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Spin-Glass Freezing above the Ordering Temperature for the Kondo Antiferromagnet $CeNi_2Sn_2$

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Measurements of electrical resistivity, magnetic susceptibility and specific heat on an as-cast polycrystal sample $CeNi_2Sn_2$ are reported. From the frequency and field dependence of the χ_{ac} and χ_{dc} above T_N, a spin glass state with two freezing temperatures $T_{f1} = 3.9\,K$ and $T_{f2} = 4.4\,K$ corresponding to the tetragonal and monoclinic phases of $CeNi_2Sn_2$, separately, are proposed. Some comparable intriguing experimental facts are the behaviors with anomalies observed in $C(T)$, $\chi_{ac}(T)$ and $\chi_{dc}(T)$ measurements. A qualitative description for the anomalous physical properties of $CeNi_2Sn_2$ compound is provided from the viewpoint of spin glass.

KEYWORDS: spin-glass, Kondo lattice, magnetic order, $CeNi_2Sn_2$

The problem of the spin-glass phenomenon has been of interest to both experimentalists and theorists since the late 1960's. An upsurge of enthusiasm in spin glasses may be due to its novel comportment. As reported by Gschneidner *et al*.,[1)] false indications of heavy fermion behavior can arise from spin-glass magnetism as well as the existence of low lying crystal field levels in Ce- and U-based compounds. In fact, frustration of magnetic interactions and Kondo effects are thought to be the two possible main reasons which block the establishment of long range order[2–5)] and may lead to a nonmagnetic or low ordering temperature ground state specific-heat enhanced compounds. Some recent related papers are listed in refs. 6–12.

In a recent study of ternary $CeNi_2Sn_2$ intermetallic compound it has been established that there exists two crystallographic structure phases depending on preparation.[13–20)] From the literature data, the as-cast sample generally crystalizes in the tetragonal $CaBe_2Ge_2$-type structure with space group P4/nmm.[14–17)] However, annealing process will cause a monoclinic distorsion[13,19,20)] of the previous structure and the space group turns out to be $P2_1$. Since both crystallographic structures have only small differences in the magnitude of their unit cell parameters, the badly crystallized sample even can be hardly resolved from the powder X-ray diffraction patterns. This is the why for there has been some controversy about $CeNi_2Sn_2$ crystallographic structure for the past years. In addition to its crystallographic structure, the $CeNi_2Sn_2$ compound attracts much interest mainly due to its intriguing heavy fermion behavior at low temperatures. This compound is an anisotropic Kondo-lattice system with an antiferromagnetic ordering temperature $T_N = 2$–$2.2\,K$ and a specific heat coefficient γ value approaching between 0.27 and $0.65\,J/mol{\cdot}K^2$, depending on authors and the temperature range concerned.[14,16,18,19,21,22)] The magnetic entropy $S_m(T_N)$ associated with a modulated magnetic structure for $CeNi_2Sn_2$ is only 35% of 2Rln2, corresponding to a reduction of $\sim$ one-third of the cerium moment.[16)] The large magnetic reduction was attributed to Kondo effect. However, to fit the magnetic specific heat anomaly for $T > T_N$, Pierre *et al*. took the sum of the magnetic/Kondo contribution from the ground state doublet and 50% of the calculated Schottky anomaly, which led to a questionable conclusion that only a small contribution arising from short range order might be present between T_N and 3.5 K. In fact, this 50% scaling procedure was obscure, as pointed out by Gómez Sal *et al*. recently.[23)] Therefore, it is speculated that to assess wholly for the anomalous magnetic behavior, a complementary contribution is needed in addition to the familiar models of mixing Kondo, crystal electric field (CEF) and Rudermann, Kittel, Kasuya, and Yosida (RKKY) interactions. The aim of the present article is to report ac susceptibility and history-dependence magnetization performed in an as-cast $CeNi_2Sn_2$ sample, to discuss the role of spin glass, and to provide a useful qualitative description.

