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# Anomalous thermal expansion of MnN

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#### Abstract

The MnN compound is prepared as a single phase by d.c. reactive sputtering. The crystal structure of MnN is tetragonally distorted NaCl type (fct) one. The temperature variation of lattice constants for MnN is measured by X-ray diffraction experiments in the temperature range from 289 to 803 K. It is found that the MnN compound shows anomalous thermal expansion and the crystal structure of MnN has changed from fct structure to fcc one at about 650 K. On the other hand, we found formerly that MnN was an antiferromagnetic compound with a Néel temperature of 650 K. The tetragonal distortion below about 650 K is well explained by the strain dependence of the exchange interaction on the basis of molecular field theory.

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### 1. Introduction

It has been known that there are four phases ( $\varepsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$ ) in the Mn–N system [1-10]. MnN which contains the most nitrogen among these compounds belongs to the  $\theta$ -phase. Lihl et al. prepared a series of Mn–N compounds with 20.9–47.9 at.% N by reacting N<sub>2</sub> or NH<sub>3</sub> with Mn amalgams [1]. The most N-rich phase has an fct crystal structure with the lattice constants a=4.221 Å, c=4.113 or 4.115 Å (45.8 at.%N) and a=4.214 Å, c=4.148 Å (47.9 at.%N). Otsuka et al. prepared Mn-N films by nitriding vacuum-evaporated Mn films with NH<sub>3</sub> gas at 300 °C [9]. The nitride film has an fct structure with the lattice constants a=4.214 Å, c=4.144 Å. The specimen composition is Mn<sub>8</sub>N<sub>5.32</sub>. They investigated the temperature variation of the lattice constants for the compound by means of electron diffraction. They reported that its tetragonal structure turned to an fcc one at about 680 K. They concluded that the observed phase transition is of the second order or of the first order very close to the second order because thermal hysteresis was not observed at the transition. Above the transition temperature the temperature variation shows a peculiar behavior where the lattice constant decreases with increasing temperature. Besides, Nishiyama and Iwanaga reported that they prepared Mn nitrides by nitriding Mn powder with ammonium [8]. Among the prepared samples, they found a MnN compound which was not an fct structure but an fcc one with a large lattice constant a=4.435 Å (=51 at.%N).

We prepared the MnN compound as a single phase by d.c. reactive sputtering whose crystal structure was an fct one [11]. According to the results of magnetic measurements, the magnetic susceptibility of MnN showed a maximum around 650 K [11]. We also showed by powder neutron diffraction studies that the values of the magnetic moment of the Mn ion in MnN was found to be 3.3  $\mu_B$  at 16 K, 3.2  $\mu_B$  at 295 K and 2.1  $\mu_B$  at 450 K, respectively [12]. The magnetic structure of MnN was determined to correspond to the first kind of antiferromagnetic structure of the fcc structure. Therefore, we concluded that MnN is an antiferromagnetic compound with a Néel temperature of 650 K.

On the other hand, Leineweber et al. performed neutron diffraction measurements on  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> and  $\theta$ -Mn<sub>6</sub>N<sub>5.26</sub> [13]. Both phases show an antiferromagnetic ordering of the first kind with magnetic moments between 3.3 and 3.8  $\mu_{\rm B}$ .  $\theta$ -Mn<sub>6</sub>N<sub>5.26</sub> has an fct structure with the lattice constants a=4.2193 Å, c=4.1287 Å. Moreover, they

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reported that the collinear magnetic moments in  $\theta$ -Mn<sub>6</sub>N<sub>5.26</sub> were tilted by 23° relative to the tetragonal *c*-axis at ambient temperatures, and at about 550 K the magnetic moments aligned parallel to the *c*-axis, and up to the critical temperature of 660 K they decreased continuously to zero. The tetragonal distortion of the unit cell decreases and finally approaches an fcc structure.

