Calorimetric evaluation of magnetic ordering and spin reorientation in Er_3Ge_4

Y. Y. Chen, Y. D. Yao, and Y. S. Lin

Institute of Physics, Academia Sinica, Taipei, Taiwan, Republic of China

C. L. Chang

Department of Physics, Tamkang University, Tamsui, Taiwan, Republic of China

H. H. Hamdeh and J. C. Ho

Department of Physics, Wichita State University, Wichita, Kansas 67208

Calorimetric measurements have been made on orthorhombic Er_3Ge_4 having two crystallographically distinct Er sites. The temperature dependence of specific heat shows a peak near 7 K, confirming the antiferromagnetic ordering of both Er sublattices as suggested by neutron diffraction. A spin reorientation in one of the Er sublattices of the highly canted magnetic structure prevails as a second peak in specific heat around 3.5 K. Both magnetic transitions exhibit no thermal hysteresis. By further taking into account the relatively small contributions from lattice and crystal-field effect, as well as $3R \ln 2$ for the ordering of all Er^{3+} with a ground-state doublet, entropy analysis results in a 30 J/mol energy associated with the spin reorientation process.

Rare-earth-base compounds often undergo magnetic ordering at low temperatures. Among the different experimental techniques, specific-heat measurements play a unique role in providing thermodynamic quantities including energy and entropy associated with the transition and related processes. This paper describes such a calorimetric study on Er_3Ge_4. The binary compound was first identified by Eremenko and Obushenko.[1] An orthorhombic structure (Cmcm space group) with two crystallographically distinct Er sites (Er_1 and Er_2 in the ratio of 2 to 1) was determined through x-ray diffraction by Oleksyn and Bodak.[2] Based on neutron-diffraction data, Schobinger-Papamentellos *et al.*[3] further demonstrated that both Er sublattices order antiferromagnetically below $T_N = 7.3$ K, resulting in a triangular canted moment arrangement. In comparison, Er_1 appears to behave normally with the ordering process almost completed at 5 K. However, the angle between the moments and the b axis of the orthorhombic structure increases from 31° just below T_N to 34.4° between 4 and 5.8 K, then to above 35° below 4 K. Meanwhile, the c-axis-confined Er_2 moments vary continuously with temperature below T_N. A small anomaly near 4 K is attributed to the Er_1-spin reorientation effect.

The polycrystalline sample was prepared following the same procedure as in the earlier studies. A mixture of 99.99% pure erbium and germanium was arc melted to form Er_3Ge_4, which was then annealed at 800 °C for 3 weeks in an evacuated quartz tube, followed by water quenching. The expected orthorhombic structure is verified by x-ray diffraction. Calorimetric measurements between 1 and 13 K were made using a thermal-relaxation-type calorimeter. A mg-size specimen was thermally anchored with a minute amount of grease to a sapphire holder, which has a Cernox temperature sensor and a nickel-chromium alloy film as Joule-heating element. The holder was linked thermally by four Au-Cu alloy wires to a copper block, the temperature of which can be raised or lowered in steps but held constant when a heat

pulse is applied to the specimen. Following each heat pulse, the specimen temperature relaxation rate was monitored to yield a time constant τ. Heat capacity was then calculated from the expression $c = \kappa \tau$, where κ is the thermal conductance of the Au-Cu wires. The heat capacity of the specimen holder was measured separately for addenda correction. The specific heat of the specimen was then obtained from $C = (c - c_{\text{addenda}})/(m/M)$ with m and M being the specimen mass and the molar mass of Er_3Ge_4 (792.14 g/mol), respectively. Because of the strong magnetic frustration in the canted structure, measurements were carried out also in the cooling direction from 9 to 2 K, thus to check magnetic hysteresis, if present. Such an approach is practically impossible in more conventional adiabatic calorimetry.

The results are shown in Fig. 1 as the temperature dependence of specific heat in units of J/mol K. One peak near 7 K clearly reflects the antiferromagnetic ordering in corroboration with the neutron-diffraction data. A second, more rounded peak centers at 3.5 K. It is believed to be associated with the Er_1-spin reorientation. In either case, specific-heat
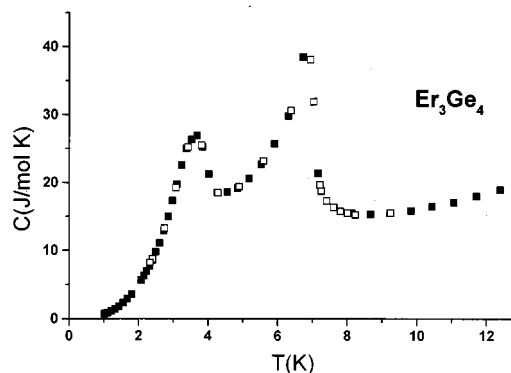

FIG. 1. Temperature dependence of specific heat showing two peaks. Closed symbols: heating path; open symbols: cooling path.
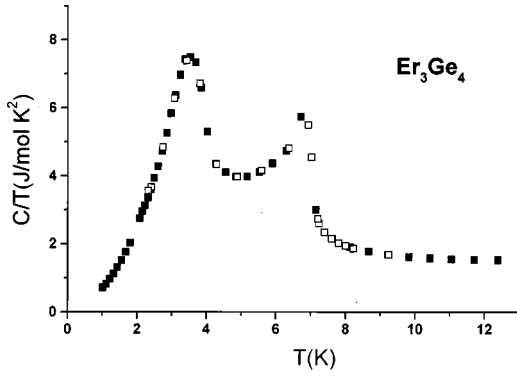
FIG. 2. C/T versus T as basis for entropy determination.

