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Spin reorientation in MnBi

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Abstract

High purity MnBi was prepared by arc-melting under He gas. The prepared samples have the property of being hard to oxidize in air and progress of oxidation was not observed by X-ray diffraction 1 year later. It is easy to pulverize a good quality sample into powder even in air. We confirmed that coercive force at room temperature depends on the powder size and takes a value of 8 kOe for less than 400 mesh. The permeability has a hysteresis in a temperature range between 77 and 300 K and exhibits a maximum at 100 K corresponding to the spin reorientation temperature T_t. The pressure (P) dependence of T_t was examined by measuring the permeability at various pressures. The value of dT_t/dP was obtained to be 9.6 K/kbar. The results of thermal expansion revealed that both the lattice parameters a and c increase abruptly near 250 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: MnBi; Ferromagnet; Spin reorientation; Pressure effect; Thermal expansion; Permeability

1. Introduction

It is well known that the intermetallic compound MnBi has a NiAs-type crystal structure and exhibits unusual ferromagnetic properties with the ferromagnetic transition temperature of 633 K on heating. At this temperature a ferromagnetic low temperature phase (FLTP) with a NiAs-type structure transforms to a paramagnetic high temperature phase (PHTP) with a distorted Ni_2In-type structure [1]. Therefore, temperature dependence of magnetization for MnBi exhibits a hysteresis and the magnetic transition temperature on cooling is 600 K [2]. Chen reported that the HTP of MnBi was a separate compound with chemical formula $Mn_{1.08}Bi$ [3]. By a neutron diffraction study Roberts confirmed that MnBi is in the paramagnetic state in the temperature range from 623 (cooling)/633 K (heating) to 718 K and a Mn atom in FLTP has a magnetic moment of 3.9 ± 0.5 μ_B [4]. At room temperature MnBi has a very high magnetocrystalline anisotropy energy [5]. The magnetizing process for MnBi oriented in the c-axis direction exhibits strong magnetic anisotropy, where the magnetic easy direction is the c-axis [2]. The anisotropy constant decreases rapidly with decreasing temperature and changes its sign at 84 K, where the magnetic moments rotate from the c-axis of the NiAs-type crystal structure into the basal plane [6]. This spin reorientation has been also investigated by NMR [7]. Robert et al. [4] carried out the neutron diffraction measurements on the MnBi sample at 77.3 K and at zero magnetic field. Their experimental result indicates that a part of the moments rotate away from the c-axis. After their work, Andresen [8] reexamined it and concluded that the spin turning is practically complete at 78 K. The pressure effect on the magnetic transition from FLTP to PHTP was investigated by Samara et al. [9]. The pressure derivative of the ferromagnetic transition temperature is -0.75 K/kbar. Adams et al. [10] attempted to prepare a permanent magnet of MnBi, because of its high magnetic crystal anisotropy. Their magnet has a large coercive force of 3.1 kOe and an energy product $(BH)_{MAX}$ of 4.3 MGOe.

How to prepare a high quality MnBi sample still remains an important problem for basic science and application. In this paper the preparation of highly pure MnBi by He-arc melting, the pressure effect on the spin reorientation temperature and the thermal expansion of MnBi are presented.

2. Sample preparation

When the high purity manganese metals Mn (5N) obtained commercially were melted by arc melting, columns of black smoke shot up into the vessel chamber. This

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black smoke is caused not only by the vaporization of Mn but also by included gas. In order to produce high quality samples, it is important to make Mn metals degas before sampling. Then, the commercial Mn metal was at first arc melted at a half of atmospheric pressure of He gas in order to degas. The commercial Mn metals are porous and with dull lustre. However, the degassed ones are hard and with a metallic brightness. The strongly oriented MnBi samples were prepared with such pretreated Mn and Bi by arc melting in He gas. Magnetic measurements were carried out to examine the transformation between high temperature phase (HTP) and low temperature phase (LTP). Magnetization in HTP was measured by VSM in the temperature range from 77 up to 750 K to examine the phase transition. Fig. 1 shows a thermomagnetic curve for the quenched MnBi alloy. The starting temperature of the measurement is room temperature and the maximum temperature is 773 K. When temperature increases, the magnetization decreases initially and has a shallow minimum around 433 K and then increases gradually. The abrupt increase was observed near 544 K ($=T_m$) which is a melting point of Bi. At 636 K, the value of the magnetization drops abruptly to near zero. According to the phase diagram of MnBi by Chu et al. [3], the molar formula of MnBi in HTP, which has a distorted Ni_2In-type crystal structure, is $Mn_{1.08}Bi$ and it has been reported that its Curie temperature (T_C) is 433 K [3]. The above minimum arises at the Curie temperature of HTP accompanying a transformation to LTP. The increase of magnetization above 433 K is due to the growth of LTP. The abrupt decrease of magnetization at 636 K is due to the transformation from FLTP to PHTP. With further increase of temperature up to 773 K, there arises a small decrease of the magnetization at 730 K as shown with an arrow in the inset. When temperature decreases again after heating up beyond 773 K, the magnetization keeps a very small value down to 440 K and increases gradually with further decrease of temperature. This means that MnBi in HTP decomposes into α-Mn and Bi above 730 K and a small amount of MnBi compound is again synthesized during cooling down to room temperature. When the temperature variation of magnetization is restricted under 643 K, the magnetization decreases abruptly at 633 K on heating and increases abruptly at 603 K on subsequent cooling (refer to Fig. 2 in Ref. [2]). The magnetic transition shows a hysteresis and is of the first order accompanying a crystal phase transition. The magnetization continues increasing although the temperature decreases through T_m.