Furthermore, as seen in the results of our experiments, the lattice constants a and c which were measured at room temperature for the samples annealed in vacuum for 2 h became smaller with increasing the annealing temperature above about 650 K because of the escape of nitrogen from the sample [11]. These results are consistent with the fact reported by Otsuka et al. [9] that the lattice constant a is smaller with increasing temperature above about 670 K, while the crystal structure is of fcc type above this temperature.

In this paper, in order to investigate the tetragonal distortion of MnN below about 650 K in more detail, the temperature variation of lattice constants of MnN is investigated. The results are discussed on the basis of a model taking account of the strain dependence of the exchange interaction.

## 2. Experimental procedure

The MnN sample was prepared by a high rate-type triode d.c. reactive sputtering in a mixture gas of  $Ar+N_2$  [11]. The sputtering conditions were as follows: target voltage, 0.22 kV; target current, 60 mA; total gas pressure,

 $3.0 \times 10^{-2}$  Torr; N<sub>2</sub> partial gas pressure,  $0.80 \times 10^{-2}$  Torr; residual gas pressure,  $1.70 \times 10^{-7}$  Torr; and target-substrate distance, 23 mm. A manganese disk of 99.9% purity was used as a target, and a water-cooled Cu plate was used as a substrate. The thickness of the deposited Mn–N film was about 170 µm and it was stripped off from the substrate mechanically, and then this stripped film was powdered. Finally, the powder sample was annealed at 510 K for 4 h in vacuum in order to relieve stress.

According to the result of the chemical analysis, the nitrogen content in the prepared MnN compound is estimated to be larger than 48 at.% N. Therefore, the atomic ratio of manganese to nitrogen in the sample is almost 1:1. Fig. 1 shows the X-ray diffraction pattern using Cu K $\alpha$  at room temperature for the annealed powder sample of MnN. Its crystal structure was determined to be an fct one. The lattice constants of the fct structure are a=4.256 Å and c=4.189 Å with c/a=0.9843 at room temperature [11]. The values of the lattice constants are a little larger than those obtained by Lihl et al. [1], Otsuka et al. [9] and Leineweber et al. [13], but the value of c/a is almost the same.

In order to investigate the temperature variation of the lattice constants of MnN, the X-ray diffraction measurements were carried out in a flow of He gas. The measurement was carried out at 289 K, and then carried out successively at every 20–30 K in the temperature range from 323 to 803 K with increasing temperature. But when the X-ray diffraction measurements were performed in the range of higher temperatures, there was a possibility that nitrogen atoms escaped from the MnN sample. Therefore,



Fig. 1. X-ray diffraction pattern of the powdered MnN compound at room temperature.

the X-ray diffraction measurements were also carried out under high pressure of 3.0 GPa at several temperatures to prevent the nitrogen escape from the sample, where the sample was air tightly enclosed in a capsule of h-BN.

## 3. Experimental results

## 3.1. Temperature variation of lattice constants

Fig. 2 shows the X-ray diffraction pattern for the MnN sample in the range of  $2\theta$  from  $30^{\circ}$  to  $55^{\circ}$  and Fig. 3 from  $55^{\circ}$  to  $80^{\circ}$  at various temperatures, respectively. In the figure, the indices of diffraction lines are shown with hkl (hkl) related to the tetragonal structure of MnN. As shown in the figure, the lines of 200 (002), 220 (202) and 311 (113) split into two lines at temperatures from 289 K up to 643 K. These lines indicate that the crystal structure is a tetragonal one below 643 K. But these lines come close to each other with increasing temperature and merge together into one line above 668 K. The lines above 668 K are well indexed as an fcc structure whose lattice constant decreases with increasing temperature as seen in the figures. However, whether it is the NaCl type structure or the ZnS type one is ambiguous from the relative intensities of the 111 line and the 200 line.

