Magnetovolume effects and the p-T magnetic phase diagram of UNi_2Si_2

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The thermal expansion of single-crystalline UNi_2Si_2 along the a and c axes has been measured with high accuracy. The linear thermal expansion is found to be highly anisotropic and to show a spontaneous magnetostriction. In the ground state, the spontaneous volume magnetostriction reaches 4×10^{-4}. The lattice volume changes abruptly at $T_1=43$ K and $T_2=103$ K, where UNi_2Si_2 undergoes the magnetic phase transitions. When increasing temperature, a considerable volume expansion (by 3.6×10^{-8} $m^3\,mol^{-1}$) at T_1 and tiny shrinkage (by 6.5×10^{-10} $m^3\,mol^{-1}$) at T_2 have been observed. On the other hand, no apparent volume effect is observed around the magnetic ordering temperature $T_N=124$ K. Thermal expansion data are analyzed using thermodynamic relations in order to elucidate the previously published pressure dependences of temperatures of magnetic phase transitions T_1, T_2, and T_N.

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I. INTRODUCTION

UNi_2Si_2 crystallizes in the tetragonal $ThCr_2Si_2$-type structure shown in Fig. 1, which consists of basal-plane layers of U atoms alternating with Si-Ni_2-Si slabs along the c axis.[1] The lattice parameters are $a=3.99$ Å and $c=9.53$ Å at room temperature. The distance between the nearest U neighbors is $d_{U\text{-}U}=a=3.99$ Å. The tetragonal crystal symmetry and the anisotropic layout of ligands of the U atoms are expected to cause anisotropy of electronic properties.

Below $T_N=124$ K, this compound exhibits magnetic order, which is characterized by several magnetic phases consecutively appearing with decreasing temperature.[2] The first ordered phase that is stable down to 103 K is an incommensurate longitudinal spin-density wave (ILSDW). At $T_2=103$ K, UNi_2Si_2 undergoes a magnetic phase transition to a simple body-centered tetragonal antiferromagnetic structure (AF-I). Finally, below $T_1=53$ K ($T_1\approx43$ K in Ref. 3) it exhibits an uncompensated antiferromagnetic (UAF) structure with $q=(0,0,2/3)$.[2] The value of T_1 is somewhat sample dependent, which may be connected with stoichiometry variations. For the crystal used in our study, $T_1=43$ K.[4–6] In all three magnetically ordered phases, the moments (only the U atoms carry detectable magnetic moments) are aligned along the c axis and coupled ferromagnetically within the basal plane. The coupling along the c axis determines the type of a magnetically ordered state; e.g., the $(+\ -\ +\ -)$ coupling defines the AF-I phase whereas the UAF phase is characterized by the $(+\ +\ -)$ coupling. The latter phase is then characterized by a spontaneous magnetic moment that amounts to 1/3 of the uranium moment. The magnetic phase transitions at T_1, T_2, and T_N are accompanied by distinct anomalies in the temperature dependence of electrical resistivity and thermal expansion.[7,8]

From neutron-diffraction experiments a magnitude of the

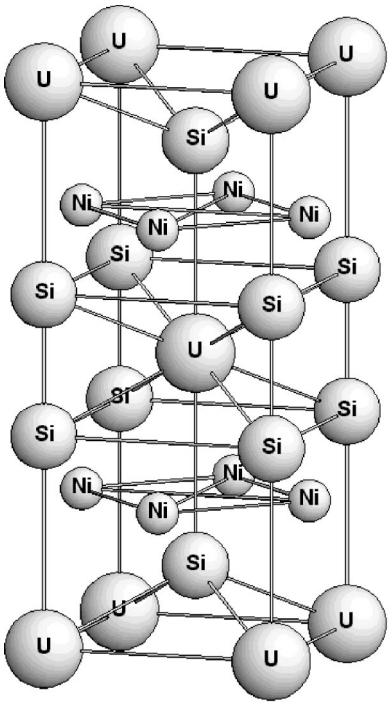

FIG. 1. A schematic picture of the crystal structure of UNi_2Si_2.

U magnetic moment of 2.2 μ_B has been determined in the ground-state phase. In this view, UNi_2Si_2 has been classified as a material with rather well-localized $5f$ electrons.[2] However, *c*-axis magnetization data obtained on the same crystal as used in our study point to a considerably lower value of 1.6 μ_B than that given in Ref. 2.

