Magnetic properties of alloys MnSb and $Mn_{1.11}Sb$ after subjection to high pressures and temperatures

N. P. Grazhdankina, I. V. Medvedeva, A. V. Pasheev, and Yu. S. Bersenev

Institute of Metal Physics, Ural Science Center, Academy of Sciences, USSR
(Submitted 14 March 1981)
Zh. Eksp. Teor. Fiz. **81**, 1064–1070 (September 1981)

The ferromagnetic alloys MnSb and $Mn_{1.11}Sb$ were subjected to the action of pressure $P = 77$ kbar and of temperatures $T = 700$ to 1400 K. This led to a sharp decrease of the magnetization σ and of the Curie temperature T_c and to an anisotropic change of volume of the elementary cell of the alloy, without change of its symmetry. The effect of hydrostatic pressure (up to 10 kbar) on T_c and σ was investigated in alloys $Mn_{1.11}Sb$ and MnSb previously subjected to thermobaric treatment at $P = 77$ kbar and $T = 1200$ K. A change of sign of the temperature coefficient of electrical resistivity was detected in the region $T \geq T_c$, and a correlation was established between the changes of T_c and the ratio c/a of the crystal lattice parameters, for the alloys investigated. The experimental results are interpreted on the basis of the assumptions that exchange interactions of different signs exist in MnSb and that there is a distinguished $3d$ band, whose shape varies under pressure.

PACS numbers: 75.30.Cr, 75.30.Kz, 75.50.Cc, 62.50. + p

INTRODUCTION

The ferromagnetic alloy MnSb belongs to the class of compounds with hexagonal structure, of the NiAs type (space group $P6_3/mmc$. A characteristic of such compounds is the presence of vacancies in the sublattices of the metal and of the metalloid and, as a consequence of this, the existence of a broad homogeneity range $MN_{1+\delta}Sb (0 \leq \delta \leq 0.22)$, which leads to a sharp lowering of the Curie temperature T_c and of the magnetization σ with increase of δ.[1] At present there is no single idea about the mechanism of exchange coupling in MnSb, since the reasons are not known for the change of T_c and of σ when structural vacancies are filled by interstitial manganese atoms in $Mn_{1+\delta}Sb$. Experiments on diffuse scattering of polarized neutrons in these alloys[2] suggest that the interstitial Mn atoms carry no magnetic moment but lead to changes of the electronic energy spectrum; these, however, are not yet explicit. It should be noted that the paper of Yamaguchi and Watanabe[2] does not allow for the possibility of a strong effect of the volume on T_c and σ in these alloys.

In a short communication published earlier,[3] we presented the first results of an investigation of the magnetic properties of the alloy MnSb, obtained in an attempt to bring about filling of the structural vacancies in MnSb under the action of high pressures and temperatures, at constant chemical composition of the alloy. The present paper reports complex magnetic, electric, and x-ray investigations of manganese-antimony alloys, in which the filling of structural vacancies was accomplished by three different methods: a) on the basis of synthesis of compounds $Mn_{1+\delta}Sb$ (where $\delta = 0$, 0.08, and 0.11); b) by thermobaric treatment of the alloy MnSb at $P = 77$ kbar and $T = 700$ to 1400 K; c) by means of the combined action of the two factors mentioned above, by investigation of $Mn_{1.11}Sb$ after subjection of it to high pressures and temperatures.

The effect of isotropic hydrostatic compression (up to 10 kbar) on the Curie temperature T_c and on the magnetization σ was investigated in these alloys; this made it possible to separate the volume factor in the change of T_c and of σ. A correlation was established between the changes of T_c and the ratio c/a of the crystal lattice parameters. On the basis of the experimental data, possible mechanisms of exchange coupling of the spins in these alloys are discussed.

EXPERIMENTAL METHOD

The preparation of the $Mn_{1+\delta}Sb$ alloys ($\delta = 0, 0.08, 0.11$) proceeded similarly to the method described by Yamaguchi, Watanabe, and Suzuki.[4] Finely ground and well mixed powders of the original chemically pure elements Mn (99.8% purity) and Sb (99.99% purity), taken in the necessary proportions, were pressed in the form of a bar and placed in an evacuated quartz ampule. The synthesis of the alloys proceeded in three stages: 1) the pressed bars were placed in a furnace, where they remained for three days at 713 K, after which the temperature of the alloys was lowered to room temperature along with the turned-off furnace: 2) the alloys obtained were crushed, and the whole cycle 1 was repeated again; 3) the alloys, ground after the second stage of preparation, were again pressed and placed in an evacuated quartz ampule, and annealed for 20 hours at 1200 K; then they were cooled at the rate of 0.5 degree per minute to 970 K, and at this temperature they were quenched in water.