An appearance of a slight wave near 433 K on decreasing temperature is due to quenching of a small amount of MnBi in HTP. These results give us a condition to transformation from a quenched sample to MnBi in LTP; the suitable temperature range for transformation is between 544 and 603 K, and the reaction time is desirably more than 1 h. We carried out X-ray diffraction to examine the orientation of the bulk sample. The (00*l*) line in the NiAs-type crystal structure was observed for the powder sample, but not observed for the bulk one. This shows that the *c*-plane of the present bulk sample grew up in the direction perpendicular to the bottom face of the Cu hearth. The obtained lattice parameters *a* and *c* are 4.289 and 6.103 nm. It has been reported that MnBi was unstable to oxidation in air. Even though the sample prepared above is exposed to air for more than 1 year, there was no observed variation on magnetic properties and X-ray diffraction pattern except the appearance of pure Bi metal on the surface. The SEM photograph and X-ray diffraction spectrum for an MnBi sample made with regular Mn metals and Bi by Ar-arc melting were also taken and examined. We observed four kinds of area in the photograph as shown in Fig. 2. According to mapping for contents of oxygen, a weird dark and large area contains MnBi and oxygen, and especially small dark spots in the SEM

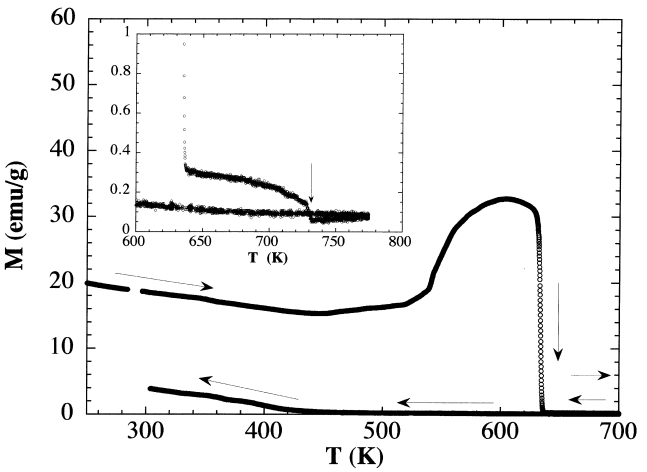

Fig. 1. Thermomagnetic curve for MnBi alloys prepared by He-arc melting. The inset shows the decomposition of MnBi in HTP at 730 K.

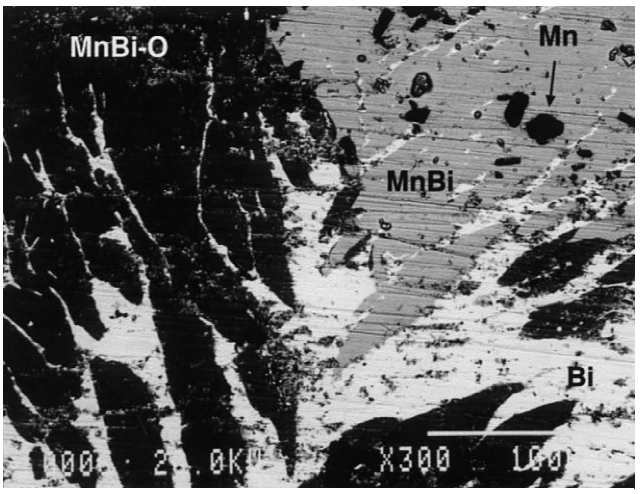

Fig. 2. Compositional image of SEM photograph of an MnBi sample made with regular Mn metals and Bi by Ar-arc melting.

photograph show high oxygen concentration. In the X-ray pattern, there are observed peaks of MnO and α-Mn. The intensity of peaks for α-Mn becomes stronger compared with that for the present powder sample prepared by He-arc melting. It means that MnBi is decomposed into active α-Mn and Bi together with oxygen and MnO and the condensed Mn exposed to the air will react with oxygen. It was found that arc-melting under He gas is the most suitable processing for the preparation of such good quality MnBi.