Electrical resistivity studies of UNi_2Si_2 exerted to an external hydrostatic pressure revealed that the value of T_1 (T_2) becomes strongly increased (weakly decreased), whereas T_N seems to be pressure invariant.[5,6,9] As a result of pressure effects on T_1 and T_2, the temperature range of the stability of AF-I is narrowing and vanishes above 3.2 GPa.[6] To discuss these phenomena from a thermodynamic point of view, highly accurate thermal expansion data of UNi_2Si_2 at ambient pressure were strongly desired. Therefore, we measured the precise thermal expansion and estimated the spontaneous magnetostriction on a single crystal along the *a* and *c* axes.

In our previous paper,[5] we estimated the spontaneous magnetostriction using a slightly higher Debye temperature $\Theta_D=370$ K available from specific-heat measurement data in Ref. 10. In the present paper, we use recently obtained $\Theta_D=283$ K,[11] which can explain the paramagnetic part of the thermal expansion much better.

II. EXPERIMENTAL PROCEDURE

The sample used for our experiment has been cut by spark erosion from the same single crystal of UNi_2Si_2 as reported in Refs. 4–6. The crystal was grown by means of the tri-arc Czochralski technique. The linear thermal expansion along the *a* and *c* axes was measured simultaneously by two strain gauges, having a resistance of 120Ω each (type KFL-02-120-C1-11 made by the Kyowa Electric Institute, Japan). They were glued by strain gauge cement (PC-6) on the clean surface of the *a*-*c* plane in UNi_2Si_2. In order to increase a measurement accuracy, we adopt the two gauge (active and dummy) method. In this method, we use dummy material as a standard, whose strain with respect to the temperature (thermal expansion) has already known exactly. Here we used a copper (99.999%) disk as a standard material. The thermal expansion coefficient of copper at ambient pressure has been investigated in detail by Kroeger and Swenson.[12] We put them in the circular of a Wheatstone bridge with other two constant resistors (120 Ω). The signal related to the difference between the relative change of the electrical resistance of strain gauges glued on the sample and dummy is amplified by a strain amplifier (type DPM-711B made by the Kyowa Electric Institute, Japan).

In such a way, these strain gauges provide data of the relative length change with an error smaller than $\pm 1 \times 10^{-6}$. We used a gold-Chromel thermocouple as a thermometer. The experimental error of the temperature is less than 0.1 K.

III. RESULTS AND DISCUSSION

The relative length change $(\Delta L/L)_i$ $(i=a,c)$ along the *a* and *c* axes, respectively, with respect to increasing temperature is shown in Fig. 2. Due to technical difficulties, we only are able to measure thermal expansion on the heating process. It is clearly seen that the linear thermal expansion is strongly anisotropic and shows several distinct anomalies accompanying the magnetic phase transitions, which is consistent with previously published thermal expansion results along the *c* axis.[8] With increasing temperature, the lattice expands along the *a* axis discontinuously at T_1, $(\Delta L/L)_a \approx 0.4\times 10^{-4}$, and shrinks along the *c* axis, $(\Delta L/L)_c \approx -0.3 \times 10^{-4}$. On the other hand, a lattice shrinkage is observed along the *a* axis ($\approx -0.3\times 10^{-4}$) and expansion along the *c* axis ($\approx 0.4\times 10^{-4}$) at T_2. These results indicate the first order magnetic phase transitions at T_1 and T_2. The magnetic phase transition at T_N is accompanied only by a change of slope of the $(\Delta L/L)_i$ vs T curves, where $i=a,c$, without showing any discontinuity in $(\Delta L/L)_i$. Above T_N, the lattice expands along the *a* axis with increasing temperature, while along the *c* axis it is nearly temperature independent.

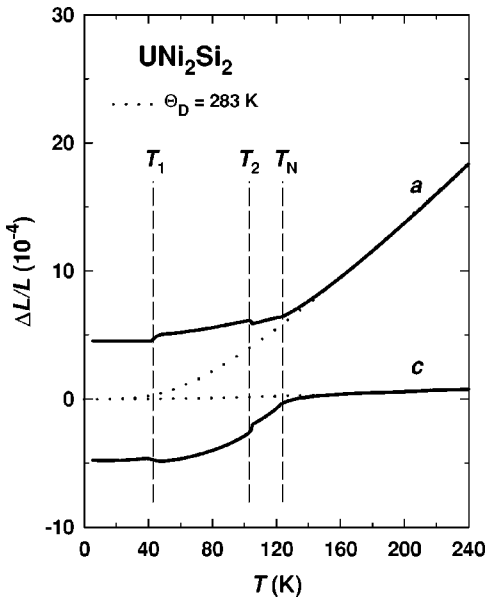

FIG. 2. The linear thermal expansion of UNi_2Si_2 along the *a* and *c* axes at ambient pressure for heating process. The dotted lines represent the phonon contribution to the thermal expansion estimated using the Debye temperature value $\Theta_D=283$ K.