On the other hand, as seen in Figs. 2 and 3, another Mn–N compound which has quite a different lattice constant appears above 693 K. In the figure, the lines of this compound are designated by the index [*hkl*]. The lines of this compound are well indexed as an fcc structure. The lattice constant of this compound is a = 4.47 Å (at 803 K) and does not change considerably with increasing tempera-



Fig. 2. X-ray diffraction pattern of the powdered MnN compound in the temperature range from 289 to 803 K (I)  $2\theta = 30-55^{\circ}$ .



Fig. 3. X-ray diffraction pattern of the powdered MnN compound in the temperature range from 289 to 803 K (II)  $2\theta = 55 \sim 80^{\circ}$ .

ture. It is considered that the structure of this compound is like a NaCl type one, because the intensity of [111] line is a little smaller than that of the [200] one. From the figures, it is found that the relative amounts of this compound is growing gradually with increasing temperature. It is noted that the lattice constant of this new compound is almost the same as the lattice constant a=4.435 Å of the MnN compound reported by Nishiyama and Iwanaga [8].

The temperature variations of the lattice constants of MnN are shown in Fig. 4. In the figure, an open circle represents the lattice constant a and an open triangle the lattice constant c of MnN whose structure is tetragonal, where a is derived from 200 line and c from 002 line. An open square represents  $V^{1/3}$  which is the cubic root of the unit cell volume of MnN in the tetragonal phase. A closed circle represents the lattice constant a of the compound which has changed from the tetragonal structure to the fcc structure, where a is derived from the 200 line. As seen in the figure, with increase of the temperature, the lattice



Fig. 4. Temperature variations of the lattice constants of MnN: an open circle represents a, an open triangle c and an open square  $V^{1/3}$  (V is unit cell volume) of MnN. A closed circle represents a of the fcc compound which has changed from the tetragonal MnN.

constant a ( $\bigcirc$ ) increases at first and decreases above about 550 K, and c ( $\triangle$ ) increases gradually at first and increases rapidly above 600 K. The lattice constants a ( $\bigcirc$ ) and c ( $\triangle$ ) coincide at 668 K, where the tetragonal structure of MnN changes into the fcc one with the lattice constant a = 4.260 Å ( $\bullet$ ). Above 668 K the lattice constant a ( $\bullet$ ) decreases remarkably with increasing temperature, and then approaches 4.212 Å at 803 K. Such negative thermal expansion is considered to be unreasonable in usual normal thermal expansion behaviour above  $T_N$ . It is considered that the observed negative thermal expansion is caused by the nitrogen escape from the sample in the high temperature range in this experiment.

Such contraction was also observed for MnN annealed at 738 K for 2 h, where it was found by chemical analysis that nitrogen escape from the sample actually occurred although the crystal structure of MnN still remained up to 753 K [11]. Thus it is considered that the MnN compound does not change into another compound even in the present experiment and only the crystal structure changes at about 650 K. It is considered that the tetragonal structure of MnN in the range from room temperature to about 650 K is caused by exchange striction due to the Mn–Mn distance dependence of the exchange interactions. The result shown in Fig. 4 is very similar to that obtained by Otsuka et al. [9].

#### 3.2. X-ray diffraction under high pressure

As seen in Section 3.1, the crystal structure of MnN has changed from the fct structure into the fcc one at about 650 K. The lattice constant of the fcc structure decreases with increasing temperature, which is considered to be caused by nitrogen escape from the sample. Therefore, in order to investigate the temperature variation of the lattice constant of MnN when the nitrogen escape from the sample is prevented, X-ray diffraction measurements under a high pressure of 3.0 GPa were carried out where the sample was air tightly enclosed in the h-BN compound.

The experiments were performed at the temperatures 675, 700, 725 and 750 K. The diffraction patterns show an fcc structure. It is found that the lattice constant a of MnN increases with increasing temperature in the region of high temperatures above 650 K, as seen in normal thermal expansion. This is considered as being due to the prevention of the nitrogen atom to escape from the sample.

