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MAGNETIC TRANSITIONS IN DEGENERATE MAGNETIC SEMICONDUCTORS+

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The specific heat C, ESR, and the effect of magnetic field on the thermopower α of $Sn_{1-x}Mn_xTe$ have been measured. Two distinct peaks in the C-T curves and the ESR anomalies in the g-value and linewidth were observed around the two characteristic temperatures of T_{AHE} (=5-6 K) and T_m (=4-5 K), indicating the two magnetic transitions associated with the structural phase transition of the host SnTe crystal. A brief report on the various types of magnetisms in Sn_{1-x}-$(Me)_xTe$ with Me=Cr, Fe, Co and Ni is also presented.

I. Introduction

In the solid solution of the degenerate semiconductor SnTe with Mn impurities as solutes or the $Sn_{1-x}Mn_xTe$ system, the magnetic impurities are in the paramagnetic state (or EPR centers) and the magnetic susceptibility obeys the paramagnetic Curie-Weiss law over a wide range of temperature, while at liquid helium temperatures the magnetic spins have been known to align ferromagnetically through indirect exchange interactions via conduction carriers. As a result, various spin-dependent behaviors are observed, such as a resistivity anomaly (a small peak or an abrupt decrease in the resistivity) appearing at a magnetic transition temperature T_m (=4-5 K) [1], the anomalous Hall effect due to the presence of a magnetization in the sample which vanishes above another characteristic temperature denoted by T_{AHE} (=5-6 K) [2], and a small peak or a shoulder in the thermopower α near a temperature denoted by $T_{\alpha max}$ (=20-25 K) which arises from some sort of spin fluctuations before the complete magnetic orderings in the spin system [3]. In order to understand these properties further, we have carried out the measurements of specific heat C, ESR, and the effect of a magnetic field on α of this system over the temperature range covering these characteristic temperatures. A brief report will also be given on various types of magnetisms in other degenerate magnetic semiconductor systems of $Sn_{1-x}(Me)_xTe$ with different 3d transition metals Me=Cr, Fe, Co, and Ni. Here we have been primarily concerned with the $Sn_{1-x}Mn_xTe$ system.

II. Experimental

The single crystals of $Sn_{1-x}Mn_xTe$ were grown by the conventional Bridgman technique. Some of the grown crystals were isothermally

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annealed in Zn-vapor followed by quenching to reduce the carrier concentration. Normally the carrier concentration of the as-grown crystals is in the range $p=(6\text{-}10) \times 10^{20}$ cm^{-3} and that of the annealed ones is $(1\text{-}4) \times 10^{20}$ cm^{-3} at room temperature, determined by the Hall effect measurements.

The thermopower α was measured in a steady state method using a home-made cryostat with a superconducting magnet, where two different sample holders were employed; one for the magnetic field applied parallel to the thermal flux flow along the rectangular sample (typically 2 x 2 x 7 mm^3) and the other for the transverse direction. The specific heat measurements were made with a home-made adiabatic calorimeter and the data were taken using the heat-pulse method, in which a heat pulse of short duration was applied to the bulk crystal (13.6 mm in diameter and 15-20 mm in length). Furthermore, commercial X-band spectrometer and vibrating sample magnetometer were used for ESR and magnetization measurements of some samples, respectively.

III. Results and Discussion

Figure 1 shows the typical results of the molar specific heat of the as-grown and annealed $Sn_{1-x}Mn_xTe$ crystals with x=3 at.%; for comparison are also shown the data for the undoped SnTe crystal (x=0), which are in good agreement with the values of Bevolo et al.[4].

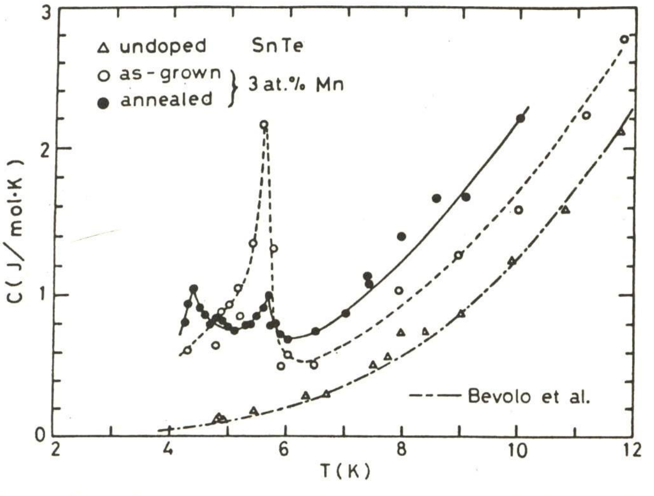

Fig. 1 Temperature dependence of the molar specific heat for the undoped (annealed) SnTe crystal (x=0), as-grown and annealed Sn_{1-x}-Mn_xTe crystals (x=3 at.%)

It should be emphasized that the specific heat for the annealed crystal with x=3 at.% has clearly two peaks at two different temperatures (4.41 and 5.70 K), which correspond to the two characteristic temperatures of T_m and T_{AHE} as found from the transport measurements of this magnetic semiconductor, such as the resistivity and the anomalous Hall effect [2]. Such anomalous behaviors of both the specific heat and resistivity at two distinct temperatures are also known in rare-earth metal like Dy with the hcp structure, which are associated with two magnetic transitions from paramagnetic to antiferromagnetic phases at the Neel temperature T_N and from antiferromagnetic to ferromagnetic phases at the Curie temperature T_c, the antiferromagnetic ordering being a screw structure in the basal plane of the hcp structure [5].

