Specific-Heat and Magnetocaloric Effect in UNiGa

de Boer, F.R.; Havela, L.; Suzuki, T.; Bruck, E.H.; Ikeda, S.; Nishigori, S.; Sechovsky, V.; Fujita, T.

Specific heat and magnetocaloric effect in UNiGa

V. Sechovský[a], L. Havela[a], F.R. de Boer[b], E. Brück[b], T. Suzuki[c], S. Ikeda[c],
S. Nishigori[c] and T. Fujita[c]

[a]*Department of Metal Physics, Charles University, Prague, Czechoslovakia*
[b]*Van der Waals–Zeeman Laboratory, University of Amsterdam, The Netherlands*
[c]*Faculty of Science, Hiroshima University, Japan*

Temperature dependence of the specific heat was measured on a single crystal of UNiGa in magnetic fields. The value $\gamma = 40.9 \, \text{mJ/mol K}^2$ does not change with the field-induced transition. The magnetic entropy is larger in the high-field (ferromagnetic) state ($0.55 \times R \ln 2$) than in the AF ground state ($0.50 \times R \ln 2$). Thermodynamic analysis shows that the high-field state is a true ferromagnetic state.

1. Introduction

UNiGa crystallizes in the ZrNiAl-type hexagonal structure. Its complex magnetic phase diagram is displayed in fig. 1 [1]. All magnetically ordered phases are collinear with moments pointing along the c-axis. The phases differ by the type of c-axis stacking of U magnetic moments coupled ferromagnetically within basal plane sheets. The ground state structure denoted 4 is characterized by the stacking $(+ + - + - -)$ of U moments of $1.4\mu_B$. High-field phase 6 with ferromagnetic stacking can be achieved either via the hatched hysteresis region or via ferrimagnetic phase 5 $(+ + -)$. Phase 7 is paramagnetic, whereas low-field phases 1, 2 and 3 are incommensurate, modulated commensurate, and equal-moment structures with the stacking

$$(+ + - + - - + - + -) ,$$

respectively. Metamagnetic transitions are accompanied by giant negative magnetoresistance effects reaching $\Delta\rho/\rho \simeq 90\%$ [2]. A reconstruction of the Fermi surface and consequent reduction of $N(E_F)$ was considered as one possible reason for the drop of ρ related to the breakdown of the antiferromagnetism. The temperature dependence of specific heat was studied first on a polycrystal showing a significant maximum around $T_C = 37 \, \text{K}$ [3]. Here we present the results of specific heat measurements on a single crystal in various magnetic fields. The primary goal, be-

Correspondence to: V. Sechovský, Department of Metal Physics, Charles University, Ke Karlovu 5, CS-121 16 Prague 2, Czechoslovakia.
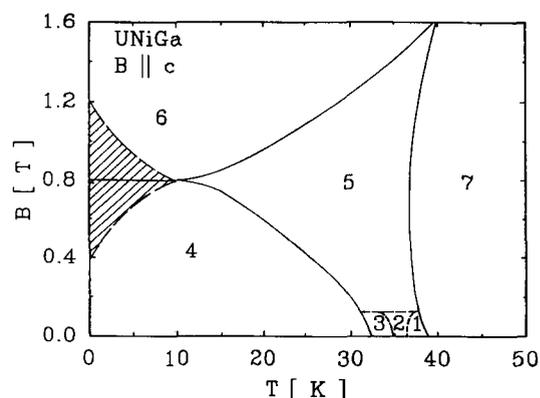
Fig. 1. Magnetic phase diagram of UNiGa determined by neutron diffraction [1]. For the description, see text.

sides direct observation of development of magnetic phase transitions in external field, is to inspect possible changes of density of electronic states at E_F with field-induced transition from the ground state antiferromagnetic to the field-induced ferromagnetic state.

2. Results and discussion

A single crystal of UNiGa was prepared by the Czochralski technique in a tri-arc furnace. The specific heat C was studied in fields of 0, 1 and 2 T applied along the c-axis, and in the temperature range 1.2–80 K. In the low-temperature part ($<15 \, \text{K}$), the C/T versus T^2 plots are straight lines, which are, surprisingly, practically identical in all applied fields. To illustrate the invariability, we give the results of a

linear regression leading to value of the γ-coefficient of 40.89, 40.93 and 40.91 mJ/mol K^2 for 0, 1 and 2 T, respectively.

