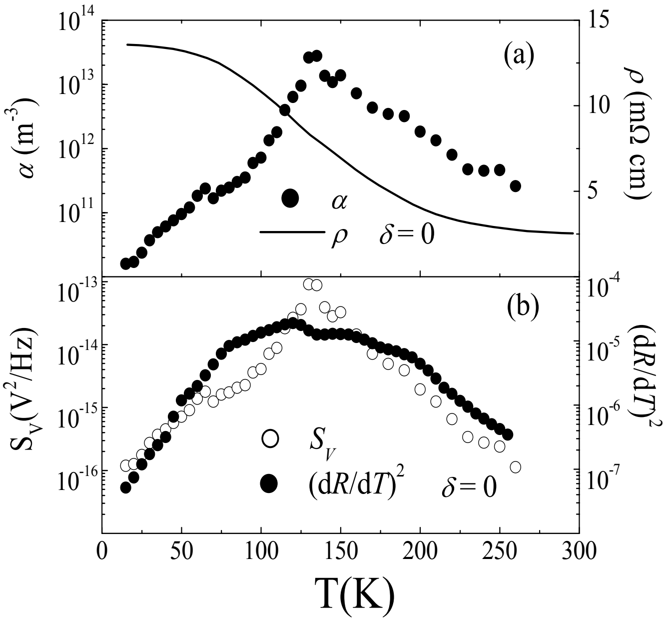

Fig. 4. Resistivity and normalized noise α as a function of temperature are plotted in panel (a). Panel (b) shows that the noise power does not scale as square of the rate of change of the resistance with temperature.

We parameterize the noise magnitude of specimens that exhibit a 1/*f*-like power spectrum by defining a phenomenological parameter, $\alpha \equiv \dfrac{f \times n \times S_V}{I^2 R^2}$, where R is resistance and n is the density of charge carriers [9,10]. n was determined from the low temperature Hall coefficient data. (n is 2.5×10^{17}cm^{-3}, 1.25×10^{18}cm^{-3}, 6.25×10^{16}cm^{-3}, and 3.12×10^{16}cm^{-3}, for $\delta \approx -0.0005$, 0, 0.0005, and 0.0009, respectively.) All reported values of α are for $f = 50$ Hz. We note that within our experimental sensitivity that α is independent of magnetic field, at least up to a few kOe. The temperature dependence of the noise, α(T), is plotted in Fig. 4a. $\alpha(T)$ is nonmonotonic, exhibiting a maximum in the intrinsic regime at a temperature (~ 135 K) that depends somewhat on the value of δ. The noise magnitude decreases rapidly on either side of the maximum; for some samples, α drops by a factor of 1000 over our temperature range. At high temperatures, the resistance of the samples is sufficiently low such that we were unable to resolve the $1/f$ noise near room temperature. Although the nonmonotonic behavior of $\alpha(T)$ emerges as a general feature of all the samples, variations in the magnitude of α from sample to sample for fixed δ can be large (a factor of 3 is typical). Taking this variance into account, the non-stoichiometric samples ($\delta \neq 0$) have nominally the same values of α and are on average somewhat noisier than the stoichiometric compound.

$1/f$ noise in semiconductors is generally attributed to some form of charge trapping-detrapping [10]. An alternative explanation based on a temperature fluctuation model [11] predicts, in the simplest case, that $S_V \propto \left(dR/dT\right)^2$. As evident in Fig. 4b, the data do not support such a scaling. The nonmonotonic form of $\alpha(T)$ and the $1/f$-like spectrum are consistent with a Dutta, Dimon and Horn (DDH) picture for $1/f$ noise [12,13]. For thermally-activated fluctuations in trap occupation the spectrum around some frequency f at any temperature T comes mainly from sites having thermal activation energies $E \approx k_B T \ln\left(f_0/f\right)$, where $f_0 \sim 10^{12}$ Hz is an attempt frequency of the order of the phonon frequency. If the spectral shape results from a broad but not arbitrarily broad distribution of energies $D(E)$ then the spectral exponent is not quite one and is temperature dependent. The relation between the temperature dependence of the spectral slope and the spectral density are shown in Fig. 5. The spectral slope is observed to cross through 1 at nearly the same temperature that $\alpha(T)$ is a maximum.