Here we note the critical-point exponents β and β' for specific heats, defined by $C \sim (\varepsilon)^{-\beta}$ for $T > T_c$ and $C \sim (-\varepsilon)^{-\beta'}$ for $T < T_c$ with $\varepsilon = T/T_c - 1$. A graphical rough evaluation for our material system, the crystal with x=3 at.%, gives the following values; $\beta \simeq \beta' \simeq 1/8$ at T_{AHE} =5.70 K, which are in reasonable order of magnitudes with reference to those in representative ferro- or anti-ferromagnets [6]. The values at $T_m \simeq 4.41$ K are β=0.07 and $\beta' \simeq 0.8$; these are less accurate compared with those for the higher critical temperature.

Our previous ESR studies on the $Sn_{1-x}Mn_xTe$ system in the temperature range 300-120 K have shown that for $x < 0.2$ at.% the spectrum consists of the six hyperfine-resolved lines while for $x > 0.2$ at.% it becomes a single broadened line [7]. Since the low temperature behavior down to 4.2 K of the latter is found to be monotonic [8], we have here carried out the measurements on the former. The results for the g-value is shown in Fig. 2 for the sample with x=0.04 at.%;

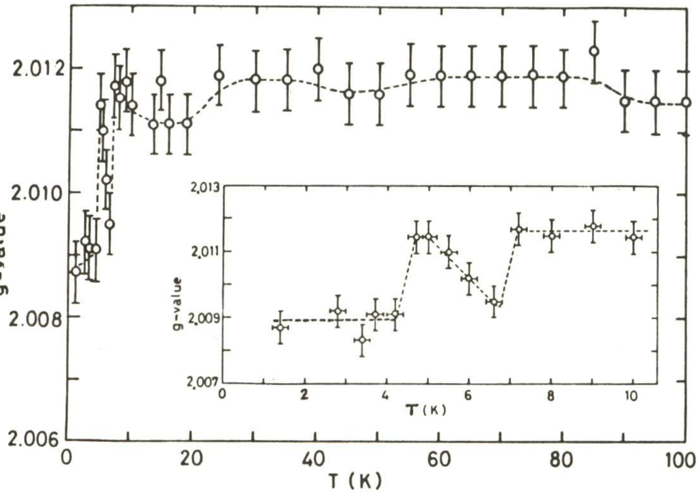

Fig. 2 Temperature dependence of the g-value of the ESR spectra for the $Sn_{1-x}Mn_xTe$ (x=0.04 at.%); the inset is an enlarged behavior at low temperatures

the inset is the expanded behavior. It is quite interesting that the g-value also shows a remarkable change around the two temperatures corresponding to T_m and T_{AHE}; similar changes in the linewidth ΔH of a hyperfine-resolved line were observed.

On the other hand, the application of a magnetic field on α leads to a reduction in the small peak or the shoulder near $T_{\alpha max}$, indicating that the spin alignment reduces the fluctuations towards the carriers contributing to the thermoelectric power.

Furthermore, we have recently extended the study to other systems of degenerate magnetic semiconductors $Sn_{1-x}(Me)_xTe$ with different 3d transition metals Me=Cr, Fe, Co, and Ni. Table I summarizes the results of the magnetic and spin resonance experiments on the Bridgman-grown crystals all with x=1 at.%. Detailed studies will be reported elsewhere.

Table I. Results of the magnetic and ESR experiments for $Sn_{1-x}(Me)_xTe$ with x=1 at.%

Me	Magnetism	Spin resonance
Cr	F	FMR
Fe	F	No signal
Co	D	No signal
Ni	D	No signal

F: Ferromagnetic D: Diamagnetic FMR: Ferromagnetic resonance is observable

IV. Summary

For the $Sn_{1-x}Mn_xTe$ we have found the specific heat and ESR anomalies in their temperature dependence at two different temperatures of T_m and T_{AHE} which exactly correspond to the two characteristic temperatures of this system as identified by the transport measurements. Together with the following facts, we may conclude that these results support the possibility of two magnetic transitions; one from paramagnetic to antiferromagnetic at T_{AHE} and the other from antiferromagnetic to ferromagnetic at T_m. The host SnTe is known to be a "near ferroelectric" material analogous to the perovskite ferroelectrics like $SrTiO_3$ and $BaTiO_3$, which undergo a structural (ferroelectric) phase transition at a critical temperature. The crystal symmetry in SnTe changes from a cubic to a rhombohedral structure, resulting in an anisotropy in the crystalline environment around the magnetic impurities at low temperatures. As a result, this could induce a preferred direction for the magnetic spins to orientate along with and thus produce the two magnetic phases through indirect exchange interactions; we may thus call this as "structural transformation-induced magnetism". We have also briefly reported on the effect of a magnetic field on α and the various types of magnetisms in $Sn_{1-x}(Me)_xTe$.

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