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Possible Evidence for Specific Heat Anomaly due to Interaction between Very Fine Ferromagnetic Microcrystalline Particles and the Host Crystal in the $Sn_{1-x}Cr_xTe$ Mixed System

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A marked specific heat anomaly has been observed for well prepared samples of the mixed system $Sn_{1-x}Cr_xTe$ at temperatures corresponding to the Curie point of CrTe. The anomaly is associated with very fine ferromagnetic particles, but it is far from being accounted for by the entropy change due to effective spins. It is necessary to suppose some sort of interactions between the particles and the host crystal;the interactions must be of a sort by which the total electronic energy of the interacting system is appreciably lowered, but with the total magnetic moment unchanged.

1. Introduction

SnTe in its pure form is a p-type degenerate semiconductor with a high carrier concentration (due to holes) of the order of 10^{20} to 10^{21} cm^{-3}. It crystallizes in the NaCl structure and is believed to undergo a trigonal deformation below 80K via a displacive structure phase transition.[1] SnTe doped with chromium, $Sn_{1-x}Cr_xTe$, manifests new kinds of magnetism such as not observed for Mn-doped SnTe crystals. (As to the Mn-doped crystals, we reported their diversity in magnetism in previous papers.[2]) The present system, for example, exhibits a ferromagnetic ordering at the Curie temperature Tc, which varies from 150K to 300K depending

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on heat treatment[3];at low temperature, however, the system shows a dominant order of paramagnetic spins along an applied field.[4] Of another and most interest is a marked anomaly in specific heat corresponding to Tc, as observed for some specimens.[5]

In this paper attention is paid on the specific heat of well prepared samples. The preparation of Bridgman-grown $Sn_{1-x}Cr_xTe$ (x=0.5, 1 at.%) polycrystalline samples is described elsewhere[3];in short, some of the as-grown crystals with carrier concentration more than 4 x 10^{20} cm^{-3} were isothermally annealed in Zn vapor at 600°C , followed by quenching into water to reduce the carrier concentration. Calorimetric measurements were carried out by an ordinary heat pulse method. For alternative examination of magnetism, magnetization measurements were also made on representative samples using a vibrating sample magnetometer;part of the results has been reported elsewhere.[4] All the sample used were unoriented.

2. Results and Discussion

A typical pattern of specific heat versus temperature curves of well prepared samples of $Sn_{1-x}Cr_xTe$ is shown is Fig.1 for x=0.5 and 1 at.%. They display a disorder-order type of magnetic phase transition around 282K corresponding to a Curie temperature Tc. Figure 2 shows a temperature dependence of specific heat of CrTe measured, for reference, on dopant material in the temperature region where the magnetic transition occurs. The critical point is 278K, and is very close to the 282K above.

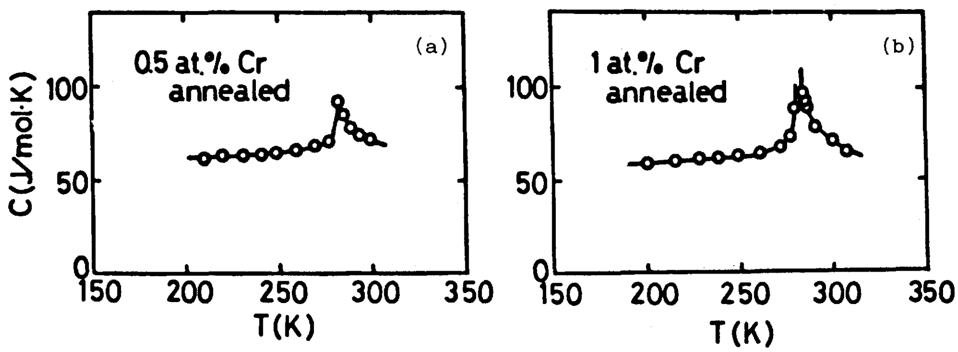

Fig. 1. Temperature dependence of molar specific heat of $Sn_{1-x}Cr_xTe$ with x = 0.5 (a) and 1 (b) at.%.

It is instructive to glance at temperature dependences of the magnetization of representative samples measured in the wide temperature range, one of which is shown in Fig.3 for x=1 at.%. The magnetization shows a broad peak around 150K and increases drastically below 20K, following nearly the Curie-Weiss law. The magnetization curve of the same sample, though not shown in the figure, reveals a ferromagnetic characteristic at room temperature showing nearly a saturation, whereas at 4.2K it exhibits an apparently paramagnetic-like curve, but still having a minor hysteresis curve. These behavior of the magnetization, together with the close agreement between the critical points for Cr-doped SnTe and dopant CrTe as observed in the specific heat experiments (Figs. 1 and 2), suggest that there exist in the Cr-doped SnTe some sort of ferromagnetic entities such as clusters of chromium ions, or rather (very fine) microcrystalline particles of CrTe, within each of which ferromagnetic characteristics similar to those observed for chromium telluride itself[6] are still present. At the same time, however, attention should be also paid on the drastic increase in magnetization at low temperatures. It suggests that the chromium ions in the mixed system is uniformly distributed throughout the crystal, thereby acting as isolated paramagnetic spins, only a part of which migrates to form the

