Magnetic Transformation in MnBi†

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Manganese bismuth loses its spontaneous magnetization very sharply at 633°K. At the same temperature drastic changes occur in the lattice constants. Previous workers have interpreted both these phenomena as arising from a ferromagnetic-antiferromagnetic transition. The present work indicates that the phase existing above 633°K is actually a ferromagnetic one with a Curie temperature of about 470°K.

INTRODUCTION

PREVIOUSLY MnBi had been studied principally by Guillaud.[1] The present investigation was initiated because the interpretation of the transition at 633°K as a ferromagnetic-antiferromagnetic change was felt to be unsatisfactory. (MnBi loses its ferromagnetism very sharply at 633°K. Coincident with the loss of ferromagnetism are a decrease in the *c*-axis of the order of 3 percent and an increase in the *a*-axis of the order of 1.5 percent.)

The samples used in the present work were prepared by Dr. A. J. Cornish of this laboratory. X-ray analysis[2] showed the room-temperature phase of MnBi and that quenched from above 633°K to have essentially the same lattice constants as reported by Guillaud. The results are summarized in Table I.

EXPERIMENTAL RESULTS AND DISCUSSION

All measurements of saturation magnetization and susceptibility were made by using the gradient method, which is considered accurate to within ±1 percent. The saturation magnetization curve shown in Fig. 1 possesses the same general characteristics as that recorded previously[1]: (1) the sudden loss of magnetization at 633±2°K,[3] and (2) the thermal hysteresis at the transition point. The important difference is the fact that I_s extrapolates to a value of $3.9_5\mu_B$ at 0°K rather than $3.52\mu_B$ as recorded previously.[1] This present value agrees well with a theoretical value of $4\mu_B$ based on the assumptions that MnBi has a *g*-factor of 2 (MnSb, a compound chemically and structurally similar to MnBi, has a measured *g*-factor of 1.96[4]) and that Mn is present as Mn^{+++}.

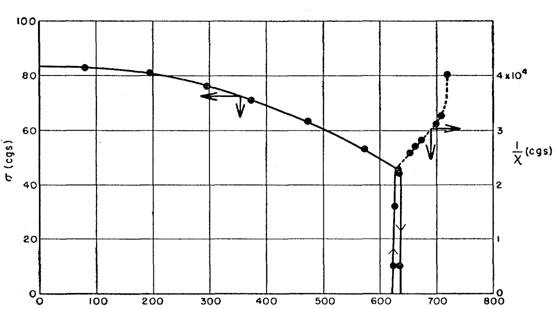

FIG. 1. Saturation magnetization and susceptibility of MnBi.

Also shown in Fig. 1 is the curve of reciprocal susceptibility *versus* temperature. It has been predicted[5] that the behavior of MnBi above its "Curie point" should be similar to that of MnAs (Fig. 2). This is found not to be the case. It should be noted that the extrapolation of the reciprocal susceptibility to zero value occurs at 440°±10°K. (The sharp bend in the curve at 720°K is due to the decomposition of the compound at the peritectic temperature.) For a normal ferromagnet one finds that this extrapolated value is very close to the Curie point. However, in the present case a different phase exists above 633°K. Therefore, the fact that the curve of $1/\chi$ extrapolates to 440°K would indicate that the high-temperature phase (the phase existing above 633°K) would be ferromagnetic with a Curie point of 440°K if it could be retained at room temperature. To test this hypothesis a sample of MnBi was quenched from 650°K. The x-rays showed the sample to be mainly the high-temperature phase. The measurement of saturation magnetization as a function of T is shown in Fig. 3. The point at which the curve turns up is dependent on the rate of heating, indicating that the quenched

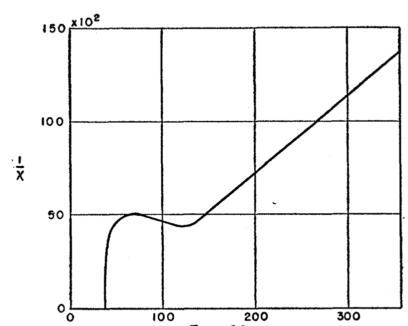

FIG. 2. Reciprocal susceptibility *versus* temperature for MnAs.

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[1] C. Guillaud, thesis, Strasbourg, 1943 (unpublished).

[2] Only lines attributable to MnBi appeared in the x-ray photograph.