Figure 2 shows the temperature dependence of the specific heat of UNiGa in various fields. Besides the temperature range 30–50 K, where the magnetic phase transitions occur, the dependencies are identical. The dashed line represents a tentative reference 'nonmagnetic' specific heat, which was constructed from the Debye-type function to conform to both high- and low-temperature parts of experimental curves. In zero field, one can see four magnetic phase transitions in the range 35–40 K, which can be well reconciled with the magnetic phase diagram. The character of the anomaly found around 37.5 K (sharp λ-type anomaly) suggests a first-order magnetic phase transition between phases 1 and 2. A similar, but even more pronounced, anomaly in $C/T(T)$ is observed in $B = 1$ T, where the boundary between paramagnetic phase 7 and ferrimagnetic phase 5 exists. The first-order transition can also be traced in $\chi(T)$ [4] and $\rho(T)$ dependences [4]. Note that phases 2 and 5 have the same fundamental component of the propagation vector of the type $\pm[0,0,1/3]$. The other anomaly in $B = 1$ T marks the transition between the ferri- and the ground-state AF phase. In $B = 2$ T only a single anomaly at 41 K is found, which corresponds to the transition from the para- to ferromagnetic range. Although no convenient nonmagnetic compound, which would provide us the 'background' specific heat, is available, we can make at least a rough estimate of the magnetic entropy using the background sketched in fig. 2. The entropy $\Delta S(T)$ calculated by integrating the difference $C/T - C_{bcg}/T$ leads, at 80 K, to the values

of $0.50 \times R \ln 2$ for 0 and 1 T, and $0.55 \times R \ln 2$ for $B = 2$ T (fig. 3). Assuming the same entropy in the paramagnetic range, the entropy in the low-temperature limit is thus lower for $B = 2$ T (i.e., in the ferromagnetic state) than for lower fields (antiferromagnetic state). Both values are, however, much smaller than expected for a local-moment system.

A thermodynamic analysis (Clausius–Clapeyron equation) of an antiferromagnet with a simple phase diagram yields a higher entropy at given temperature for the high-field metamagnetic phase than for the antiferromagnetic phase. However, for our type of phase diagram, we do not have the usual standard negative $\partial B_c/\partial T$ (B_c is the critical field of the metamagnetic transition). Instead, as the temperature of the magnetic ordering increases slightly with applied field, $\partial B_c/\partial T$ is positive, and the lower entropy of the metamagnetic state is understandable. We would like also to point out that for standard antiferromagnets the magnetic specific heat anomaly disappears in fields above B_c (0 K). In UNiGa the transition survives up to the highest fields studied, which means that the high-field state is a true ferromagnetic state.

Additional information on the thermodynamics can be obtained from the magnetocaloric effect, i.e., the temperature variations of an adiabatically mounted sample induced by sweeping the magnetic field. Here we concentrate on an analysis of temperature steps related to field-induced transitions. For adiabatic processes with $S = $ constant, one should observe a decrease in T at a transition from a low- to a high-entropy state, and vice versa. However, at low temperature we always observe a significant heating with
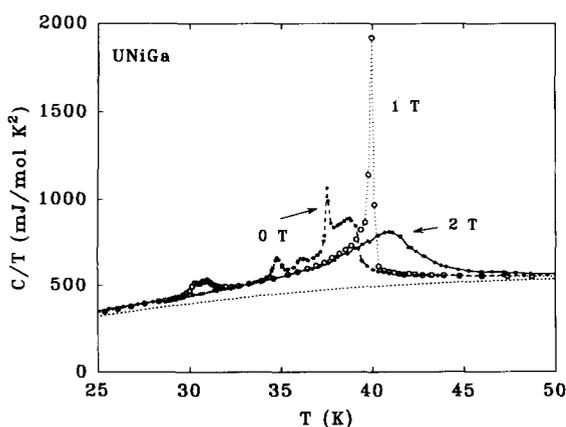

