Exchange Scattering in a Ferromagnetic Semiconductor

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Experimental studies of magnetoresistance and magnetization on the degenerate magnetic semiconductor $(GeTe)_{99}(MnTe)_1$ indicate that the transport properties correlate with the square of the magnetization both above and below the ferromagnetic transition. A simple spin-flip scattering mechanism yields a value for $|J_{s-d}|$ of 0.8 eV in agreement with the dependence of the Curie-Weiss temperature on manganese concentration.

I. INTRODUCTION

The pseudobinary system $(GeTe)_{1-x}(MnTe)_x$ is a degenerate magnetic semiconductor which orders ferromagnetically[1,2] with a Curie temperature dependent on manganese concentration. Recent studies[3,4] have shown that for manganese concentrations below 10 at.%, the paramagnetic Curie-Weiss temperature Θ varies linearly with temperature, while the manganese moment is localized with a spin of $\frac{5}{2}$. Carefully prepared samples show sharp ferromagnetic transitions with narrow hysteresis loops in the ordered state.[3] The interaction between the manganese ions is believed to be of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type,[3,5] which proceeds via a coupling between the ion and the mobile charge carriers with an exchange constant J_{s-d}. This coupling also reflects itself in the electrical resistivity, whose properties[1,2,4] indicate a substantial contribution from manganese ion scattering.

The purpose of the present work has been to (a) investigate the scattering in the paramagnetic state, from this to determine the exchange constant J_{s-d}, and to compare this with the value found from the magnetic properties; (b) investigate the scattering in the ferromagnetic state and to see if any correlation exists between this and the total magnetic moment.

To examine the above points we have chosen a sample containing 1-at.% MnTe with a paramagnetic Curie-Weiss temperature of 3.3 K and a carrier concentration of 1.0×10^{21} holes/cm^3. This sample orders at a temperature high enough to allow detailed examination both above and below the transition, but well below the temperature at which phonon scattering begins to affect the resistivity.

II. SAMPLE PREPARATION AND METHODS OF MEASUREMENT

Pure GeTe was made by melting the components together in a sealed and evacuated quartz ampoule at 800 °C for 3 h. Pure MnTe was made by dissolving Mn powder in molten Te in a graphite crucible under vacuum at 900 °C for 24 h. X-ray powder photographs were then taken to check that both had the correct crystal structure. $(GeTe)_{99}(MnTe)_1$ was then made by mixing GeTe and MnTe in the desired proportions in an evacuated, sealed quartz ampoule and heating first at 850 °C for 6 h and then at 720 °C for 24 h. X-ray powder photographs showed that the resultant compound still had the structure of GeTe,[6] while a microprobe analysis revealed a uniform concentration of MnTe of 1.0 at.% to within the resolving power of the instrument (0.25 at.%). A sample of rectangular form with dimensions $1.8\times1.8\times15$ mm was then spark cut from the polycrystalline ingot and was used *both* for the resistivity *and* the magnetization measurements. Prior to these measurements, however, the Hall voltage was measured at 300, 77, and 4.2 K in fields up to 40 kG. These measurements indicated a charge-carrier density of 1.0×10^{-21} holes cm^{-3}, independent of temperature, while no evidence was seen for the existence of any other type of carrier. Furthermore, the Hall voltage was independent of magnetic field direction, indicating no measurable anomalous component.

The magnetization was measured by a vibrating sample magnetometer designed to operate in the longitudinal field of a 60-kG superconducting magnet as described by Springford *et al.*[7] The magnetic moment could be resolved to 5×10^{-4} emu.

Both resistivity and Hall voltages were measured by a four terminal technique using an ac current of 33 Hz. The block diagram of the circuit is shown in Fig. 1. Sample resistance was about 5 mΩ. Once the apparatus was fully warmed up, short-term current stability was 3 parts in 10^5, while long-term drift was better than 2 parts in 10^4. With such stability, changes in resistance could easily be measured to better than 1 part in 10^4. The major advantage of the ac technique over the more usual dc is that thermal voltages developed in the circuit do not interfere with the measurement, so that small changes in voltage may easily be observed, provided precautions are taken to minimize inductive coupling between the current and potential circuits.