3. Experimental results and discussion

3.1. Magnetization

The magnetization process was measured with a SQUID magnetometer at temperatures from 4.2 up to 300 K and a VSM one at room temperature. The results are shown in Fig. 3. A spin easy direction is that of the *c*-axis and the value of the coercive force H_c is small being $\sim 10^2$ Oe. There is observed a tendency of magnetic saturation near 10 kOe and the magnetic moment per Mn atom takes a value of 3.3 μ_B (70 emu/g) at 10 kOe, which is consistent with the previous results: 3.3 at 10 kOe and 3.8 μ_B at 140 kOe [2]. The temperature dependence of the magnetization at 10 and 55 kOe for bulk samples is shown in Fig. 4 where the value of magnetization was taken from the magnetization curve at a constant temperature. The curve at $H = 10$ kOe has a maximum near 100 K which gives the magnetic moment of 4.2 μ_B/formula. The appearance of the peak is due to the reorientation of spins with temperature. It was confirmed that the remanence is almost zero below room temperature within the measurement accuracy, though the temperature dependence of remanence for the bulk sample is not presented here. The magnetization vs. temperature curves at 50 kOe for the powdered sample are shown in Fig. 5a. The magnetization decreases slightly with temperature except at 4.2 K. The remanence as shown

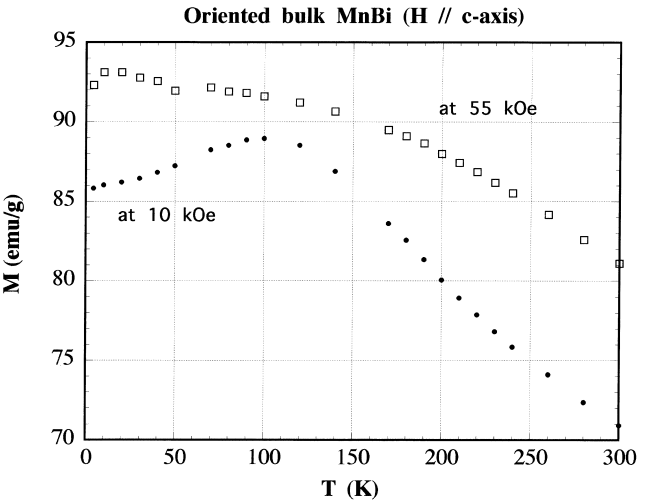

Fig. 4. Temperature dependence of the magnetization at 10 and 55 kOe for the oriented bulk MnBi.

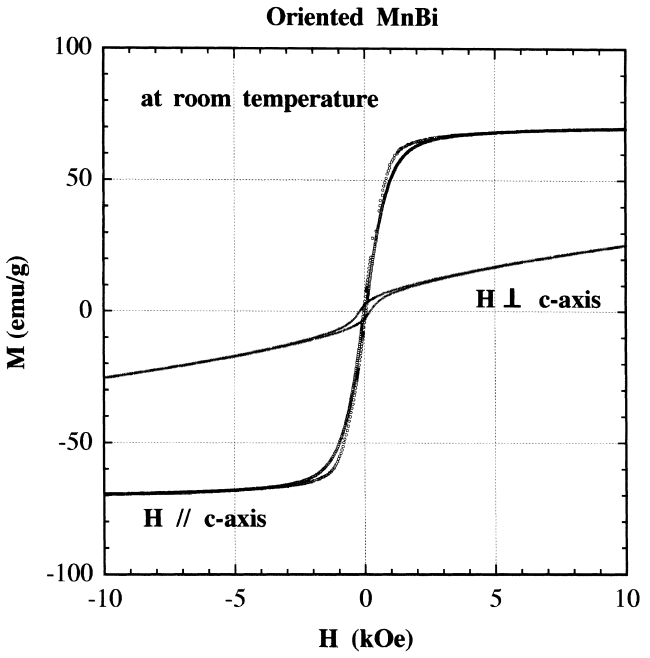

Fig. 3. Hysteresis loops of an oriented MnBi sample measured at room temperature.