As mentioned above, it is considered that the tetragonal structure of MnN below the transition temperature is caused by exchange striction. Therefore, if MnN would not be in a magnetically ordered state, the crystal structure of MnN would be of the fcc type in the whole temperature range. So the temperature variation of the lattice constant *a* of MnN in the non-magnetic state below the transition temperature was determined by using the linear expansion coefficient above the transition temperature.

## The calculation procedure is as follows:

First, the bulk modulus *B* is derived from the difference of the lattice constants *a* under normal pressure and a high pressure of 3.0 GPa at room temperature. *B* is obtained to be  $1.66 \times 10^{11}$  N/m<sup>2</sup>. Next, the Grüneisen parameter  $\gamma$  is derived.  $\gamma$  is given as

$$\gamma = \frac{3B\alpha}{C_v} \tag{1}$$

where  $\alpha$  represents the linear expansion coefficient and  $C_v$ represents the specific heat at constant volume. The value of  $\gamma$  is determined to be 2.21 from Eq. (1), where  $\alpha$  is  $1.878 \times 10^{-5}$  (1/K),  $C_v$  is  $4.24 \times 10^6$  J/m<sup>3</sup>·K and B 1.66×  $10^{11}$  N/m<sup>2</sup> as obtained above. The value of  $\alpha$  is obtained by using the least-squares method for the lattice constants *a* which are derived from the 220 line at 675, 700, 725 and 750 K.  $C_v$  is the lattice specific heat at 690 K, supposing that the Debye temperature of MnN is 530 K [14]. Assuming that  $\gamma$  and *B* are almost independent of temperature within the whole range of temperature, they can be taken as constant. The value of  $\alpha$  in non-magnetic state below 650 K can be calculated by the following expression

$$\alpha = \frac{\gamma C_v}{3B} \tag{2}$$

The lattice constants *a* for the non-magnetic state at temperatures below the transition temperature are derived by using  $\alpha$  at each temperature, as obtained from Eq. (2). In this calculation,  $C_v$  is the value at each temperature. The results are shown in Fig. 5. In this figure, the solid line below the transition temperature represents the calculated lattice constant *a* for the non-magnetic state. The open squares above 675 K are derived from the experimental data obtained in the X-ray diffraction measurements under a high pressure of 3.0 GPa, where the values at each temperature fluctuate somewhat. The solid line above the transition temperature is derived by using a least-squares



Fig. 5. Temperature variations of the lattice constants of MnN. An open circle represents a and an open triangle c of MnN. A solid line represents the calculated lattice constant a in non-magnetic state. An open square represents a which is obtained from the X-ray diffraction measurements under high pressure of 3.0 GPa.

method from the experimental data. Open circles (triangles) represent the experimental values of the lattice constant a (c) of MnN, as already shown in Fig. 4.

#### 4. Discussion

Bean et al. studied a first-order magnetic transition and pressure variation of  $T_c$  of a ferromagnetic compound MnAs, considering the volume dependence of a single exchange interaction [15]. On the other hand, Adachi et al. [16] and Abe et al. [17] discussed the magnetic properties of CrSb, considering two kinds of strain dependent exchange interactions. The present results of MnN are discussed in a way similar to those of Refs. [16,17].

We reported that the magnetic structure of MnN is an antiferromagnetic one, as shown in Fig. 6 based on neutron diffraction studies [12]. The magnetic moment of the Mn-ion extrapolated to 0 K was found to be 3.3  $\mu_B$  and to lie in the (001) plane. This is known as the first kind antiferromagnetic ordering of the fcc lattice. The direction of the magnetic moment within the (001) plane cannot be determined by a powder neutron diffraction measurement [18]. In the magnetic structure shown in Fig. 6, a Mn-ion has 12 first nearest neighboring Mn-ions. Four of them are in the same (001) plane, and couple ferromagnetically with the central Mn-ion. And eight of them are in the adjacent (001) planes, and couple antiferromagnetically with the central Mn-ion. A given Mn-ion has also six second