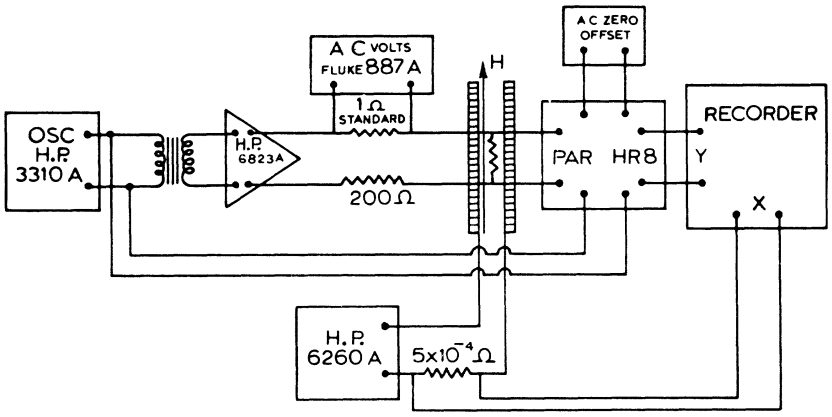

FIG. 1. Block diagram of the circuit used for measuring resistivity and Hall voltage.

III. EXPERIMENTAL RESULTS

Figures 2(i) and 2(ii) show graphs of the magnetization and magnetoresistance of 1-at.% MnTe in GeTe as a function of magnetic field up to 55 kG at 4.2 and 1.06 K. At 1.06 K the magnetization is saturated at fields beyond 45 kG. In magnetoresistance the normal orbital term is positive and varies as H^2. To verify this the magnetoresistance in a specimen of *pure* GeTe was measured and found to vary exactly as H^2 for all fields with a slope of $(2.10\pm0.5)\times10^{-3}\rho_0\ \mathrm{kG}^{-2}$ at both 4.2 and 1.06 K, where ρ_0 is the resistivity of the specimen in zero field at 4.2 K. Figure 2(iii) shows the magnetoresistance of $(GeTe)_{99}(MnTe)_1$ at 1.06 K plotted as a function of H^2. For fields over 45 kG this varies linearly with a slope of $(2.50\pm0.05)\times10^{-3}\rho_0\ \mathrm{kG}^{-2}$, a figure close to that of pure GeTe, the difference arising from slightly different mean free paths and carrier concentrations. We therefore assume that below 8 K, the resistivity in the $(GeTe)_{99}$ $(MnTe)_1$ sample can be written

$$\rho(H,T)=\rho_0+\rho_{\mathrm{orb}}(H)+\rho_m(H,T), \qquad (1)$$

where $\rho_0=\rho(0, 4.2\ \mathrm{K})=(1.4\pm0.2)\times10^{-4}\ \Omega\,\mathrm{cm}$, the zero-field resistivity at 4.2 K, is used as the reference value in the magnetically disordered regime; $\rho_{\mathrm{orb}}(H)=(2.50\times10^{-3})H^2\rho_0$ is the orbital magnetoresistance which is assumed independent of temperature; and $\rho_m(H,T)$ is the *negative* spin resistivity arising from the presence of Mn and it is this quantity which we analyze in the remainder of the paper.

The low-field behavior of the magnetization is shown in Figure 3(i). At 4.2 K there is only a slight precursor of the ordering, whereas at 1.06 K a characteristic hysteresis loop is observed with a remanent moment between $\frac{1}{3}$ and $\frac{1}{2}$ the saturated value. On the other hand, the resistivity shows *no* hysteretic behavior below the ordering temperature. This is illustrated in Figure 3(ii), which shows the low-field dependence of the total resistivity plotted as