Treatment of the MnSb alloys by high quasihydrostatic pressures $P = 77$ kbar was carried out in cells of the "toroid" type, on a hydraulic press DO 137 A, at temperatures 700, 800, 1000, 1200, and 1400 K. A seamless specimen of MnSb alloy (diameter 3 mm, length 4.5 mm) was placed in a nichrome heater (diameter 4 mm, length 7 mm) and was insulated from it with mica and from the ends with spacers of catlinite. The time that the specimen was kept at the high P and T was 50 min. The raising and lowering of the pressure was accomplished over a period of 10 min. The taking of the x-ray pictures and the measurements of magnetization and of electrical resistivity were carried out directly after the lowering of the pressure.

 0038-5646/81/090564-04$02.40

The x-ray pictures were taken with powder specimens, in a PKD-57.3 camera, by the asymmetric method, in chromium and iron radiation. The periods of the lattice were determined by graphical extrapolation to zero of the relation $a, c = f(\varphi)$:

$$\varphi = \cos^2\theta/\sin\theta + \cos^2\theta/\theta.$$

The magnetization was measured with a pendulum magnetometer of the Domenicali type,[11] in fields up to 16 kOe. The measurements of magnetization at high hydrostatic pressures (up to 10 kbar) were made by a method similar to that described earlier.[5]

The electrical resistivity of MnSb alloys was measured by the usual potentiometric method, at constant current. At high temperatures, to prevent oxidation of the specimens, the measurements were made in a vacuum.

RESULTS

Measurements of the temperature dependence of the magnetization of the alloy MnSb after subjection to pressure 77 kbar, at various temperatures from 700 to 1400 K, showed that in all cases there occurs a sharp decrease of the magnetic moment and of the Curie temperature as compared with the alloy in its original state.[3] For $P = 77$ kbar and $T = 1400$ K, the ferromagnetism disappears over a wide temperature interval. An increase of the magnetization in the high-temperature range and a merging of all the curves with approach to the T_c of the original MnSb is apparently due to a return of the alloy to a state of thermodynamic equilibrium, close to the original state.[1)] It must be mentioned that the magnetization curves of all the alloys, measured at 77 K, have the form of the $\sigma(H)$ curve that is characteristic of ferromagnets, with saturation of the magnetization.

X-ray investigations, the results of which are presented in Table I, showed that the changes of the magnetic properties of MnSb under the action of high P and T are accompanied by strain of the crystal lattice without change of its symmetry. Thus, for example, treatment of the alloy at $P = 77$ kbar and $T = 800$ K leads to a sharp decrease of the parameter c and to an insignificant increase of the parameter a, as a result of which the volume of the elementary cell decreases by ~2%; the shift of the Curie temperature with change of volume is $\Delta T_c/\Delta V = 107.3$ deg/Å^3, which is six times larger than its rate of change under isotropic compression.[6] Under the action of $P = 77$ kbar and $T = 1200$ K, the volume of the elementary cell increases, primarily because of increase of the parameter a, and as a result the ratio $\Delta T_c/\Delta V$ is negative. Pressure $P = 77$ kbar and temperature $T = 1400$ do not lead to a significant change of the lattice parameters as compared with the preceding case, but a change of intensity of the x-ray lines indicates the possibility of a filling of crystallographic vacancies.

TABLE I. Curie temperature T_c, lattice parameters a, c, and c/a, and volume of the elementary cell, for alloys MnSb and $Mn_{1.11}Sb$ after treatment at high T and at $P = 77$ kbar.