Fig. 6. Antiferromagnetic structure of the MnN compound. Magnetic moments lie in the (001) plane.  $J_{1d}$  is defined as  $J_1$  related to the eight ions in the adjacent (001) planes and  $J_{1a}$  as  $J_1$  related to the four ions in the same (001) plane, where  $J_1$  represents the exchange interaction between the first nearest neighboring Mn-ions.  $J_2$  represents the exchange interaction between the second nearest neighboring Mn-ions.

nearest neighboring Mn-ions. Four of them are in the same (001) plane, and two of them are in the *c*-direction. All of these neighbors couple ferromagnetically with the central Mn-ion.

The exchange interaction  $J_1$  between the first nearest neighboring Mn-ions and  $J_2$  between the second nearest neighboring Mn-ions are estimated on the basis of molecular field approximation for the first kind antiferromagnetic ordering in the fcc structure as proposed by Smart [19]. We obtained that  $J_1$  and  $J_2$  are -29 and 24 K, respectively, by using  $T_N = 650$  K, the magnetic susceptibility value  $\chi_g =$  $2.3 \times 10^{-5}$  emu/g at 650 K obtained experimentally and S = 3/2 [12]. If  $J_1$  and  $J_2$  are, respectively, the 90° and 180° superexchange interactions proceeding via N-ions, the signs of the exchange interactions in MnN are contradictory to those of  $d^3$  (Mn) in the model of Goodenough and Kanamori [20–22].

Here,  $J_{1d}$  is defined as  $J_1$  related to the eight ions in the adjacent (001) planes and  $J_{1a}$  as  $J_1$  related to the four ions in the same (001) plane as shown in Fig. 6. So,  $J_1$  is  $J_{1d}$  or  $J_{1a}$ . The number of Mn-ions related to  $J_2$  is six. All these ions are coupled ferromagnetically and can be separated into four which are in the same (001) plane and two which are in the direction of the *c*-axis. Therefore,  $J_{2a}$  is defined as  $J_2$  related to the four ions in the same (001) plane and  $J_{2c}$  as  $J_2$  related to the two ions in the direction of *c*-axis. So,  $J_2$  is  $J_{2a}$  or  $J_{2c}$ .

Hence, exchange energy per unit volume of MnN can be described in the following way:

$$-\frac{1}{2}N \cdot 8J_{1d}S^{2} \cdot (-\sigma^{2}) - \frac{1}{2}N \cdot 4J_{1a}S^{2}\sigma^{2}$$
$$-\frac{1}{2}N \cdot 4J_{2a}S^{2}\sigma^{2} - \frac{1}{2}N \cdot 2J_{2c}S^{2}\sigma^{2}$$
(3)

where *N* is the number of Mn-ions per unit volume, *S* the spin quantum number and  $\sigma$  the relative magnetic moment. Therefore, the Gibbs-free energy per unit volume of the system including striction energy in addition to the exchange energy can be expressed as

$$G = -NS^{2} \left( -4J_{1d}\sigma^{2} + 2J_{1a}\sigma^{2} + 2J_{2a}\sigma^{2} + J_{2c}\sigma^{2} \right) + \frac{1}{2} \left( 2\frac{e_{a}^{2}}{K} + \frac{e_{c}^{2}}{K} \right) + p(2e_{a} + e_{c}) - T(\phi_{l} + \phi_{s})$$
(4)

where  $e_a$  and  $e_c$  are strain components in the direction of the *a*- and *c*-axes, *K* the compressibility, *P* the pressure, *T* the temperature and  $\phi_1$  and  $\phi_s$  the lattice and spin parts of the entropy.

