THE CRYSTAL STRUCTURE OF MANGANESE BETWEEN 77 AND 300°K

V. A. FINKEL'

Physico-technical Institute, Academy of Sciences, Ukrainian S.S.R.

Submitted January 5, 1968

Zh. Eksp. Teor. Fiz. 54, 1697–1699 (June, 1968)

The crystal structure of the α and β modifications of manganese between 77 and 300°K is studied by a low-temperature x-ray diffraction technique. An anomaly in the temperature dependence of the crystal lattice constant is detected in α-Mn at 98°K and ascribed to a transition from the paramagnetic to the antiferromagnetic state.

THE investigation of the crystal structure of manganese is of considerable interest. The metal exists in four modifications, the two low-temperature modifications (α and β) having unique structures: the complex cubic crystal lattice of α-Mn consists of 58 atoms in four distinct states,[1,2] and in the cubic lattice of β-Mn there are 20 atoms in two states.[3] A neutron diffraction study of the modifications of manganese showed[4,5] that α-Mn is a collinear antiferromagnet ($T_N \sim 95°K$) in which only three types of atoms (34 out of 58 atoms) have magnetic moments; no magnetic ordering was observed in β-Mn. Anomalies in the thermal, electronic, and magnetic properties of manganese have been observed at 95–100°K.[6-10] Anomalies have also been observed in the region of the Néel temperature in studies of the crystal structure of α-Mn.[2,11] The structure of β-Mn has not been studied at low temperatures.

The purpose of this work is a precise study of the crystal structure of the α and β modifications of high-purity manganese between 77 and 300°K by means of x-ray structure analysis. The investigation was carried out on polycrystalline manganese obtained by vacuum distillation and of purity no worse than 99.99 percent. The initial samples consisted only of the α modification. In order to obtain the β modification, the metal was annealed in evacuated quartz ampoules for one hour at 900°C and quenched in water. Only β-Mn lines were present in the diffraction patterns.

The low-temperature x-ray diffraction patterns of manganese were obtained by a method which essentially did not differ from that described previously in [12]. The photographs were obtained on a URS-50I instrument provided with a low-temperature attachment. The (633) peak of α-Mn ($\theta \sim 71°$) or the (510) peak of β-Mn ($\theta \sim 68°$) were determined at large diffraction angles using chromium Kα radiation. The temperature of the sample was measured with a chromel-alumel thermocouple with an accuracy no worse than ±0.2°K; the lattice constants of α-Mn and β-Mn were determined with an accuracy of $\sim 10^{-4}$ Å.

The results of the measurements of the lattice constants of the α and β modifications are presented in Fig. 1. It is seen that at ~98°K a sharp bend is observed on the a(T) curve for α-Mn; no anomalies are observed on the a(T) curve for β-Mn. The thermal expansion of α-Mn in the magnetically ordered (antiferromagnetic) state is thus negative. Bends in the curves of the temperature dependence of the atomic volumes

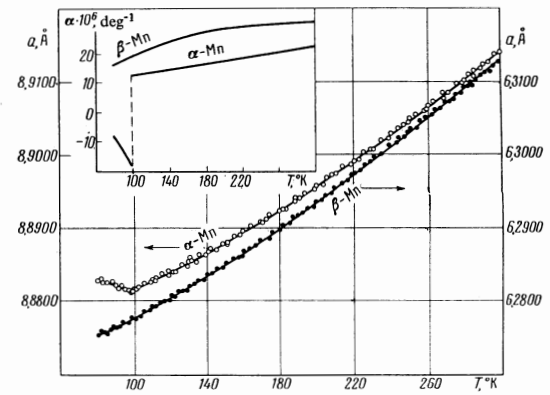

FIG 1

have previously been observed in a series of hexagonal rare-earth magnets;[12-14] among the cubic metals such an anomaly on the $V_{at}(T)$ curve (Fig. 2) is apparently only observed in the case of α-Mn. In all instances the anomaly is obviously connected with an appreciable contribution of the spin waves to the thermal expansion.[15]