Alloy	T, K	T_c, K	a, Å	c, Å	c/a	V, Å^3
MnSb	(initial)	596	4.149	5.772	1.391	86.05
	700	405	4.150	5.644	1.360	84.18
	800	420	4.160	5.635	1.356	84.37
	1200	300	4.225	5.660	1.338	87.70
	1400	250	4.256	5.660	1.330	88.78
$Mn_{1.11}Sb$	(initial)	423	4.200	5.716	1.360	87.32
	1200	350	4.220	5.700	1.351	87.91
	1000	224	4.285	5.671	1.323	90.17

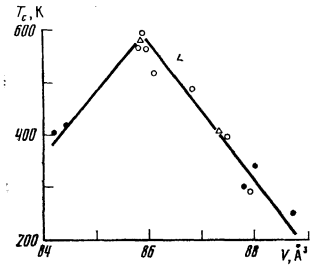

FIG. 1. Variation of the Curie temperature with volume of the elementary cell for alloys $Mn_{1+\delta}Sb$: △, data of the present paper; ○, according to the data of Ref. 1; ●, MnSb after subjection to high P and T.

Analogous features can be noted also for the volume change of σ. As we established earlier,[7] under isotropic compression of the alloy MnSb the value of $\Delta\sigma/\Delta V$ is positive, whereas after subjection to $P = 77$ kbar and $T = 800$ K this quantity is also positive but much larger, and for $P = 77$ kbar and $T = 1200$ and 1400 K the ratio $\Delta\sigma/\Delta V$ has a negative sign.

The results presented above indicate that by the combined action of high pressures and temperatures, it is possible to produce in MnSb alloys volume strains of different types: a) uniaxial compression; b) anisotropic volume expansion; c) enlargement of the elementary cell of the crystal because of filling of structural vacancies. This leads to the complicated, nonmonotonic variation of T_c with V shown in Fig. 1, where results for alloys $Mn_{1+\delta}Sb$, obtained by us and taken from the paper of Teramoto and van Run,[1] are also given. It is evident from the $T_c(V)$ graph that MnSb can have the same Curie

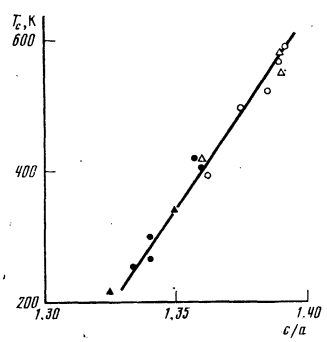

FIG. 2. Variation of the Curie temperature with the ratio c/a of the lattice parameters: △, $Mn_{1+\delta}Sb$ alloys ($\delta = 0$, 0.08, 0.11); ○, according to the data of Ref. 1; ●, MnSb after subjection to high P and T; ▲, $Mn_{1.11}Sb$ after subjection to high P and T.

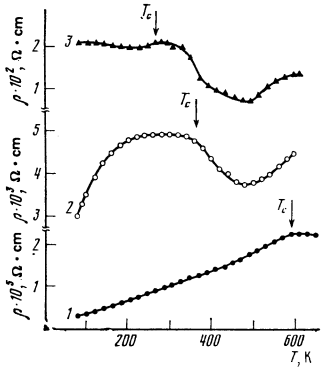

FIG. 3. Temperature dependence of the electrical resistivity of MnSb alloy in the initial state (1) and after subjection to pressure: 2, $P = 77$ kbar, $T = 700$ K; 3, 77 kbar, $T = 1200$ K.

temperature at different V. For example, $T_c = 400$ K can be obtained by uniaxial compression of the crystal along the c axis ($V = 84.2$ Å^3) and for $V = 87.3$ Å^3, when the increase of volume of the elementary cell of the crystal occurs because of partial filling of structural vacancies (as in the alloy $Mn_{1.11}Sb$). It is very important that the change of T_c with the ratio c/a of the crystal lattice parameters is linear for all the MnSb and $Mn_{1+\delta}Sb$ alloys investigated by us,[1] as is clearly seen from Fig. 2. We observed similar variations of the Curie temperature with the volume of the elementary cell of the crystal and with the ratio c/a also for the alloy $Mn_{1.11}Sb$. These data are shown in Table I and in Fig. 2.