Polycrystalline samples investigated for this work were synthesized by arc melting together with stoichiometric amounts of the constituent elements in a Zr-gettered arc furnace on a water-cooled Cu hearth under purified argon of about one atmosphere. The rare-earth elements of $> 99.9\%$ (3N) purity were obtained from the Materials Preparation Center of the Ames Laboratory. The 4N purity Ni and 5N purity Sn were purchased from Gredmann, Inc. Weight losses during arc melting were less than 0.5% due to the sufficiently low vapor pressures of these elements at the melting temperature of the ternary compounds. A Mac Science microcomputer-controlled powder diffractometer equipped with copper target and graphite monochromator for CuKα radiation was used to obtain the powder X-ray-diffraction patterns at a scan rate 0.4°/min. The dc electrical resistivity measurements were made on rectangular samples of uniform thickness (approximate dimensions $1 \times 1 \times 6\,mm^3$) between 2.0 and 300 K in a system fully automated for temperature stability and data acquisition. The ac and static magnetic susceptibility measurements were carried out with a commercial Quantum Design SQUID (superconducting quantum interference device) magnetometer. The specific heat was measured with a semiadiabatic calorimeter using a standard heat-pulse technique in the temperature from 0.5 to 20 K.

Analysis of powder X-ray-diffraction patterns shows that the as-cast samples crystalize in a tetragonal $CaBe_2Ge_2$-type structure with space group P4/nmm. No traces of secondary phases were observed. As determined by the method of least squares fit, the refined lattice parameters $a = 0.44325(5)$ nm, $c = 1.01421(5)$ nm for $CeNi_2Sn_2$ are in good agreement with the literature.[14,15,19)]

Figure 1 displays the temperature dependence of the resistivity of $CeNi_2Sn_2Z$ and $LaNi_2Sn_2$. The magnetic resistivity

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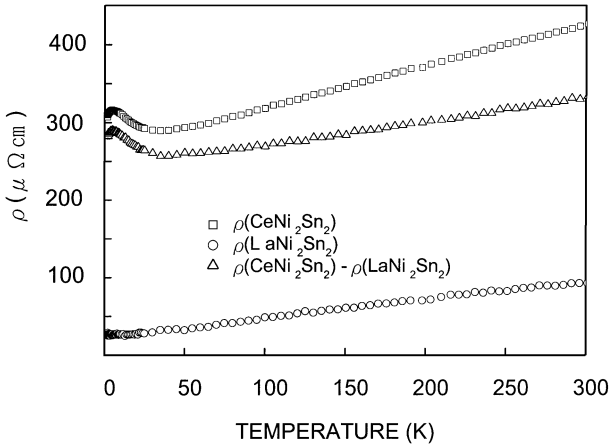


Fig. 1. Resistivity vs temperature of $CeNi_2Sn_2$, $LaNi_2Sn_2$ and the difference between these two compounds from 2.0 to 300 K.

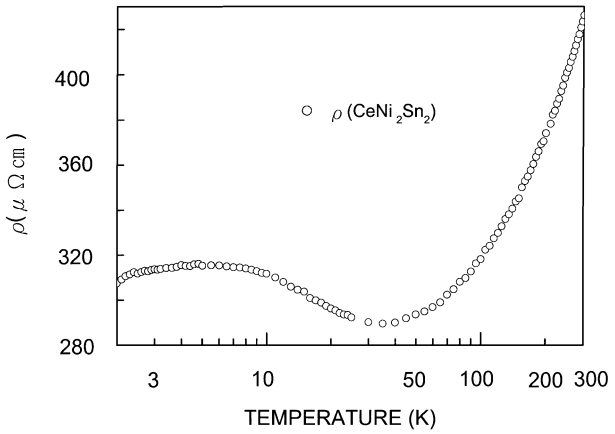
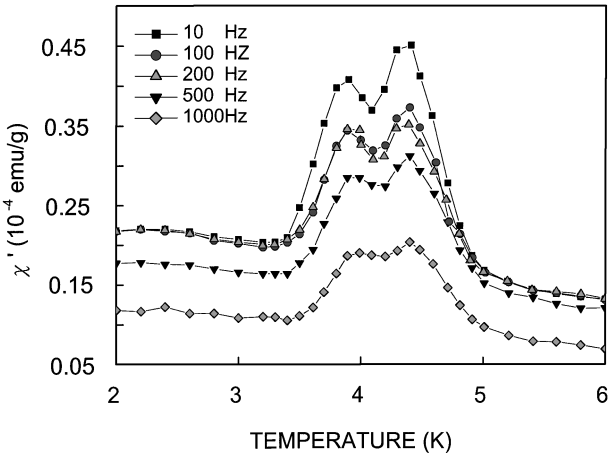
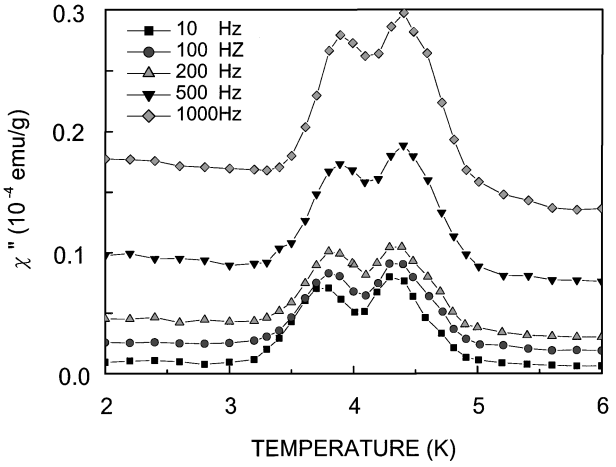