[3] A few samples were measured which did not possess the transition at 633°K but instead had a normal Curie temperature at about 700°K. At present their occurrence is not understood.

[4] F. Galavics, Helv. Phys. Acta 12, 581 (1939).

[5] C. Guillaud, Grenoble Conference Papers, 1950.

TABLE I. Lattice constants of MnBi (NiAs structure).

	Room-temperature phase	High-temperature phase
Present data	c—6.118 A a—4.287 A	c—5.964 A a—4.339 A
Guillaud's data	c—6.12 A a—4.30 A	c—5.83 A a—4.32 A

material is transforming into the stable low-temperature phase. If, after heating to just below the transition temperature of 633°K, the MnBi is cooled, it then returns along the original curve of the low-temperature phase. It can be seen that upon extrapolation to $I_s=0$, a Curie point is found at about 470°K. Because of the inaccuracies involved, this second estimate of the Curie point of the high-temperature phase is considered to be in good agreement with the value derived from the reciprocal susceptibility curve. (The fact that the quenched form of MnBi is ferromagnetic was first observed in our Laboratories by Himmel and Jack.[6])

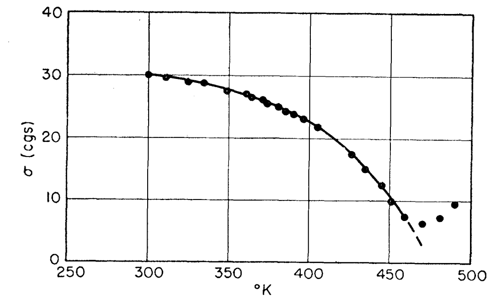

FIG. 3. Saturation magnetization of quenched MnBi.

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[6] L. Himmel and K. Jack, (unpublished work).

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Heat Capacities of Vanadium and Tantalum in the Normal and Superconducting Phases*

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The heat capacities of two samples of vanadium and two of tantalum have been measured in the normal and superconducting phases in the temperature interval between 1.7° and 5°K. Below the transition temperature T_0, the superconducting heat capacity of both metals could be represented accurately by the relation $C_s=AT+BT^2$. In the normal phase the data obeyed the usual relation $C_n=\gamma T+(464/\theta^3)T^3$. From these data H *vs* T curves were calculated and values of H_0, the threshold field at absolute zero, were obtained. For the better vanadium sample the values of the various constants were found to be $T_0=4.89$°K, $A=-1.97\times10^{-3}$ cal/mole deg², $B=1.69\times10^{-3}$ cal/mole deg³, $\gamma=21.1\times10^{-4}$ cal/mole deg², $\Theta=273$°K, and $H_0=1340$ oersteds; for the better tantalum sample $T_0=4.38$°K, $A=-1.45\times10^{-3}$ cal/mole deg², $B=1.33\times10^{-3}$ cal/mole deg³, $\gamma=13.0\times10^{-4}$ cal/mole deg², $\Theta=231$°K, and $H_0=860$ gauss. The measured heat capacities were compared with the predictions of the Koppe theory and the α model.

1. INTRODUCTION

An experimental study of the electronic contribution to the heat capacity of metals in the superconducting phase is of fundamental interest in the theory of superconductivity. Vanadium and tantalum are well suited to such a study for they have a high zero field transition temperature, a large electronic heat capacity, and a relatively small lattice heat capacity. In addition, the heat capacities of these two metals are of interest in their own right for comparison with the results of magnetic measurements of the threshold fields which destroy their superconductivity.

There is a great disparity in the threshold fields which have been reported for vanadium,[1,2] and, prior to the present measurements, no calorimetric data existed for the purpose of comparison. The more recent work[2] indicates that the threshold fields for this metal depend markedly on the amount of internal strain in the sample, due either to mechanical work or to the presence of interstitial gaseous impurities which distort the lattice structure. The effect of these quantities on the heat capacities of vanadium has been studied in these experiments.

Tantalum has been the subject of two earlier heat capacity investigations. The first of these was carried out by Keesom and Désirant in 1941.[3] Since their results did not agree with the magnetic measurements

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[1] Webber, Reynolds, and McGuire, Phys. Rev. 76, 293 (1949).
[2] A. Wexler and W. S. Corak, Phys. Rev. 85, 85 (1952).
[3] W. H. Keesom and M. Désirant, Physica 8, 273 (1941).