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Thermal expansion of MnRhP

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Abstract

The temperature dependence of the lattice parameters of MnRhP was determined in the temperature range from 80 K to 593 K by X-ray diffraction. The temperature dependence of the exchange strictions of MnRhP was estimated from the experimental results by using a Grüneisen relation. Based on the molecular field theory, we estimated the pressure derivative of the Curie temperature to be +1.7 K kbar^{-1}, which is in good agreement with the value obtained by direct measurement. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: MnRhP; Manganese rhodium phosphide; Thermal expansion; Compressibility

1. Introduction

The ternary intermetallic compound MnRhP crystallizes in the hexagonal Fe_2P-type. As shown in Fig. 1, the P atoms form tetrahedral and square-based pyramids both stacked in triangular channels along the hexagonal *c*-axis. The Rh atoms are located on the tetrahedral sites of one channels and the Mn atoms on the pyramidal sites of the adjacent channels. So, this compound has the character of a pseudo two dimensional crystal structure along the *c*-axis. MnRhP is a metallic ferromagnet with the Curie temperature T_c of 400 K [1]. The magnetic moment of MnRhP at 4.2 K was found to be 3.0 μ_B per formula unit and the spontaneous magnetization σ_s at 4.2 K is independent of pressure in the pressure range up to 7.6 kbar [2,3]. Kanomata et al. reported that the Curie temperature T_c of MnRhP increases linearly with pressure and the value of $\partial T_c/\partial p$ is +1.2 K kbar^{-1} [2]. Recently, Sato et al. reported that the value of $\partial T_c/\partial p$ for MnRhP is +1.5 K kbar^{-1} [3].

In order to examine the above experimental results from a different point of view, the temperature dependence of the lattice parameters of MnRhP was determined by X-ray diffraction at various temperatures between 80 and 593 K. The pressure dependence of the lattice parameters was also

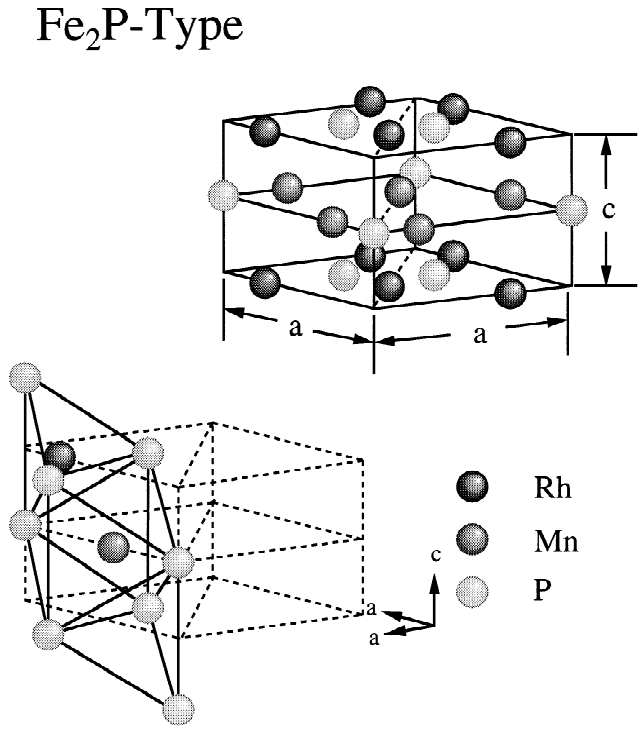

Fig. 1. Crystal structure of MnRhP.

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studied at room temperature. From these data, we obtained the temperature dependence of the exchange striction. The pressure derivative of the Curie temperature was estimated by the molecular field theory proposed by Bean and Rodbell [5].

2. Experimental

Polycrystalline sample of MnRhP was prepared from powders of Mn (99.99%), Rh (99.9%) and granules of P (99.9999%). They were mixed in the desired proportion, sealed in evacuated silica tubes and heated at about 400°C for 1 day. They were then heated at 850°C for 3 days and quenched in water. The reaction product was pulverized, mixed and annealed at 850°C for 3 days. The X-ray diffraction lines of the prepared sample were indexed with the hexagonal Fe_2P-type structure and no extra lines due to an impurity phase were observed. The lattice parameters were found to be $a=6.223$ Å and $c=3.585$ Å. These values are in good agreement with those reported by Fruchart [6]. X-ray diffraction analysis using Cu K_α radiation was carried out at various temperatures between 80 K and 593 K for a powdered sample of MnRhP. Lattice parameters were calculated from the three diffraction lines (111), (201) and (210) with strong intensity. The compressibility of MnRhP was measured at room temperature by high-pressure X-ray diffraction using a diamond anvil cell and Mo K_α radiation. The pressure dependence of the lattice parameters were determined using all diffraction lines from the $2\theta=3.69°$ to 35.5° at room temperature, where θ is the diffraction angle.