Fig. 2. Magnetic resistivity ρ_m vs $\ln(T)$ of $CeNi_2Sn_2$ between 2.0 and 300 K.



(a)

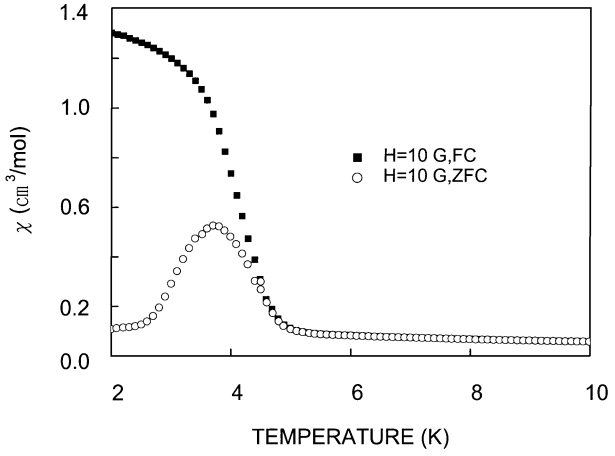


(b)

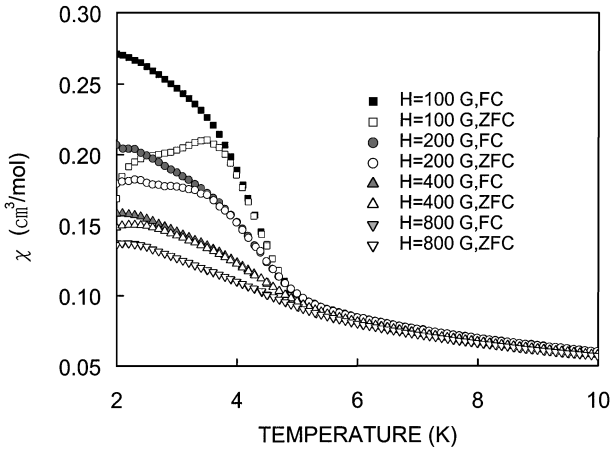
Fig. 3. (a)(b) The temperature dependence of real and imaginary compounds of ac susceptibility for $CeNi_2Sn_2$ in a driving field of 1.0 G at 10, 100, 200, 500 and 1000 Hz.

$\rho_m(T)$ is estimated by sustracting the resistivity of isostructural $LaNi_2Sn_2$ from that of $CeNi_2Sn_2$. Both the resistivity of $CeNi_2Sn_2$ and the magnetic resistivity $\rho_m(T)$ decrease almost linearly to a minimum value at 35 K as temperature is lowered from room temperature then show a Kondo-like increase at lower temperature down to 5 K where the maxima appear. Upon further cooling, a drop in the magnetic resistivity curve below 5 K is attributed to the onset of coherence between Kondo states at Ce sites as well as the magnetic phase order transition. The data for $\rho_m(T)$ are plotted as a function of $\ln(T)$ in Fig. 2. A $\ln(T)$ dependence is seen in the temperature region $10\,K < T < 30\,K$, which is one of the characteristic features of dense Kondo systems. Compared to the electrical resistivity measurements on single crystal $CeNi_2Sn_2$ as reported by Takabatake *et al.*,[16] our resistivity data have about five times larger value in magnitude probably due to the existence of the disorder and deficiciency in the nonmagnetic sublattice of our polycrystal sample. Moreover, our resistivity maximum in the resistivity curve appears at $1 \sim 2.5$ K lower temperature.