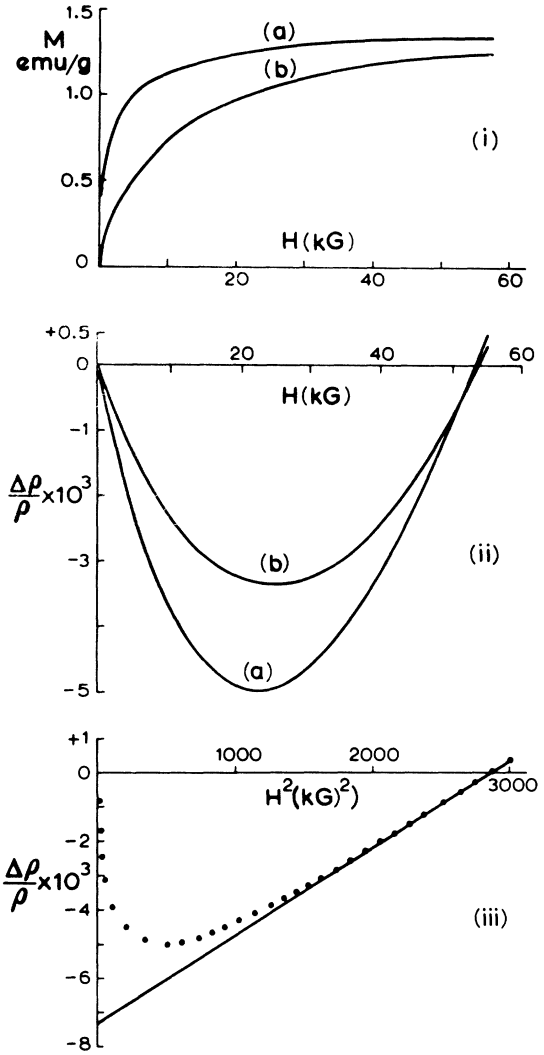

FIG. 2. (i) Measured magnetization of $(GeTe)_{99}(MnTe)_1$ as a function of field at (a) $T=1.06$ K; (b) $T=4.2$ K. (ii) Measured change in total resistivity $\Delta\rho/\rho=[\rho(H,T)-\rho(0,T)]/\rho(0,T)$ as a function of field at (a) $T=1.06$ K; (b) $T=4.2$ K. (iii) Curve 2 (ii) (a) above replotted against the square of the magnetic field.

$$\frac{\Delta\rho}{\rho} = \frac{\rho(H,T) - \rho(0,T)}{\rho(0,T)}$$

both above and below the ordering temperature. From this we can conclude that there is no appreciable contribution to the resistivity from domain-wall scattering, a result consistent with the low mean free path (~ 100 Å).

However, the appearance of magnetic order does lead to a change in the resistivity as shown in Figs. 3(iii) and 3(iv). The former is a plot of the remanent moment which increases with decreasing temperature below 3 K. The latter presents the temperature dependence of the relative change in the total resistivity $\Delta\rho/\rho_0$ in zero field. From 8 to 3 K, the resistivity is constant and then decreases as the remanent moment increases. Again for comparison, the resistivity of pure GeTe was measured and found constant for all temperatures below about 8 K.

Thus, the above results suggest very strongly that all changes in the resistivity below 4.2 K are caused by changes in spin scattering from the Mn ions.

IV. DISCUSSION OF RESULTS

We wish to discuss the results above in terms of an s-d exchange between the conduction electrons and the manganese ions which affects the resistivity through spin-flip scattering and also couples manganese ions through indirect exchange. Yosida[8] was the first to carry out a calculation of the influence of spin scattering on the resistivity, a calculation since extended by a number of authors.[9,10] There are two significant contributions to the resistivity: (a) a simple spin-flip scattering process given by second-order perturbation; application of an external field or the onset of magnetic ordering freezes out the impurity spin degree of freedom and the resistance decreases; (b) a double spin-flip process given by third-order perturbation; for $J_{s-d} < 0$ this leads to the well-known Kondo logarithmic temperature dependence of the resistivity.

In the present system no evidence whatever is seen for the Kondo effect. At zero field, only a decrease in resistivity is observed, coinciding with the onset of ordering [Figs. 3(iii) and 3(iv)]. It seems clear, therefore, that to describe the resistivity only a simple spin-flip process need be considered. If we assume that the exchange scattering is less than the Coulomb scattering (a ratio of 1 to 10 is sufficient), then the resistivity can be written,[9] to second order in J_{s-d},

$$\rho_m = KJ_{s-d}^2 A(\alpha), \tag{2}$$

where K is a constant and $A(\alpha)$ is a field- and temperature-dependent function accounting for the freeze out of spin-flip scattering. More explicitly,

$$K = 2\pi N(0) mc/zne^2 h,$$

where $N(0)$ is the density of states at the Fermi energy, c is the atom fraction of Mn, m is the charge-carrier effective mass (here essentially the same as the free electron mass[11]), e is the electronic charge, z is the valence of the solvent, n is the number of atoms per cm^3, and

$$A(\alpha) = 4\langle S_z\rangle^2 + \langle S_z\rangle (\coth \tfrac{1}{2}\alpha - \tfrac{1}{2}\alpha/\sinh^2 \tfrac{1}{2}\alpha),$$

where $\alpha \equiv g\mu_B H/kT$, μ_B being the Bohr magneton.