3. Results and discussions

The temperature dependence of the lattice parameters are shown in Figs. 2 and 3. Lattice parameter a decreases linearly as the temperature is decreased to the Curie temperature of $T_c=390$ K and hereafter decreases more quickly. The fast decrease in lattice parameter at temperatures below T_c is probably due to the negative exchange striction. In contrast, lattice parameter c decreases linearly with decreasing temperature through T_c, showing no exchange striction within experimental accuracy. In Fig. 4 the temperature dependence of the unit cell volume of MnRhP is shown. The solid lines in Fig. 4 are normal thermal expansion curves deduced by the Grüneisen relation, assuming the Debye temperature Θ_D to be 1000 K. The discrepancy between the normal thermal expansion curve and the thermal expansion curve observed is indicative of the temperature dependence of the exchange striction. The pressure dependence of the lattice parameters for MnRhP is shown in Figs. 5 and 6. To evaluate the pressure dependence of the lattice parameters, the lattice parameter $a(p)$ and $c(p)$ are fitted by the expression

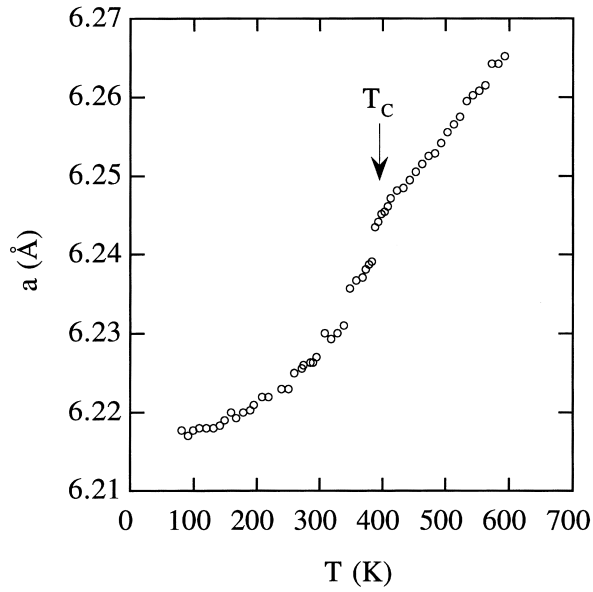

Fig. 2. Temperature dependence of lattice parameter a for MnRhP.

$$a(p) = a_0 + K_a a_0 p + \delta_a a_0 p^2$$

$$c(p) = c_0 + K_c c_0 p + \delta_c c_0 p^2 \quad (1)$$

a_0 and c_0 are the lattice parameters at $p=0$.

This gives the linear compressibility K_i ($i=a$ or c), which is normalized and thus independent of the size of the lattice parameter. The parameter δ_i ($i=a$ or c) indicates the change of the linear compressibility with increasing pressure. These numerical values of the coefficients are found by the least-squares method: $K_a=2.15\times10^{-4}$ kbar^{-1}, $\delta_a=2.46\times10^{-7}$ and $K_c=2.68\times10^{-4}$ kbar^{-1}, $\delta_c=3.37\times10^{-7}$. The volume compressibility K is obtained as

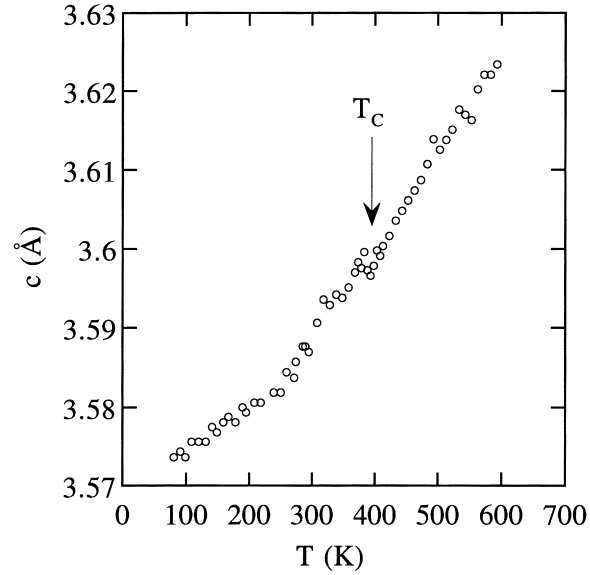

Fig. 3. Temperature dependence of lattice parameter c for MnRhP.