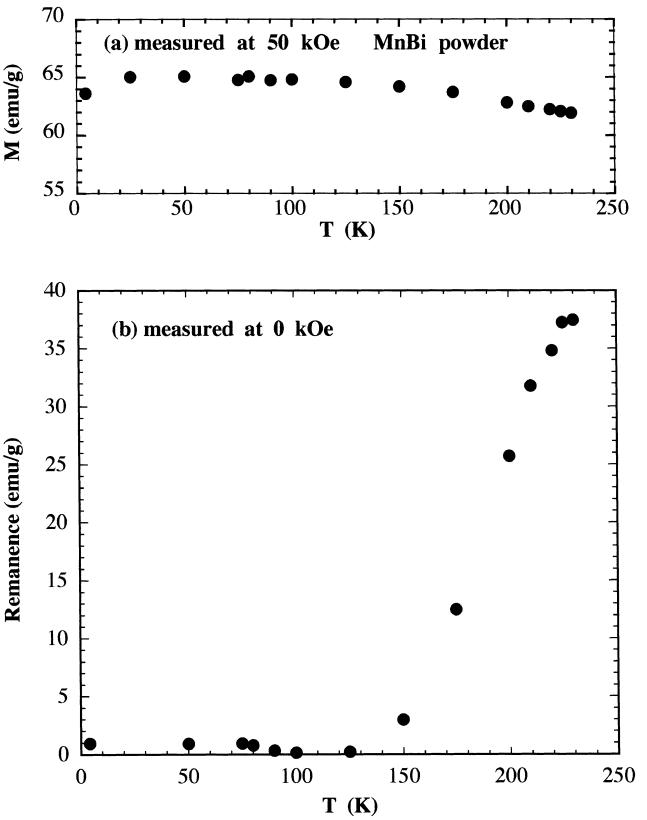

Fig. 5. Thermomagnetic curve of powder MnBi samples at 50 kOe (a) and at 0 kOe (=remanence) (b), respectively.

in Fig. 5b starts to have a finite value from 150 K with increasing temperature. It is quite different from that of the bulk sample mentioned above. The magnetization at 4.2 K for both bulk and powdered sample has a smaller value comparing with those in the higher temperature range. It suggests that there may exist a certain antiferromagnetic interaction at 4.2 K which yields the forces to tilt the spins in the ferromagnet. The good quality sample has a preference of an orientation along the *c*-axis. Since it has a large anisotropy at room temperature, the magnetic loop has a larger coercive force. In Fig. 6 the hysteresis curve for two kinds of powder size samples are shown. These show that the value of coercive force strongly depends on the grain size. These results are consistent with those by Shur et al. [11,12]. They have examined the magnetic domain of manganese–bismuth alloy in particles of various sizes and observed that as a function of particle size. It was found that the value of H_c decreases with the domain wall number in a systematic manner. One origin of the coercive force for the powdered samples is due to the crystalline anisotropy of the single domains. The number of the domain and the decrease of the magnetic anisotropy makes H_c smaller. The remanence of powder samples at temperatures lower than 150 K shown in Fig. 5b has an almost zero value because of diminishing the single domain structure with decreasing anisotropy energy. There is a critical diameter size of particle (D_c) to realize the single domain. This size is proportional to the root of the magnetic anisotropy constant (K_c). The diminishment of the residual magnetization at temperatures lower than 150 K is ascribed to the decrease of K_c [11,12].

3.2. Permeability and pressure effect

It was reported that the intermetallic compound MnBi has a large magnetic anisotropy at room temperature and its temperature dependence is particular. The spin easy direction at room temperature is along the *c*-axis and the strength of the anisotropy is reduced with decreasing temperature down to ~90 K. At lower temperatures than ~90 K, the Mn spin rotates into the *c*-plane. In general, the permeability μ_{ac} is sensitive to the variation of magnetization or magnetic anisotropy. The pressure effect on T_t was examined by measuring the temperature variation of μ_{ac} at various pressures. The details of measurements are given in Ref. [13]. Fig. 7 shows the temperature dependence of the permeability at various pressures with increasing temperature. The μ_{ac} vs. T curve at normal pressure has a maximum at 100 K. Above the maximum temperature, μ_{ac} decreases simply. When temperature is decreased again, the curve shows a hysteresis, where the maximum temperature appears at 98 K. The peak corresponds to that observed in the magnetization vs. temperature curve and the peak temperature was defined as a transition temperature T_t of spin reorientation. The hysteresis in the temperature variation of μ_{ac} shows that the transition at T_t is of the first order, which is consistent with the discontinuous change of spin direction at T_t observed in NMR experiment by Hihara [7]. T_t increases linearly with pressure and its pressure derivative is $dT_t/dP = 9.6$ K/kbar. It means that the volume for the state with magnetic easy direction along the *c*-axis is larger than for the one in the *c*-plane.