From Eq. (1), we see that the total increase in resistivity in going from a totally ordered to a totally disordered state is

$$(\Delta\rho_m)_{\text{total}} = KJ_{s-d}^2(4S^2 + S). \tag{3}$$

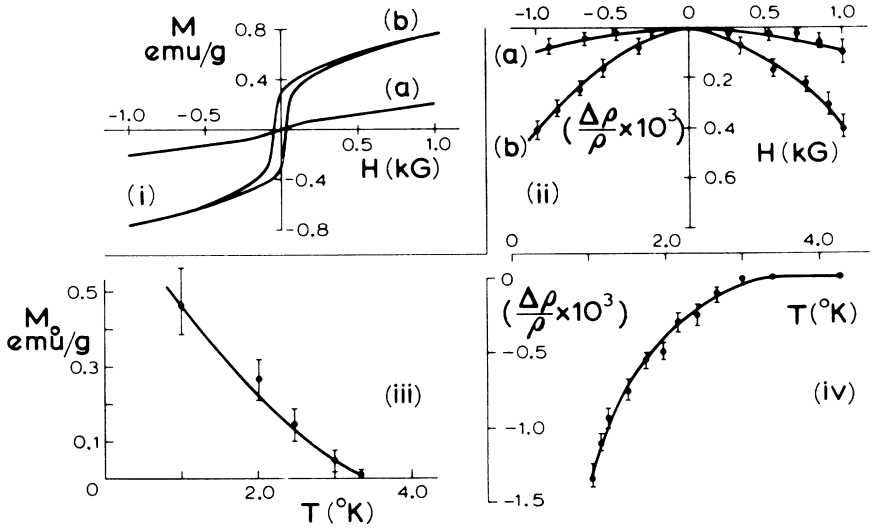

FIG. 3. (i) Low-field magnetization at (a) 4.2 K and (b) 1.06 K. (ii) Low-field magnetoresistance $\Delta\rho/\rho = [\rho(H, T) - \rho(0, T)]/\rho(0, T)$ at (a) 4.2 K and (b) 1.06 K. (iii) Remanent magnetic moment at zero field as a function of temperature. (iv) Change in *total* resistivity $\Delta\rho/\rho = [\rho(0, T) - \rho_0]/\rho_0$ as a function of temperature at zero field.

On the assumption that the spin system is totally ordered at 55 kG and 1.06 K, and totally disordered in zero field at 4.2 K, then

$$(\Delta\rho_m)_{\text{total}} = \rho_0 - \rho_m(55\text{ kG},\ 1.06\text{ K}) = (8.6\pm0.1)\times10^{-3}\rho_0,$$

where $\rho_0 = (1.4\pm0.2)\times10^{-4}\ \Omega\,\text{cm}$. Using these values and the calculated value of K assuming a parabolic band, a free-electron mass and a spin of $\frac{5}{2}$ yields a value of $J_{s\text{-}d}$,

$$|J_{s\text{-}d}| = 0.8\pm0.08\text{ eV}.$$

This figure is in good agreement with the value of 0.7 ± 0.1 eV determined from the concentration dependence of the Curie-Weiss temperature Θ on an RKKY model.[3,12]

Since Eq. (2) has been derived for an isolated magnetic impurity, we have taken account of the magnetic interactions between the manganese ions in the paramagnetic regime by making the usual mean-field approximation and writing α as $g\mu_B H/(T-\Theta)$. Furthermore, $\langle S_z\rangle$ has been determined directly from the experimentally measured magnetization M, remembering that $\langle S_z\rangle = M/Ng\mu_B$. We now define $B(\alpha) = \frac{1}{4}(Ng\mu_B)^2 A(\alpha)$, so that

$$B(\alpha) = M^2\left[1+\frac{Ng\mu_B}{4M}\left(\coth\tfrac{1}{2}\alpha - \frac{\frac{1}{2}\alpha}{\sinh^2\frac{1}{2}\alpha}\right)\right].$$

The relative change in spin resistivity in a magnetic field at 4.2 K, $\Delta\rho_m(H,\ 4.2\text{ K})/\rho_0$, has been plotted as a function of $B(\alpha)$ and is shown in Fig. 4(i). Clearly, the modified equation (2) is obeyed extremely well. Moreover, the slope of the line yields the same value for $|J_{s\text{-}d}|$, 0.8 ± 0.8 eV, as above. It should be pointed out that $B(\alpha)$ is given by M^2 to within 10%, and replacing the abscissa in Fig. 4(i) by M^2 also gives a straight line, but with a slope about 10% larger.