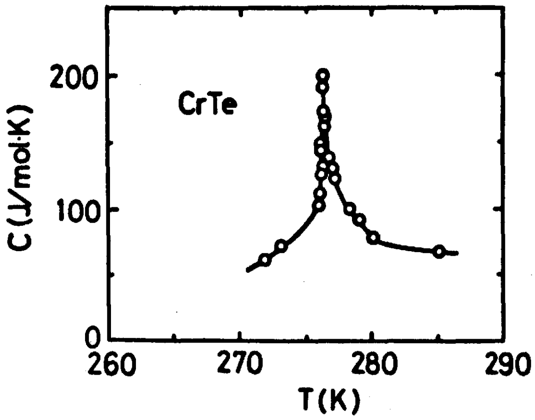

Fig. 2. Temperature dependence of molar specific heat of dopant material CrTe.

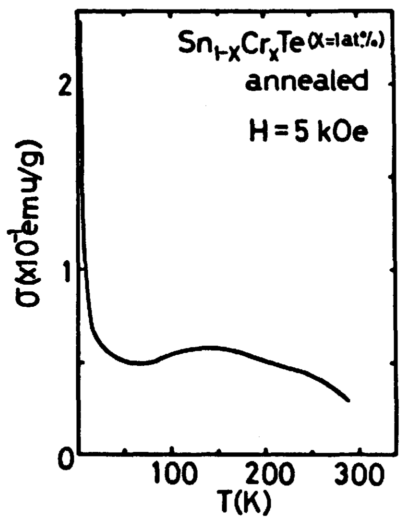

Fig. 3. An example of temperature dependence of the magnetization at 5 kOe measured in the wide temperature range 4.2–300 K for a representative sample : $Sn_{1-x}Cr_xTe$ with x = 1 at.%.

ferromagnetic entities;nevertheless, it is still the latter which is associated with the marked specific heat anomaly observed.

It is worth while tring to make a rough evaluation of an entropy change related to the specific heat anomaly. With the use of $\int(Cm/T)dt$, where T is the temperature and Cm is the magnetic term of the specific heat, which is obtained by subtracting the back ground lattice term from the observed specific heat, the entropy change is estimated to be, in unit J/mole·K , ~ 10 for CrTe, and ~ 1.5 and ~ 3 for $Sn_{1-x}Cr_xTe$ with x=0.5 and 1 at.%, respectively. According to an alternative expression for the entropy change Rln(2S+1), where R is the gas constant and S is the electron spin per chromium ion, the value ~ 10 for CrTe reduces to an effective spin of about unity per chromium ion, which is compared with the value S=2 for free Cr^{2+} ion. On the other hand an effective spin for the mixed system as calculated by the formal application of the same expression, but with the consideration of the diluted spin concentration, is far from being unity, as expected by the marked specific heat anomaly. In fact the calculated value of the entropy change with the assumption S ~ 1 is, for example, 0.1 J/mole·K for x=1 at.%, which is too small to be compared with the experimantal value of ~ 3 . Here it should be noted further that, as suggested above, it is probably only a few tenth of the total number of the doped chromium ions which migrates to form the ferromagnetic entities responsible for the specific heat anomaly.

These evaluations of the observed entropy change suggest a certain but strong interaction of the ferromagnetic entities with the host crystal. The mixed system is paramagnetic at elevated temperatures;when the system is cooled down near the Curie temperature, there occur paramagnetic-to-ferromagnetic transitions within each of the ferromagnetic particles. The ordered-spins state of each particles may be as if it were a high-spin state of a sort of 'molecule' such as composed of several CrTe molecules, i.e., such as of the form $(CrTe)_n$. Once the transition of spin configurations has occured from a low- to high-spin states in the individual $(CrTe)_n$ 'molecules', the resultant 'molecular' states of $(CrTe)_n$ might interact with Bloch orbitals of the free carriers (holes) of the host crystal and/or with orbitals of 'ligands' furnished by the surrounding host, in such a way that the total electronic energy of the interacting system is appreciably lowered, but with the total magnetic moment unchanged;as for which interaction of the two is dominant, helpful suggestions will be obtained from experiments on the system of Cr-doped PbTe because of less carrier concentration for PbTe than for SnTe (by the order of about three, in our preliminary works).

In summary, the mixed system $Sn_{1-x}Cr_xTe$ is a magnetic semiconductor in which very fine microcrystalline ferromagnetic particles are embedded in a paramagnetic matrix. The ferromagnetic particles are less dominant in number of the constituent chromium ions than the latter, but they give rise to a marked specific heat anomaly that is far from being accounted for by the entropy change due to effective spins alone. For this anomaly to be understood, it is necessary to suppose some sort of interactions between the particles and the host crystal;the interactions must be of a sort by which the total electronic energy of the interacting system is appreciably lowered, but with the total magnetic moment unchanged. Detailed studies are still being undertaken.

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