Figures 3(a) and 3(b) depict the real and imaginary parts of χ_{ac} versus T at different frequencies ν for the 1.0 G driving field. Note two prounced cusps in real χ_{ac} at 3.9 K and 4.4 K may denote two freezing temperatures. It is recalled that $CeNi_2Sn_2$ crystallizes in two crystallographic structures, one is tetragonal with $T_N = 1.8$ K[16,22] and the other one is monoclinic with $T_N = 2.1$ K.[19] Therefore the two freezing temperatures, $T_{f1} = 3.9$ K and $T_{f2} = 4.4$ K, may originate from the frustration of magnetic interactions in the tetragonal and monoclinic structures separately. In fact, Pierre *et al.*[19] also discussed the frustration of magnetic interactions in $CeNi_2Sn_2$ from the neutron diffraction data before. Our speculation is reasonable because it is very hard to tell the two phases from powder X-ray diffraction patterns due to their small difference in unit cell parameters of the two crystal structures. The frequency shifts of the maxima in χ_{ac} susceptibility yield ratios $\Delta T/[T_f \Delta(\log_{10}(\nu))] = 0.006 \pm 0.002$, which are in good agreement with values previously reported for metallic glasses.[24] In $CeNi_2Sn_2$, peaks of χ'_{ac} and χ''_{ac} occur at slightly different temperature, i.e., < 0.1 K. Figures 4(a) and 4(b) illustrate the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) static magnetic susceptibilities for the compound $CeNi_2Sn_2$ measured, in five fields, $H = 10$, 100, 200, 400 and 800 G, between 2 and 6 K with a commercial SQUID magnetometer. It is seen that, at low fields, *e.g.*, $H = 10$, 100, 200 and 400 G, the magnetization measured after zero-field-cooling is different from that in field cooling



(a)



(b)

Fig. 4. (a)(b) The temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) susceptibility of $CeNi_2Sn_2$ measured in fields of $H = 10$, 100, 200, 400 and 800 G between 2.0 and 6.0 K.

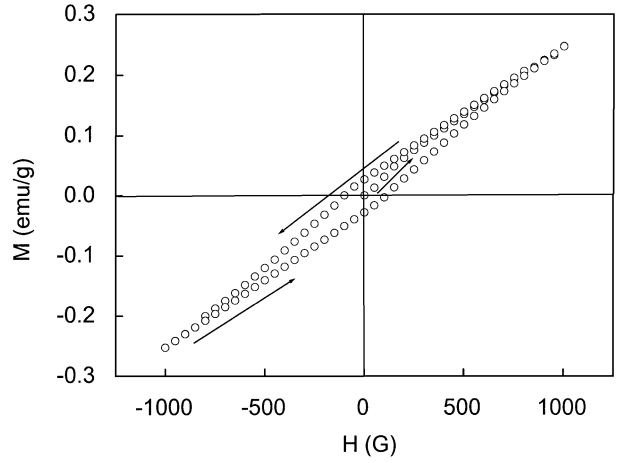


Fig. 5. The field dependence of magnetization $M(H)$ for $CeNi_2Sn_2$ at 2 K.

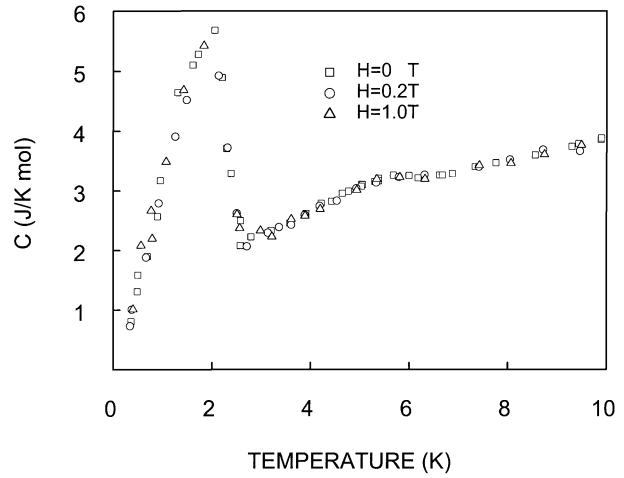


Fig. 6. The temperature dependence of specific heat $C(T)$ of $CeNi_2Sn_2$ measured in fields $H = 0$, 0.2 T and 1.0 T between 0.5 and 10 K.