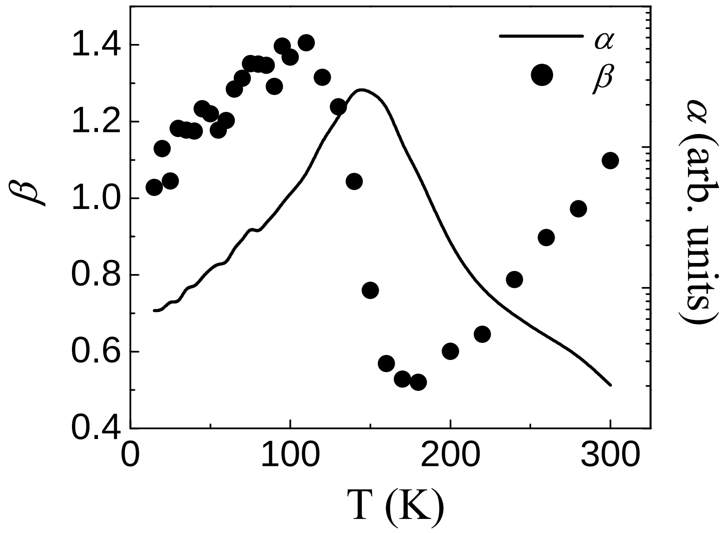

Fig. 5. The spectral slope β and the normalized noise magnitude α versus temperature are shown for an n-type sample having $\delta = 0.0005$.

Under somewhat restrictive conditions [12,13], DDH showed that the spectral slope should be related to the temperature dependence of the spectral density itself in the following way:

$$\beta = -\frac{\partial \ln S(f,T)}{\partial \ln f} = 1 + \frac{1}{\ln(f_0/f)}\left[\frac{\partial \ln S(f,T)}{\partial \ln T} - 1\right]. \tag{1}$$

Here $S(f,T) = S_\rho(f,T)/\rho^2(T)$ in order to factor out the temperature dependence of the resistivity. The predicted DDH spectral slope and the measured slope are in qualitative agreement as is demonstrated for a Ag-rich and a Ag-deficient sample in Fig. 6. Notice that some temperature dependence other than that predicted by the DDH relation is clearly present, particularly at low temperatures as indicated by the offset between the predicted and observed slopes. Even so, the common structure to both terms is clearly evident. These results support a picture for 1/*f* noise in which the noise generating processes are thermally activated.

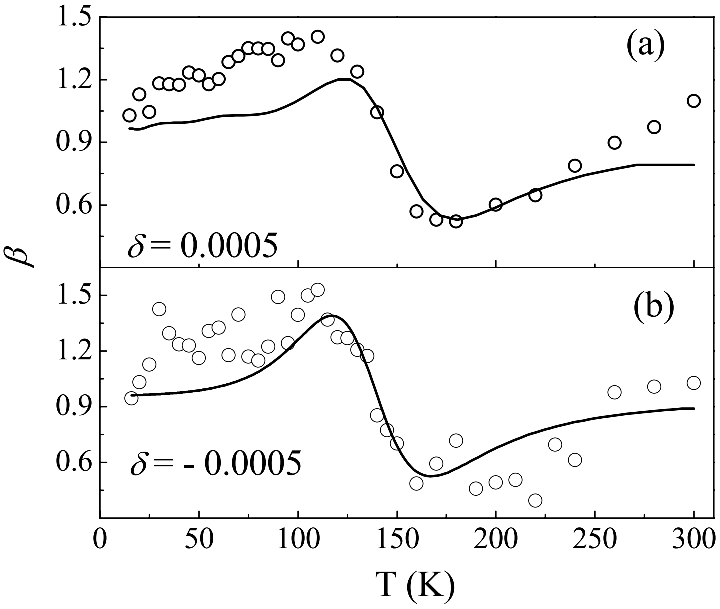

Fig. 6. Temperature dependence of the spectral slope for a nominally *n*- and *p*-type sample. The solid lines are the predicted spectral slope calculated from the DDH relation (see Eq. 1).

In the random fluctuation model of DDH, $\beta = 1$ only if $D(E)$ = const. However, it is actually necessary only that $D(E)$ vary slowly compared to k_BT for S_V to be consider 1/*f*-like noise (defined as noise with $0.6 < \beta < 1.4$). When $D(E)$ is broad on the scale of a few k_BT, it can be shown that the distribution of activation energies is given by,

$$D(E) \propto \omega S(f,T)/k_BT\ . \tag{2}$$

Figure 7 shows the energy distributions for two samples, calculated from the corresponding $S(f, T)$ using Eq. 2. The distributions have a characteristic peak at ~ 250 meV that has a width of 50 to 100 meV. This activation energy is larger than the semiconducting gap in Ag_2Te, which is only 120 meV.