Figure 3 shows the temperature variations of the electrical resistivity of MnSb in the initial state (Curve 1) and after treatment at $P = 77$ kbar and $T = 700$ K (Curve 2) and at $P = 77$ kbar and $T = 1200$ K (Curve 3). From the $\rho(T)$ graphs it is seen that the original MnSb alloy has a metallic type of conductivity over the whole temperature range investigated, and at the Curie point $T_c \sim 600$ K the bend in the $\rho(T)$ curve that is characteristic of ferromagnets is observed. In MnSb alloys treated at high P and T, the sign of the temperature coefficient of electrical resistivity changes near $T \sim T_c$, and the metallic type of conductivity, in the range $T_c < T < 500$ K, changes with increase of T to semiconductor type; at 500 K the temperature coefficient of electrical resistivity again becomes positive, apparently as a result of destruction of the metastable phase of MnSb that originated during treatment of the alloy at high P and T.

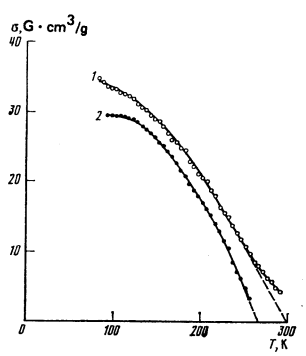

FIG. 4. Temperature dependence of specific magnetization of MnSb alloy, measured in field $H = 8$ kOe after subjection to pressure and temperature ($P = 77$ kbar, $T = 1200$). Curve 1 was taken at $P = 1$ atm, Curve 2 under hydrostatic pressure 7.7 kbar.

In conclusion, we shall present the results of an investigation of the influence of high hydrostatic pressure (up to 10 kbar) on the magnetic properties of alloys $Mn_{1.11}Sb$ and MnSb previously treated at pressure 77 kbar and temperature 1200 K. These alloys have a lower value of the Curie temperature and a larger volume of the elementary cell, as compared with the original MnSb. It may be assumed that the decrease of T_c in these cases is determined not by the change of volume, but principally by filling of structural vacancies, which leads to significant modification of the electronic energy spectrum. From experiments with hydrostatic pressures[6] it is known that in the alloy MnSb, isotropic compression leads to a lowering of the Curie temperature; but so far there are no experimental data on the influence of the volume on T_c for manganese-antimony alloys with partially filled structural vacancies.

Figure 4 shows curves of the temperature variation of the magnetization of the alloy MnSb, after treatment at $P = 77$ kbar and $T = 1200$ K, taken at atmospheric pressure (1) and under a pressure of 7.7 kbar (2). It is evident that the pressure derivatives dT_c/dP of the Curie temperature and $d\sigma/dP$ of the magnetization retain their negative signs and have the same order of magnitude as the original MnSb.[6,7] Determination of the numerical values of these derivatives in this case (because of the indicated instability of the alloys) did not seem possible. Our measurements showed that T_c for the alloy $Mn_{1.11}Sb$ also decreases under isotropic compression: $dT_c/dP = -1.7$ deg/kbar, which is smaller by almost a factor two than the value of dT_c/dP obtained for MnSb.[6]

DISCUSSION OF RESULTS

The experimental data presented indicate that the variation of T_c and of σ for manganese-antimony alloys with the volume of the elementary cell of the crystal is determined by the type of volume strain; under isotropic hydrostatic compression the derivatives dT_c/dV and $d\sigma/dV$ are positive, but the decrease of the Curie temperature and magnetization of alloys $Mn_{1+\delta}$ with increase of δ is accompanied, on the contrary, by an increase of volume, i.e., dT_c/dV and $d\sigma/dV$ have a negative sign. Thermobaric treatment enables us to produce volume strains of different types: both a decrease of volume (in this case dT_c/dV and $d\sigma/dV$ are positive) and an increase of volume, because of filling of structural vacancies, which leads to negative values of the volume derivatives of T_c and σ. It is very important that in all the cases enumerated, the Curie temperature and the magnetization are determined by the ratio c/a of the crystal lattice parameters.

The experimental results can be understood qualitatively if we assume the existence in MnSb of exchange interactions of different signs: antiferromagnetic along the hexagonal axis and ferromagnetic in the basal plane.

Both decrease of the parameter c and increase of the parameter a lead to a drop of T_c because of weakening of the ferromagnetism and strengthening of the antiferromagnetism. This deduction is in accord with the scheme of exchange spin couplings proposed by Goodenough[8] for compounds with crystal structure of the NiAs type, and with the signs postulated by him for these interactions.