Below the ordering temperature, the mean-field approximation suggests that we use the limiting value of α and express

$$B(\alpha) = M^2(1+Ng\mu_B/4M).$$

Under these conditions we have plotted the *total* spin-flip resistivity at 1.06 K, $[\rho_m(H,\ 1.06\text{ K}) - \rho_0]/\rho_0$, against $B(\alpha)$ in Fig. 4(ii) (ρ_0 being the reference value for the completely disordered spin system). Remarkably, this graph is also linear with a slope identical to that found in the paramagnetic regime [Fig. 4(i)]. A further illustration of this behavior is noted in Fig. 4(iii), which shows that the zero-field resistivity [Fig. 3(iv)] correlates with the remanent moment [Fig. 3(iii)] in exactly the same manner.

It is therefore apparent that all changes in resistivity arising from spin-flip scattering may be parametrized by the total magnetization in both the ordered and disordered states.

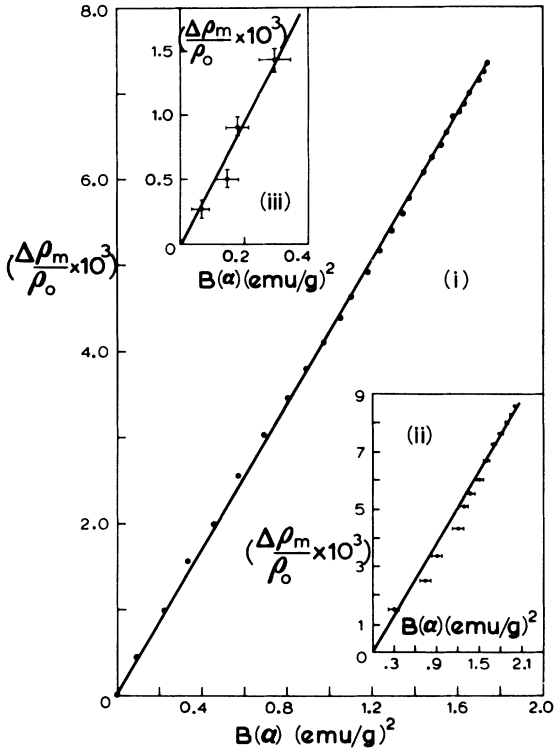

FIG. 4. Negative magnetoresistance $\Delta\rho_m/\rho_0$ as a function of $B(\alpha)$; (i) up to 55 kG; 4.2 K, $\alpha = g\mu_B H/K(T-\theta)$; (ii) up to 55 kG; 1.06 K, $\alpha = \infty$; (iii) zero field from 3.0 to 1.06 K, $\alpha = \infty$.

V. CONCLUSION

The behavior of the magnetization and magnetoresistance for GeTe containing 1-at.% Mn is in good agreement, both above and below the ordering temperature, with a simple spin-flip scattering mechanism based on an s-d exchange model. The value of the exchange coupling parameter $|J_{s\text{-}d}|$ is in excellent agreement with the previously reported value derived from the concentration dependence of the Curie-Weiss constant. The magnitude of $J_{s\text{-}d}$ is larger than in paramagnetic metal alloys exhibiting a Kondo effect. The size of the Kondo effect is such a system depends on the product of $J_{s\text{-}d}$ with the density of states $N(0)$ as well as $J_{s\text{-}d}$ having a negative sign. In the GeMnTe alloy reported here, the increase in $J_{s\text{-}d}$ more than compensates for the decrease in the density of states. The fact that no Kondo effect is observed suggests that $J_{s\text{-}d}$ is positive. This would be consistent with a direct s-d interaction (i.e., no s-d mixing), where, in general, a positive J results. The absence of s-d mixing would imply that the manganese d levels lie above the hole-conduction band.

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