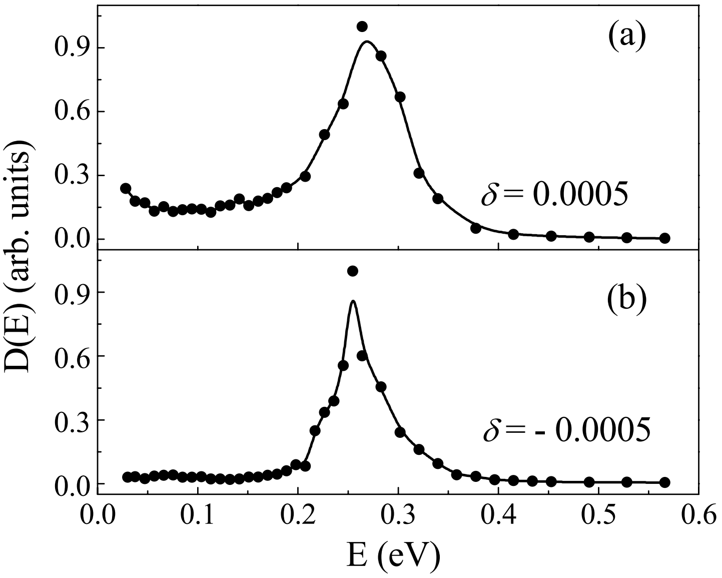

Fig. 7. Distribution of activation energies calculated from the curves in Fig. 6 using the expression in Eq. 2. Solid lines are guides to the eye.

The linear magnetoresistance in nonstoichiometric silver chalcogenides is believed to require an inhomogeneous medium with highly conducting regions, due for example to excess silver forming metallic clusters embedded in less conducting material [5,7,14]. Disorder, in the form of spatial fluctuations in conductivity, can lead to broad distributions of energy scales and time scales. If conductivity fluctuations are sufficiently large, distorted current paths may give rise to non-Gaussian noise power fluctuations [10]; however, such behavior was not observed in these samples. In our slightly nonstoichiometric $Ag_{2+\delta}Te$ samples, we speculate that the disorder is uniform on a macroscopic scale and that the broad-band noise spectra are due to charge traps located near the interfaces between highly and poorly conducting regions of the material. It would be of interest to investigate heavier doped samples ($\delta > 0.01$) that exhibit smaller field scales ($\approx$ 10 Oe) at which the magnetoresistance crosses over from quadratic to a linear dependence. Such small magnetic field values correspond to peculiarly long physical length scales that may lead to different noise properties.

Using the low-temperature magnetoresistance and noise data for a sample having δ = 0.0005, we estimate that $1/f$ resistance fluctuations lead to an effective magnetic field noise of 50 $\mathrm{mOe}/\sqrt{\mathrm{Hz}}$ at 50 Hz. This is a factor of 10^4 higher than the noise of field sensors [15] based on giant magnetoresistive materials or spin-polarized tunnel junctions [16]. Hence, the near stoichiometric ($\delta \approx 0$) silver chalcogenides may not compare favorably for low-field, low frequency applications. However, magnetic field sensors based on Ag_2Te

and Ag_2Se do have a niche in pulsed magnet applications that involve high fields and higher frequencies [17]. Other devices would likely make use of thin films of silver chalcogenide [18] that may have considerably different noise properties.

4. Summary and Conclusions

With ideal stoichiometry, the silver chalcogenide compound, Ag_2Te, is a non-magnetic, intrinsic narrow-gap semiconductor that exhibits no appreciable magnetoresistance. Interestingly, slight alterations in stoichiometry lead to a marked increase in the magnetic response. In silver rich compounds, the magnetoresistance is found to depend *linearly* on field starting from ~10 Oe and extending up to at least 55 kOe without any sign of saturation [3]. This unusual linear dependence on magnetic field is of practical importance and indicates an unusually long length scale associated with the underlying mechanism. Theoretically, both classical [19] and quantum [7] explanations require an inhomogeneous medium with highly conducting regions, due for example to excess silver embedding in less conducting material. Inhomogeneous density fluctuations, on a scale larger than the mean free path but much smaller than the sample size permit length scales to emerge that are not simply set by the cyclotron radius, and can lead to a linear field dependence of the resistivity over many orders of magnitude in H.

Low frequency electrical noise in these materials is due to resistance fluctuations with a $1/f$-like power spectrum. The noise magnitude is a strong function of temperature, peaking in the intrinsic regime. The temperature dependence of the noise power and its spectral slope are consistent with distributed, thermally activated kinetics of the noise generating processes that lead to $1/f$ noise. The distribution of activation energies is peaked near 250 meV which is at least a factor of two larger than the semiconducting energy gap. Although the precise origin of the noise mechanism is not known, a plausible explanation is charge trapping associated with the interfaces between highly and poorly conducting regions of the material.

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