We may also assume that some of the $3d$ electrons are collectivized and form a narrow, distinguished $3d$ band. The negative signs of the pressure coefficients $T_c^{-1} dT_c/dP$ of the Curie temperatures and $\sigma^{-1} d\sigma/dP$ of the magnetization, for an alloy treated at $P = 77$ kbar and $T = 1200$ K, are interpreted within the framework of the Stoner-Wohlfarth band theory of ferromagnetism,[7] according to which, under the influence of pressure, there occurs a broadening of the $3d$ band and a lowering of the density of electronic states at the Fermi level, causing a drop of T_c and σ. The presence of a correlation between changes of T_c and the ratio c/a in MnSb alloys treated at high P and T, and in the alloys $Mn_{1+\delta}Sb$, agrees qualitatively with this deduction.

As is well known,[9] metals with a hexagonal close-packed lattice the number of energy states per atom in a Brillouin zone is a function of the ratio c/a:

$$g = 2 - \frac{3}{4}\left(\frac{a}{c}\right)^2 \left[1 - \frac{1}{4}\left(\frac{a}{c}\right)^2\right].$$

Hence it is seen that a change of c/a is accompanied by a change of the electronic population, since the density of states per unit energy interval within a Brillouin zone changes, and consequently the density of states near the Fermi level changes. Thus the experimentally established linear relation $T_c(c/a)$ indicates that the lowering of the Curie temperature of the alloys investigated is caused by a decrease of the density of states. The anisotropic change of volume of MnSb under treatment at high P and T may lead to a change of shape of the $3d$ band and to distortion of the electronic energy spectrum, as is indicated by the change of character of the conductivity over a wide range of temperatures.

It must be mentioned that under the condition of coexistence both of localized and of collectivized $3d$ electrons in MnSb, a qualitative interpretation of the experimental data is also possible on the basis of the Friedel-Anderson model,[10] as for compounds with variable valence, as was proposed for the alloys $Mn_{1+\delta}$ by Yamaguchi and Watanabe.[2] For final choice of a suitable theoretical model, it would be very useful to make x-ray investigations of the $K_{\beta 5}$ spectra of $Mn_{1+\delta}Sb$ alloys with various degrees of occupancy of the crystallographic vacancies.

[1)]This instability of the magnetic properties showed up also in a rise of the Curie temperature by 20 to 40 degrees during repreated cycles of the $\sigma(T)$ measurements.

[1]I. Teramoto and A. M. J. G. van Run, J. Phys. Chem. Solids 29, 347 (1968).
[2]Y. Yamaguchi and H. Watanabe, J. Phys. Soc. Jpn. 48, 435 (1980).
[3]N. P. Grazhdankina, I. V. Medvedeva, and A. V. Pasheev, Pis'ma Zh. Eksp. Teor. Fiz. 32, 565 (1980) [JETP Lett. 32, 547 (1980)].
[4]Y. Yamaguchi, H. Watanabe, and T. Suzuki, J. Phys. Soc. Jpn. 45, 846 (1978).
[5]Yu. S. Bersenev, N. P. Grazhdankina, and M. K. Oleĭnik, Prib. Tekh. Eksp. No. 5, 158 (1969) [Instrum. Exp. Tech. (USSR) No. 5, 1271 (1969)].
[6]H. Ido, T. Kaneko, and K. Kamigaki, J. Phys. Soc. Jpn. 22, 1418 (1967).
[7]N. P. Grazhdankina, I. V. Medvedeva, and Yu. S. Bersenev, Zh. Eksp. Teor. Fiz. 71, 820 (1976) [Sov. Phys. JETP 44, 431 (1976)].
[8]J. B. Goodenough, Magnetism and the Chemical Bond, Wiley-Interscience, New York, 1963, p. 276; reprint, Krieger, 1976.
[9]H. Jones, Theory of Brillouin Zones and Electronic States in Crystals, North-Holland, 1960, p. 191 (Russ. transl., M.: Mir, 1968, p. 192).
[10]F. Friedel and P. Anderson, transl. in: Teoriya ferromagnetizma metallov i splavov (Theory of Ferromagnetism of Metals and Alloys), M.: IIL, 1963, p. 368).
[11]C. A. Domenicali, Rev. Sci. Instrum. 21, 327 (1950).

Translated by W. F. Brown, Jr.