The Mn–Mn distance for  $J_{1d}$  is almost the same in both the antiferromagnetic state and the paramagnetic state, since in the antiferromagnetic state the lattice constant *a* is larger and *c* is smaller than those in the non-magnetic state. It is assumed that the atomic distance dependence of  $J_{1d}$  needs not to be taken into consideration within a first approximation. Thus, only  $J_{1a}$  depending on  $e_a$  on the same (001) plane is taken into consideration. Therefore, the strain dependencies of  $J_{1d}$  and  $J_{1a}$  can be expressed as

$$J_{1d} = J_{10} J_{1a} = J_{10} (1 + \beta_1 e_a)$$
(5)

where  $J_{10}$  represents the value of the exchange interaction  $J_1$  in the unstrained state,  $\beta_1$  is coefficient which relates the strain component  $e_a$  to  $J_1$ .  $J_2$  can be separated into  $J_{2a}$  and  $J_{2c}$ . Since  $J_{2a}$  depends on  $e_a$  only and  $J_{2c}$  on  $e_c$  only, respectively, the strain dependencies of  $J_{2a}$  and  $J_{2c}$  can be expressed as

$$J_{2a} = J_{20}(1 + \beta_2 e_a) J_{2c} = J_{20}(1 + \beta_2 e_c)$$
(6)

where  $J_{20}$  represents the value of the exchange interaction  $J_2$  in the unstrained state,  $\beta_2$  is coefficient which relates the strain component  $e_a$  and  $e_c$  to  $J_2$ .

Substituting Eqs. (5) and (6) into Eq. (4) and using

$$\frac{\partial G}{\partial e_a} = 0 \quad \frac{\partial G}{\partial e_c} = 0 \tag{7}$$

the value of  $e_a$  and  $e_c$  that minimize the Gibbs-free energy are determined. The expression for the magnetic strain components  $e_a$  and  $e_c$  are obtained as

$$e_{a} = NS^{2}\sigma^{2}K(J_{10}\beta_{1} + J_{20}\beta_{2})$$

$$e_{c} = NS^{2}\sigma^{2}KJ_{20}\beta_{2}$$
(8)

by taking P=0 and neglecting  $\phi_1$ .

 $\sigma(T)$  is given by the Brillouin function,

$$\sigma(T) = B_S(x) \tag{9}$$

$$x = \frac{2(-8J_{1d} + 4J_{1a} + 4J_{2a} + 2J_{2c})\langle S \rangle S}{kT}$$
(10)

where  $\langle S \rangle = S\sigma$ , k is Boltzmann constant. Putting Eqs. (5), (6) and (8) into Eq. (10), we obtain

$$x = \frac{4S^2}{kT} \left( p\sigma + q\sigma^3 \right) \tag{11}$$

where

$$p = -2J_{10} + 3J_{20}$$
  

$$q = NS^{2}K(2J_{10}^{2}\beta_{1}^{2} + 4J_{10}\beta_{1}J_{20}\beta_{2} + 3J_{20}^{2}\beta_{2}^{2})$$
(12)

The Néel point  $T_{\rm N}$  is given as

$$T_{\rm N} = \frac{2S(S+1)(-8J_{1d}+4J_{1a}+4J_{2a}+2J_{2c})}{3k}$$
(13)

Putting Eqs. (5) and (6) into Eq. (13), and then using  $e_a = e_c = 0$  (:: $\sigma = 0$ ),  $T_N$  is expressed as

$$T_{\rm N} = \frac{2S(S+1)(-4J_{10}+6J_{20})}{3k} \tag{14}$$

As shown above, the magnetic strains are expressed as

functions of the strain coefficients of the exchange interactions  $\beta_i$ . The deviation of the lattice constants *a* and *c* from that of the cubic structure in the non-magnetic state below 650 K is derived.