The volume thermal expansion $\Delta V/V=2(\Delta L/L)_a+(\Delta L/L)_c$ below 150 K is shown in Fig. 3 (solid line). Pronounced anomalies are observed at T_1 and T_2: at T_1, the volume increases discontinuously by $\approx 0.5\times 10^{-4}$, and at T_2, it decreases discontinuously ($\approx -0.2\times 10^{-4}$) with increasing temperature. From these results it is found that the volume of the AF-I phase is larger than that of the other phases UAF and ILSDW. Practically complete compensation of linear strains along the *a* and *c* axes results in the absence of a volume anomaly at T_N.

The temperature dependence of the linear thermal expansion coefficients $\alpha_i=d(\Delta L/L)_i/dT$ at ambient pressure is shown in Fig. 4. The linear thermal expansion coefficients along the *a* and *c* axes are extremely anisotropic, $\alpha_a=12\times 10^{-6}$ K^{-1} at room temperature, whereas α_c is less than 1×10^{-6} K^{-1}. Sharp peaks reflecting the first-order mag-

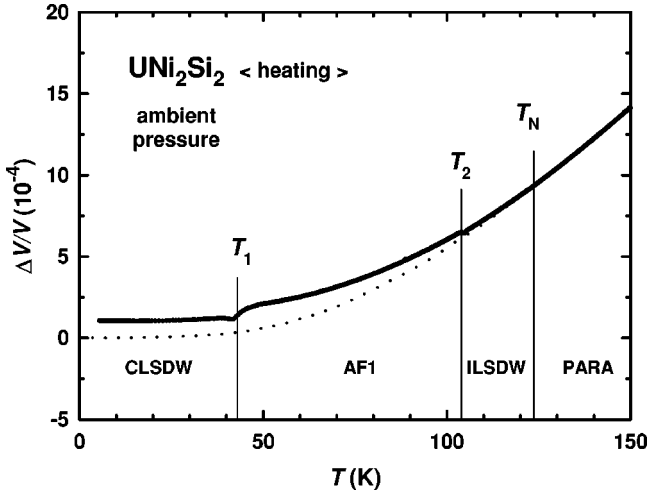

FIG. 3. The volume thermal expansion of UNi_2Si_2 at ambient pressure for heating process.

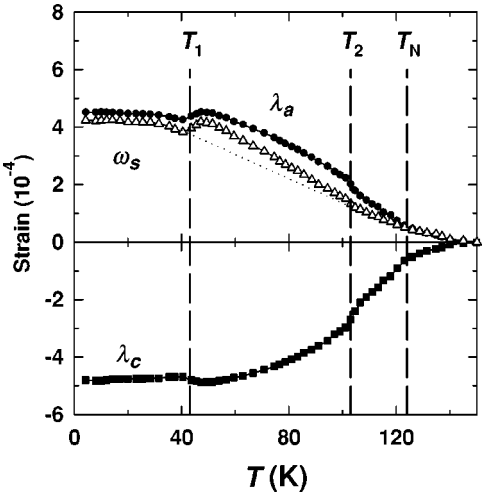

FIG. 5. Temperature dependence of linear (λ_a and λ_c) and volume (ω_s) spontaneous magnetostrictions at ambient pressure.

netic phase transition are observed at $T_1=43$ K and $T_2=103$ K. These values are in good agreement with specific-heat data.[11] At T_1, a pronounced hysteresis behavior is found in the electrical resistivity along the c axes.[6,7] The value of T_1 is also in good agreement with the averaged temperature of the resistivity anomaly between the cooling and heating processes. It is suggested that thermal hysteresis in the thermal expansion is narrower than that in the resistivity along the c axis. The transition at $T_N=124$ K is of the second-order character, which is connected with a discontinuous change of the linear thermal expansion coefficient $\Delta\alpha_a=4\times10^{-6}$ K^{-1} and $\Delta\alpha_c=-8\times10^{-6}$ K^{-1}. Then the change in the volume thermal expansion coefficient $\Delta\alpha_V$ at T_N, where $\Delta\alpha_V=2\Delta\alpha_a+\Delta\alpha_c$, is negligibly small.