The linear expansion coefficients α of α-Mn and β-Mn were determined by approximate differentiation; the corresponding $\alpha(T)$ curves are shown in the insert of Fig. 1. A negative λ anomaly on the $\alpha(T)$ curve characteristic of second-order phase transitions[16] is observed in α-Mn near the Néel temperature. The value of dT_N/dp, which turned out to be −1.64 deg/kbar, was calculated from the measured values of the jump of the linear expansion coefficient ($\Delta\alpha$) and of the atomic volume, and from the jump of the specific heat known from the literature (ΔC_p = 0.5 cal/mole-deg[7]) with the aid of the well-known equation of the theory of second-order phase transitions

$$dT_N / dp = 3\Delta\alpha V_{at} T_N / \Delta C_p$$

As far as we know, dT_N/dp for α-Mn has not been directly determined, but the obtained value is close to those obtained for other cubic antiferromagnetic metals —chromium (−5.0 deg/kbar[17]) and vanadium (−0.85 deg/kbar[18]).

It is interesting to note that in the entire investigated temperature range the atomic volume of β-Mn is larger than that of α-Mn; the thermal expansion coefficients of β-Mn are also larger than those of α-Mn (Fig. 1). Although for the complex structures of the modifications of manganese the atomic volume is an insufficiently

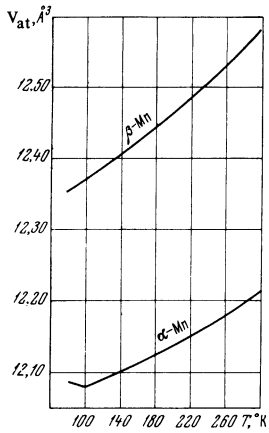

FIG. 2

correct characteristic of the compactness of the crystal lattice (owing to the presence of a broad "spectrum" of interatomic distances), it cannot be excluded that the relatively large specific volume of β-Mn prevents the appearance of antiferromagnetic ordering.

[1] A. J. Bradley and J. Thewlis, Proc. Roy. Soc. **115A**, 456 (1927).
[2] C. P. Gazzara, R. M. Middleton, R. J. Weiss, and E. O. Hall, Acta Cryst. **22**, 859 (1967).
[3] G. B. Preston, Phil. Mag. **5**, 1198 (1928).
[4] C. Shull and M. Wilkinson, Rev. Modern Phys. **25**, 100 (1953).
[5] J. S. Kasper and B. W. Roberts, Phys. Rev. **101**, 537 (1956).
[6] C. H. Shomate, J. Chem. Phys. **13**, 326 (1945).
[7] C. P. Gazzara, R. M. Middleton, and R. J. Weiss, Phys. Lett. **10**, 257 (1964).
[8] G. K. White, Proc. Phys. Soc. **86**, 159 (1965).
[9] G. T. Meaden and P. Pellous-Gewais, Bull. Am. Phys. Soc. **12**, 703 (1967).
[10] A. Arrott and B. R. Coles, J. Appl. Phys. **32**, 515 (1961).
[11] J. A. C. Marples, Phys. Letters **24A**, 207 (1967).
[12] V. A. Finkel' and V. V. Vorob'ev, Zh. Eksp. Teor. Fiz. **51**, 786 (1966) [Sov. Phys.-JETP **24**, 524 (1967)].
[13] V. A. Finkel', Yu. N. Smirnov, and V. V. Vorob'ev, Zh. Eksp. Teor. Fiz. **51**, 32 (1966) [Sov. Phys.-JETP **24**, 21 (1967)].
[14] V. V. Vorob'ev, Yu. N. Smirnov, and V. A. Finkel', Zh. Eksp. Teor. Fiz. **49**, 1774 (1965) [Sov. Phys.-JETP **22**, 1212 (1966)].
[15] A. E. Lord, J. Phys. Chem. Solids **28**, 517 (1967).
[16] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964, p. 501.
[17] A. R. Kutor and E. G. Ponyatovskiĭ, Dokl. Akad. Nauk SSSR **169**, 1318 (1966) [Sov. Phys.-Doklady **11**, 741 (1967)].
[18] H. Suzuki, S. Minomura, and S. Miyahara, J. Phys. Soc. Japan **21**, 2089 (1966).

Translated by Z. Barnea
196