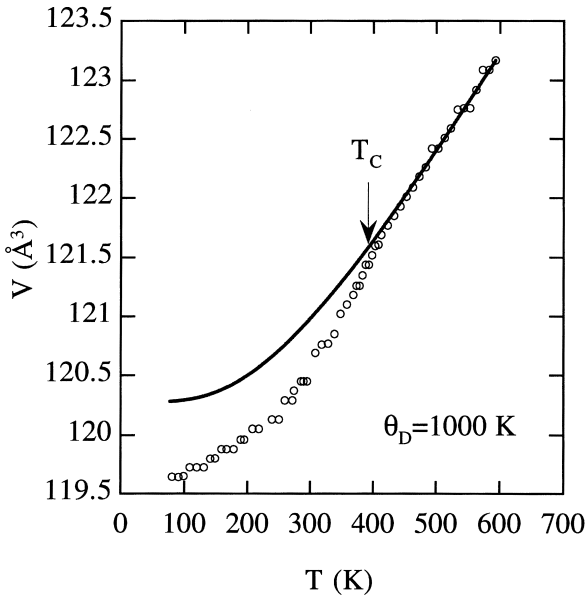

Fig. 4. Temperature dependence of the unit cell volume V for MnRhP. The solid line is a normal thermal expansion curve deduced by the Grüneisen relation, assuming the Debye temperature to be 1000 K.

6.98×10^{-4} kbar^{-1} by using the relation $K=2K_a+K_c$. No new diffraction lines were found up to 350 kbar, which indicates no change in the structure of MnRhP.

As mentioned above, the magnetic moment of MnRhP at 4.2 K is independent of pressure, indicating that the magnetic moment in MnRhP is localized. Therefore we derive expressions for the exchange strictions of MnRhP on the basis of a molecular field theory taking into account the anisotropic strain dependence of the exchange interactions. The exchange interactions J_a (>0) and J_c (>0) for MnRhP are defined as the interactions between the nearest

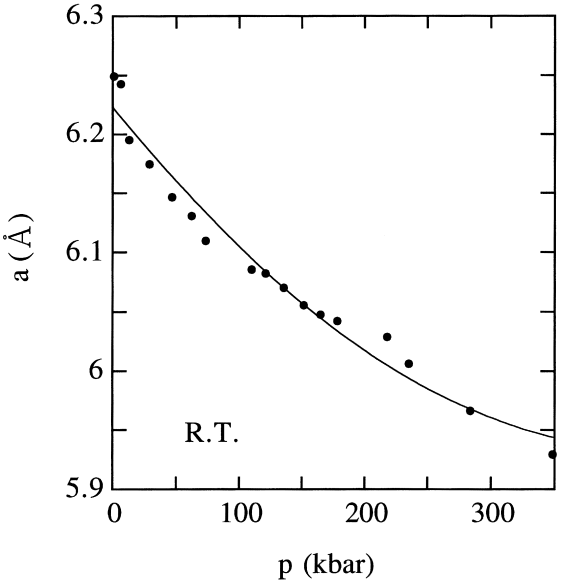

Fig. 5. Pressure dependence of lattice parameter a for MnRhP.

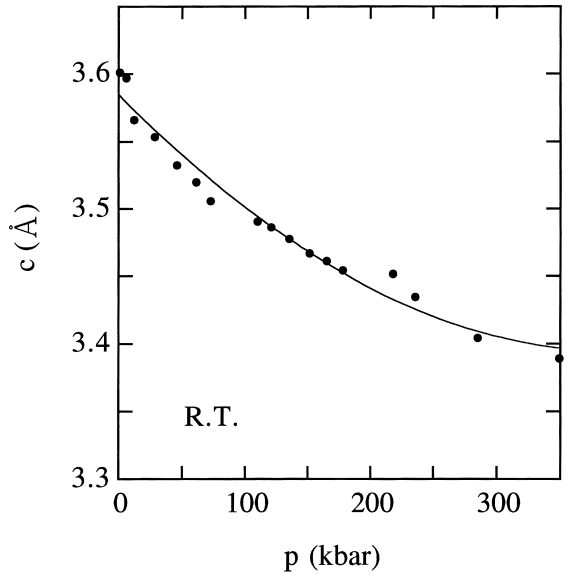

Fig. 6. Pressure dependence of lattice parameter c for MnRhP.

neighbors of the Mn ions within the c-planes and along the c-axis, respectively. Then, the Gibbs free energy per unit volume of the system can be expressed as

$$G = -3/2(S/S+1)NkT_c\sigma^2 + 1/2(2e_a^2/K_a + e_c^2/K_c) + p(2e_a + e_c) - TS(\sigma) \quad (2)$$

where p is the pressure, T the temperature, N the number of magnetic ions per unit volume, k the Boltzmann constant, S the spin quantum number, σ the relative magnetization, e_a and e_c the strain components along the a- and c-axis and $S(\sigma)$ the entropy. According to the molecular field theory, the Curie temperature can be expressed as

$$T_c = 2(z_aJ_a + z_cJ_c)S(S+1)/3k \quad (3)$$

where z_a and z_c are the numbers of the nearest-neighbor interacting magnetic ions within the c-planes and along the c-axis.