In order to determine the spontaneous magnetostriction, the $(\Delta L/L)_i$ vs T and $\Delta V/V$ vs T curves were extrapolated from the paramagnetic region ($T>T_N$) into the magnetically ordered region ($T<T_N$). The dotted lines in Figs. 2 and 3 represent the Debye function with a characteristic temperature $\Theta_D=283$ K, which has been derived from specific-heat data measured on the crystal used in the present work.[11] (It should be noticed that the previously used value $\Theta_D=370$ K taken from Ref. 10 seems to be overestimated. The new value of Θ_D does not practically affect the extrapolation along the c axis, but leads to considerable corrections along the a axis compared to Ref. 5.) The related differences between the measured and extrapolated values correspond to the linear (λ_a in the basal plane, λ_c along the c axis) and the volume $\omega_s=2\lambda_a+\lambda_c$ spontaneous magnetostrictions that are displayed in Fig. 5 as functions of temperature. One can see that λ_a is always positive, λ_c is negative, and both linear strains vary nonmonotonously with temperature due to additional contributions of opposite sign in the intermediate AF-I phase. In the ground state, λ_a reaches 4.6×10^{-4} and $\lambda_c=-4.8\times10^{-4}$ which results in $\omega_s=4.4\times10^{-4}$.

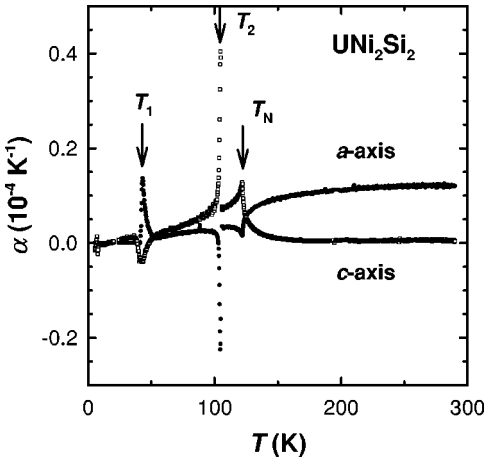

FIG. 4. The linear thermal expansion coefficients along the a and c axes for heating process. Arrows indicate magnetic phase transition temperatures.

Since the magnitudes of linear strain are of the order of 10^{-4} and moreover they are partly compensated due to their opposite sign, the spontaneous volume magnetostriction found in UNi_2Si_2 is relatively small. The compensation of linear strains having opposite sign, seems to be a common feature of uranium intermetallic compounds. For example, in the hexagonal UNiGa $\lambda_a=-0.8\times10^{-4}$, $\lambda_c=1.8\times10^{-4}$, and $\omega_s=0.2\times10^{-4}$,[13] in UNiAl, $\lambda_a=-0.4\times10^{-4}$, $\lambda_c=1.2\times10^{-4}$, and $\omega_s=0.5\times10^{-4}$,[14] and in UPtAl, $\lambda_a=-3\times10^{-4}$, $\lambda_c=2\times10^{-4}$, and $\omega_s=-4\times10^{-4}$.[16]

Figure 6 shows the pressure dependence of magnetic phase transition temperatures derived from data obtained on UNi_2Si_2 under various pressures up to 4 GPa.[6] The phase transition from the AF-I phase to the UAF structure exhibits a large temperature hysteresis. The value of T_1 represents the average value of the transition temperatures observed during the cooling and heating processes. One can see that T_1 is rapidly enhanced with applying pressure, $dT_1/dp=8.6$ K GPa^{-1}. This means that the UAF phase becomes stabilized with applying pressure on account of the AF-I phase, which is consistent with the fact that the volume of the UAF phase is reduced with respect to AF-I. On the other