The  $\beta_i$  values are determined for the difference between the experimental values and the calculated ones to be the least in the whole range of temperature below  $T_N$ . The calculation is performed by using the following data for N,  $S, K, J_{10}, J_{20}$  and taking  $\beta_i$  as fitting parameters: N = $5.27 \times 10^{22}$  (1/cm<sup>3</sup>), S = 3/2,  $K = 6.02 \times 10^{-13}$  (cm<sup>2</sup>/dyn),  $J_{10} = -29$  K ( $-40.0 \times 10^{-16}$  erg),  $J_{20} = 24$  K ( $33.1 \times 10^{-16}$ erg), where the value of N is approximated as constant in the whole range of temperature and K is the inverse of the bulk modulus B obtained in Section 3.2 and  $J_{10}$ ,  $J_{20}$ correspond to  $J_1$ ,  $J_2$  in the unstrained state [12]. A reasonable fit is obtained by taking

$$\beta_1 = -65.9 \text{ and } \beta_2 = -42.4$$
 (15)

respectively.

The results are shown in Fig. 7, together with the experimental values. In the figure, an open circle and an open triangle are the experimental values of the lattice constants *a* and *c* which are shown in Fig. 4. The upper solid line below 650 K represents the calculated values of *a*, and the lower solid line below 650 K represents those of *c*. The transition temperature is set at 650 K, so *a* and *c* have the same value at this temperature. The middle solid line below 650 K represents the lattice constant *a* of the cubic structure in the non-magnetic state which is shown in Fig. 5. The open diamonds represent  $V^{1/3}$  (*V* is volume) derived from the experimental values. The open squares represent the lattice constant *a* obtained in the X-ray diffraction measurements under high pressure as shown in



Fig. 7. Temperature variations of the lattice constants of MnN. An open circle and triangle represent the experimental values of the lattice constants *a* and *c*. An open diamond represents  $V^{1/3}$  (*V* is unit cell volume) derived from the experimental values. The upper solid line below 650 K represents the calculated value of *a* and the lower solid line below 650 K represents that of *c*. The middle solid line below 650 K represents the lattice constant *a* of the cubic structure in the non-magnetic state. An open square represents the lattice constant *a* obtained in the X-ray diffraction measurements under high pressure of 3.0 GPa and the solid line above 650 K is derived by using a least-squares method from these experimental values.



Fig. 8. Strain components,  $e_a$  and  $e_c$  versus temperature curves. The lattice constant *a* of the cubic structure in the non-magnetic state is used as a base line. The upper solid line below 650 K (1) shows the curve for the calculated value of  $e_a$ , and the lower solid line below 650 K (2) is the curve calculated for  $e_c$ . An open circle and triangle represent the strain components derived from the experimental values of the lattice constants *a* and *c*. An open diamond represents the strain component of  $V^{1/3}$  (*V* is unit cell volume) derived from the experimental values.

Section 3.2 and the solid line above 650 K is derived by using a least-squares method from these experimental values. The results of the temperature variations of strain components along the *a*- and *c*-axes,  $e_a$  and  $e_c$ , are shown in Fig. 8, together with the experimental values.

In Fig. 7, the overall agreement between the calculated and the experimental values appears to be reasonable, although the calculated value of *c* deviates from the experimental values in the temperature range from about 500 to 650 K. As is found in Fig. 7, the value of  $V^{1/3}$  ( $\diamond$ ) is a little larger than that of the lattice constant *a* in the non-magnetic state (middle solid line). It is concluded that the volume striction is positive. A study of the pressure dependence of  $T_N$  is now in progress in our laboratory in order to further clarify the atomic distance dependence of exchange interaction.

#### 5. Conclusion

The MnN compound has been prepared as a single phase by d.c. reactive sputtering. The crystal structure of MnN is of a tetragonally distorted NaCl type (fct) at room temperature. The MnN compound shows antiferromagnetism with a Néel temperature of 650 K. In this paper, the temperature variation of the lattice constants of MnN was investigated. The results showed that the crystal structure of MnN has transformed from an fct structure to an fcc one at temperatures between 643 and 668 K, which corresponds to the above transition temperature of MnN. The anomalous thermal expansion of MnN was discussed by taking into account the anisotropic strain dependence of the exchange interactions on the basis of molecular field theory.

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