below T_f. When the magnetic field increases to 800 G, the spin glass is depressed. The severe history dependence magnetization of $CeNi_2Sn_2$ is also demonstrated in the hysteresis loop measurements at temperature below T_f. As shown in Fig. 5, the hysteresis of $M(H)$ for $CeNi_2Sn_2$ at 2 K is probably due to the time dependence of $M(H)$ in a spin-glass state. The competition of ferromagnetic and antiferromagnetic interaction may creat small ferromagnetic component clusters in $CeNi_2Sn_2$.

As indicated in Fig. 6, the specific heat vs temperature $C(T)$ data curve of an as-cast $CeNi_2Sn_2$ sample measured in fields $H = 0$, 0.2 T and 1.0 T between 0.5 and 10 K shows a broad Lamda-type anomaly around 2 K and a peak value approaching 5.8 J/mol·K. We here, do not present the specific heat data of $LaNi_2Sn_2$ to get magnetic specific heat of $CeNi_2Sn_2$ due to the neglected small value of $LaNi_2Sn_2$ at low temperatures, and this does not affect our qualitative analysis. Similar anomaly measured in zero field was found by Takabatake *et al.*[16] and Beeyermann *et al.*[22] It is found that the experimental specific heat jump at the magnetic transition is only about 47% of the theoretical value calculated on the mean field ionic model for a ground state doublet of Ce^{+3} in $CeNi_2Sn_2$. This large reduction in specific heat jump as well as in the magnetic entropy at T_N was analyzed by Pierre *et al.* mainly from the viewpoints of mean field model and Kondo effect. We need to point out here that spin glass behavior as reflected in the hysteresis data for $CeNi_2Sn_2$ at 2 K in Fig. 5 may not be neglected in this situation. A more interesting behavior is the anomaly above T_N in the specific heat data curve of $CeNi_2Sn_2$. Again, the broad hump between 4 and 7 K in the specific heat data curve in Fig. 6 also reminds us the freezing of the magnetic moments as shown in the above ac susceptibility data in Fig. 3. The reason is that the existence of a broad peak in magnetic specific heat at higher temperature than T_f, i.e., about 1.3 or 1.4 times of T_f,[25,26] is one of the characteristic features of a spin glass. The two broad peaks in magnetic specific heat of $CeNi_2Sn_2$ may merge into a broad hump due to the two close freezing temperatures, $T_{f1} = 3.9$ K and $T_{f2} = 4.4$ K. Unfortunately, at present stage, there is still no persuadable theory to calculate the specific heat due to spin-glass order in a NMAD spin glass. We still can not rule out the possible contribution of crystal field (CF) splitting in $CeNi_2Sn_2$,[16,19] though Sampathkumaran *et al.*[14] has ever proposed a negligible CF splitting and no second peak in $\rho_m(T)$ dut to CF effects[27] has been observed in $CeNi_2Sn_2$.

From the present study, we conclude that the as-cast intermetallic compound $CeNi_2Sn_2$, which may crystallize in two

type structures, one is tetragonal and the other one is monoclinic, exhibits several interesting properties. Especially, some comparable experimental facts for $T > T_N$ with anomalies are observed between 3.5 and 7 K. in $C(T)$ and magnetic susceptibility measurements. This compound was found to be a Kondo lattice antiferromagnet with freezing temperature above its T_N. To further investigate the spin glass behavior in $CeNi_2Sn_2$ we have prepared a number of samples in the series $CeNi_{2-x}Cu_xSn_2$. This lengthier study of an isostructural series of compounds will be directed toward the question of the stability of the spin glass state against variations of the lattice parameters (Ce-ligand distances), magnetic susceptibility, and coherent scattering effects as measured by the electrical resistivity.

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