FIG. 3. Temperature dependence of entropy.

data as measured during heating and cooling paths coincide to suggest the lack of any hysteresis.

Data analysis is based on several contributions to the total specific heat:

$$C = C_{lat} + C_{Sch} + C_{SR} + C_{O\text{-}D}.$$

The lattice contribution, C_{lat} prevails in all solids. By assuming a reasonable Debye temperature θ_D of 400 K for the ceramic compound, $C_{lat} = 0.21 \times 10^{-3} T^3$ at least below approximately $\theta_D/50 = 8$ K. It is relatively insignificant. For example, at 8 K, $C_{lat} = 0.11$ J/mol K represents less than 1% of the total specific heat. The sizable background at higher temperatures comes from a crystal electric-field (CEF) effect. For Er^{3+} ($J = \frac{15}{2}$), CEF splitting yields most commonly a ground-state doublet. Excitations to higher energy levels lead to broad specific heat peaks known as Schottky anomalies. Obviously, what is observed here above T_N is the low-temperature tail of C_{Sch} which should drop off quickly below T_N. The spin-reorientation term, C_{SR} does not have an exact expression to follow. The same can be said for the contribution associated with the order-disorder transition, $C_{O\text{-}D}$, particularly for the complex magnetic structures and the gradually developing ordering with decreasing temperature in Er_2 sublattice. In order to delineate the energy associated with the relatively unusual spin reorientation, further analysis requires an entropy consideration.

Specific-heat data form the basis for entropy determination:

$$\Delta S = \int (C/T)dT.$$

By plotting C/T versus T in Fig. 2, a simple integration yields the increasing entropy with increasing temperature in
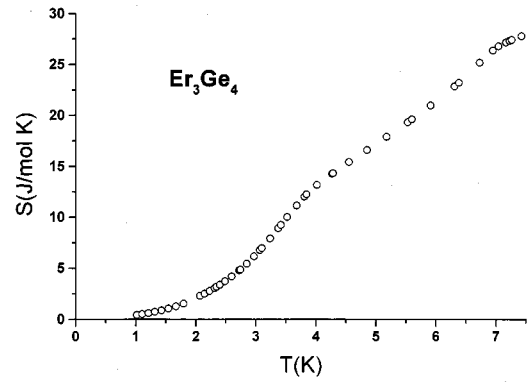
Fig. 3, reaching 27.5 J/mol K at 7.5 K just above T_N. Again, the total entropy change is the sum of individual contributions:

$$\Delta S = \Delta S_{lat} + \Delta S_{Sch} + \Delta S_{SR} + \Delta S_{O\text{-}D}$$

$$= \int (C_{lat}/T)dT + \int (C_{Sch}/T)dT$$

$$+ \int (C_{SR}/T)dT + \int (C_{O\text{-}D}/T)dT,$$

where the lattice term is negligible. In contrast, the major portion comes from the order-disorder transition. Even though the temperature dependence of $C_{O\text{-}D}$ is not available, statistical thermodynamics dictates that $\Delta S_{O\text{-}D}$ equals to $3R \ln 2 = 17.3$ J/mol K for Er_3Ge_4 with a ground-state doublet of Er ions. The factor of 3 is included, since there are 3 moles of Er ions per mole of the compound and both Er sublattices order simultaneously at the same T_N.[3] By further assigning a fair estimate of 1.5 J/mol K for ΔS_{Sch}, which should diminish rapidly below T_N, ΔS_{SR} can be calculated then as $[\Delta S - (\Delta S_{lat} + \Delta S_{Sch} + \Delta S_{O\text{-}D})] \sim 8.7$ J/mol K. With the transformation centering around 3.5 K, this entropy change corresponds to an energy of 30 J/mol, a rather impressive magnitude for a spin reorientation process at such low temperatures.

In conclusion, calorimetric data support the findings from neutron diffraction on Er_3Ge_4. Additional information is also obtained to provide a measure of the interaction strength between Er_1 and Er_2 sublattices.

[1] V. N. Eremenko and I. M. Obushenko, Sov. Powder Metall. Met. Ceram. **19**, 482 (1980).

[2] O. Ya. Oleksyn and O. I. Bodak, J. Alloys Compd. **210**, 19 (1994).

[3] P. Schobinger-Papamantellos, O. Oleksyn, C. Ritter, C. H. de Groot, and K. H. J. Buschow, J. Magn. Magn. Mater. **169**, 253 (1997).