Here we assume that the exchange interactions J_a and J_c are strain dependent and can be expressed as

$$J_i = J_{i0}(1+\beta_i' e_i), \quad i = a \text{ or } c. \quad (4)$$

where J_{i0} represents the exchange interaction in the unstrained state and the coefficient β_i' relates the strain component e_i to the change in the exchange interaction along the i-axis. Substituting Eq. (4) into Eqs. (2) and (3), and setting $\partial G/\partial e_a$ and $\partial G/\partial e_c$ to zero, we obtain the following equations:

$$e_a = 3/4(S/S+1)NkT_0\beta_a\sigma^2K_a - K_ap \quad (5)$$

$$e_c = 3/2(S/S+1)NkT_0\beta_c\sigma^2K_c - K_cp \quad (6)$$

where T_0, β_a and β_c are expressed as

$$T_0 = 2S(S+1)(z_a J_{a0} + z_c J_{c0})/3k \quad (7)$$

$$\beta_a = \beta'_a z_a J_{a0}/(z_a J_{a0} + z_c J_{c0}) \quad (8)$$

$$\beta_c = \beta'_c z_c J_{c0}/(z_a J_{a0} + z_c J_{c0}) \quad (9)$$

It is shown in Eqs. (5) and (6) that e_a and e_c are proportional to σ^2 when $p=0$. The value of β_c is estimated to be zero because no exchange striction from the lattice parameter c is observed as mentioned above. Making use of the data from the $\sigma-T$ curve [3] and then using the values $N=2.5\times10^{22}$ cm^{-3}, $K_a=2.10\times10^{-4}$ kbar^{-1}, $S=3/2$, $T_0\approx T_c=390$ K, the temperature variation of exchange striction along the a-direction, $\Delta a/a$, was calculated by using Eq. (5).

The result is shown in Fig. 7, together with the experimental values. The agreement between these data appears to be reasonable, where the value of β_a was estimated to be -20.5. Furthermore, from Eqs. (3) and (4) we obtain

$$T_c = T_0(1 + \beta_a e_a + \beta_c e_c) \quad (10)$$

The pressure derivative of the Curie temperature is given by

$$\partial T_c/\partial p = -T_0(\beta_a K_a + \beta_c K_c) \quad (11)$$

Putting the values of $\beta_a=-20.5$, $\beta_c=0$, into Eq. (11) the initial pressure derivative of T_c is calculated as $\partial T_c/\partial p=+1.7$ K kbar^{-1}. This value is in good agreement with the directly measured values [3,4].

It should be noticed that the sensitivity to the atomic distance of the exchange interactions is large in the c-plane and very small along c-axis. The measurement of the pressure change of T_c under very high pressure is in progress.

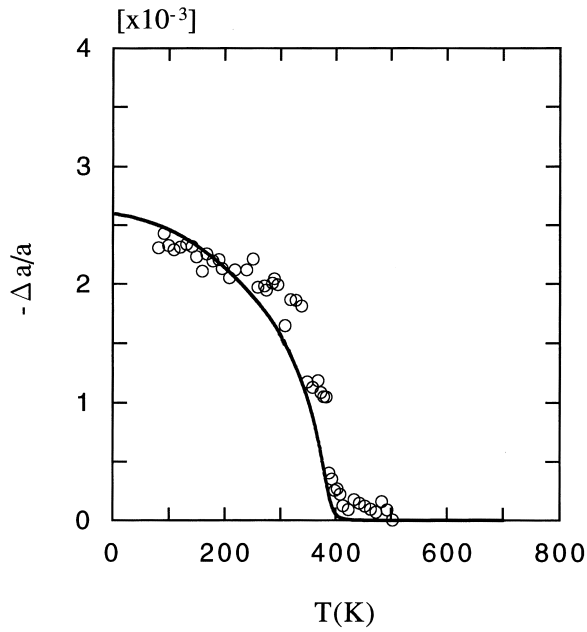

Fig. 7. Temperature dependence of exchange striction along the a-axis for MnRhP. Solid curve is calculated and open circles are the experimental results in this study.

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