Fig. 2. Detail of the temperature dependence of C/T in various magnetic fields applied along the c-axis. The dashed line represents the background specific heat mentioned in the text.
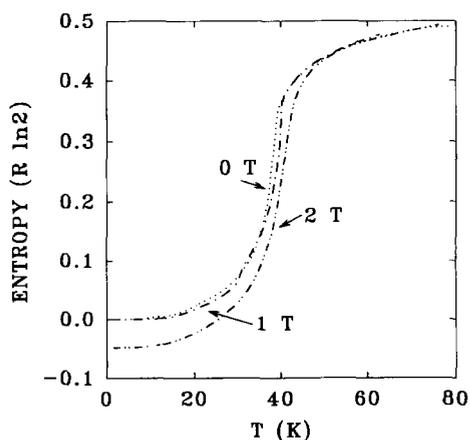

Fig. 3. Temperature dependence of the magnetic entropy in various fields. The zero entropy level is chosen arbitrarily for the low-temperature limit in zero magnetic field.

no respect to the direction of crossing the transition (fig. 4b). Keeping in mind the lower entropy of the ferromagnetic state, one would expect a heating effect when crossing B_c from below, which is indeed observed. However, the curve is not retraced with decreasing field; only the value of the step is reduced by several percent. One can speculate that the intrinsic magnetocaloric effect of the order of difference between two steps ($\simeq 0.5$ K) is obscured by a spurious heating mechanism, which can be related to, for example, magnetoelastic phenomena. This effect disappears around 10 K, i.e., with the appearance of the ferrimagnetic state. Figure 4(a) shows an example of the magnetocaloric effect at higher T. At temperatures where the ferromagnetic state is achieved via the
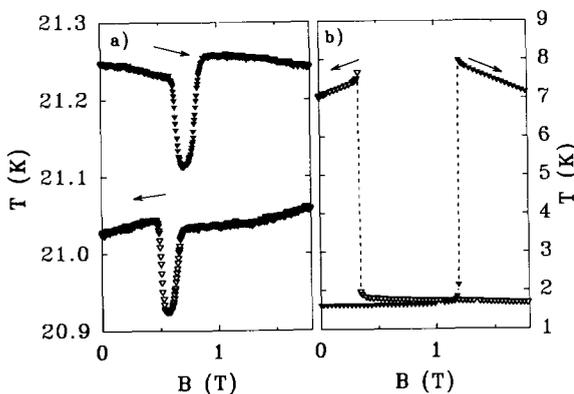
ferrimagnetic phase 5, at two-step function is observed. First, the transition from the AF to the ferri leads to a cooling, while the subsequent ferri-ferro transition heats up the sample. This corroborates the possibility of crossing of $S(T)$ branches for 0 and 1 T, seen in fig. 3. Consequently, the ferri phase can have a higher entropy than the ground state phase, while the entropy of the ferro phase is smaller throughout the whole temperature range.

Fig. 4. Magnetocaloric effect obtained with field along the c-axis. The sweeping rate did not exceed 0.2 T/min.

References

[1] P. Burlet, L. Jirman, V. Sechovský, L. Havela, M. Diviš, Y. Kergadallan, J.C. Spirlet, J. Rebizant, E. Brück, F.R. de Boer, H. Nakotte, T. Suzuki, T. Fujita and H. Maletta, in: Proc. 22 Journées des Actinides, Méribel 1992, eds. A. Blaise, P. Burlet and J.M. Fournier, CEN, Grenoble (1992) p. 125.

[2] V. Sechovský, L. Havela, L. Jirman, W. Ye, T. Takabatake, H. Fujii, E. Brück, F.R. de Boer and H. Nakotte, J. Appl. Phys. 70 (1991) 5794.

[3] V. Sechovský, L. Havela, L. Neuzil, A.V. Andreev, G. Hilscher and C. Schmitzer, J. Less-Common Metals 121 (1986) 169.

[4] L. Havela, V. Sechovský, L. Jirman, F.R. de Boer and E. Brück, J. Appl. Phys. 69 (1991) 4813.