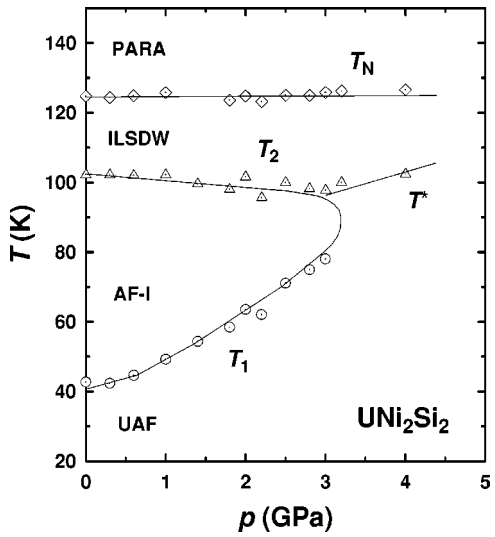

FIG. 6. Pressure dependence of magnetic phase transition temperatures of UNi_2Si_2 under high pressure up to 4.0 GPa.

hand, T_2 decreases with pressure at a rate of -1.3 K GPa^{-1} the transition becomes gradually broadened. The AF-I phase is completely suppressed in pressures above 3.2 GPa.[6]

Our thermal expansion data allow us to discuss the pressure effects on the magnetic phase transition temperatures of UNi_2Si_2 from a thermodynamical point of view. The value of the Néel temperature is found to be almost pressure independent. For the second-order phase transition, dT_N/dp is directly proportional to the discontinuous change of the volume thermal expansion coefficient, $\Delta\alpha_V$. As discussed above, there is no volume effect at T_N, $\Delta\alpha_V = 2\Delta\alpha_a + \Delta\alpha_c \approx 0$ K^{-1} within the experimental error. This result is then in good agreement with the pressure invariance of T_N, $dT_N/dp \approx 0$. The transition at T_2 from the phase AF-I to the ILSDW phase should be a first-order transition because it is accompanied by a discontinuous change of volume, $\Delta V = -6.5\times10^{-10}$ m^3 mol^{-1}. We can estimate the change in entropy, ΔS_{T_2}, at the transition by substituting these values in the Clausius-Clapeyron equation,

$$\Delta S_{T_2} = \frac{\Delta V}{(dT_2/dp)} \approx 0.5 \text{ J mol}^{-1} \text{ K}^{-1}. \qquad (1)$$

It is expected that the latent heat at this transition is large, ≈ 50 J mol^{-1}. This value is consistent with previous specific-heat data.[11,15]

The transition from the UAF phase to the AF-I phase is also the first-order transition accompanied by a discontinuous volume change, $\Delta V = 3.6\times10^{-8}$ m^3 mol^{-1} at T_1. As can be seen in Fig. 6, pressure dependence of T_1 at the lowest-pressure limit ($p \approx 0$) is not more than 8.6 K/GPa. Based on Eq. (1), the expected entropy change at the transition amounts, at least, to $\Delta S = 3.7$ J mol^{-1} K^{-1} at ambient pressure. This value is about one order of magnitude larger than the entropy change at T_2. But in reality, only a tiny anomaly is observed in the specific-heat data at T_1 which yields an entropy change of the order of 0.1 J mol^{-1} K^{-1}.[11]

From the thermodynamic point of view, the highest stability of the UAF phase is qualitatively in good agreement with our thermal expansion data obtained at ambient pressure. Note that the UAF phase has the smallest volume among all magnetic phases of this compound and the external pressure usually stabilizes a low-volume (high-density) state.

IV. CONCLUSIONS

Here we would like to conclude our study on UNi_2Si_2. The distinct anomalies in the thermal expansion of UNi_2Si_2 were observed at $T_1 = 43$ K, $T_2 = 103$ K, and $T_N = 124$ K, reflecting magnetic phase transitions. T_1 increases and T_2 decreases with increasing pressure; i.e., the intermediate magnetic phase is suppressed by pressure. T_N is almost independent of pressure up to 4.0 GPa. The thermal expansion of UNi_2Si_2 is highly anisotropic. In the paramagnetic range, the thermal expansion coefficient along the a axis is one order larger than that along the c axis. The values of the a and c linear spontaneous magnetostriction are of the order of 10^{-4} and have opposite sign, which leads to tiny volume effects. The pressure dependence of the critical temperatures T_2 and T_N of magnetic phase transitions can be explained within the thermodynamic point of view, applying the Clausius-Clapeyron equation with knowledge of thermal expansion and specific-heat data. However, questions about the small specific-heat anomaly at T_1, the complex magnetic phase diagram, and the large difference of the linear thermal expansion coefficients in the paramagnetic region remain still open. Measurements of the thermal expansion under high pressure, compressibility, and the theoretical approach are strongly desirable in order to get more information about UNi_2Si_2.

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