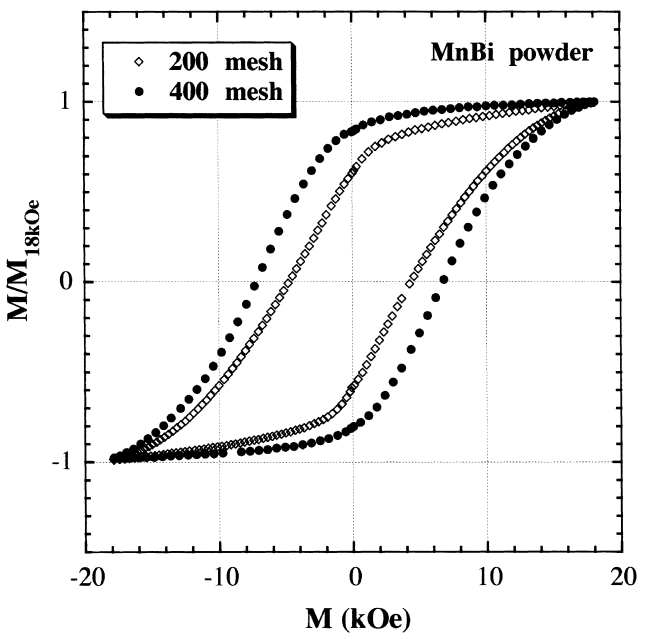

Fig. 6. Hysteresis loops of powder MnBi samples passed through a sieve with 200 mesh and 400 mesh, respectively.

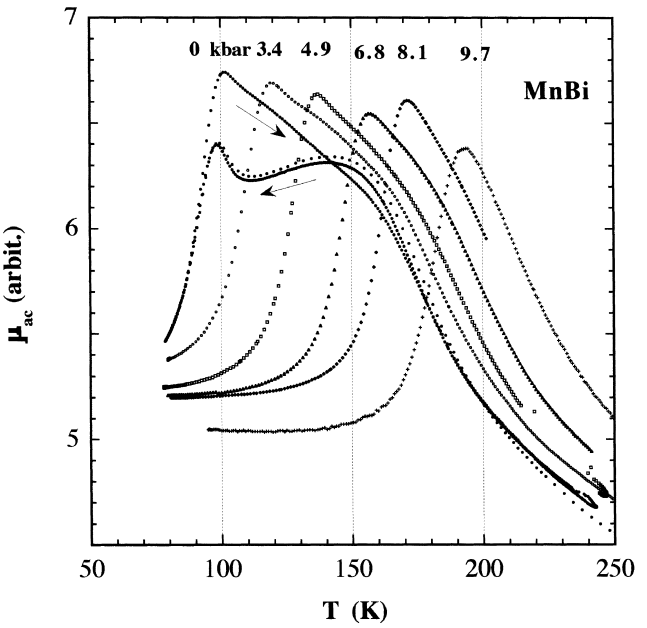

Fig. 7. The temperature dependence of permeability (μ_{ac}) at 0, 3.4, 4.9, 6.8, 8.1 and 9.7 kbar. The curve at 0 kbar shows a large hysteresis in the temperature range of 90 to about 180 K.

3.3. Thermal expansion

It is well known that Mn_2Sb with a tetragonal lattice exhibits a spin reorientation at 250 K. The anisotropy energy was explained well by the sum of the magnetic dipole interaction and the single ion spin energy [14]. The temperature dependence of the anisotropy varies in sign at 250 K. Its origin comes from two kinds of manganese atoms present in the unit cell. Different to Mn_2Sb, there exists only one kind of manganese atom in the lattice of MnBi. The temperature variation of lattice parameters *a* and *c* are examined from 100 to 450 K. The temperature dependence of *a* and *c* in the NiAs-type crystal structure and the volume of unit cell are shown in Fig. 8a–c. As seen in the figure, the curves demonstrate unexpected variations at 250 K. The volume varies abruptly by about 0.5%. The origin of such a peculiar volume variation without the break of crystal symmetry is not clear at present. The results of $dT_t/dP > 0$ mentioned above suggest that there is the anomalous volume increase through T_t. To examine an anomaly of thermal expansion at T_t, it is desired to carry out the X-ray diffraction measurement at temperatures lower than 100 K.

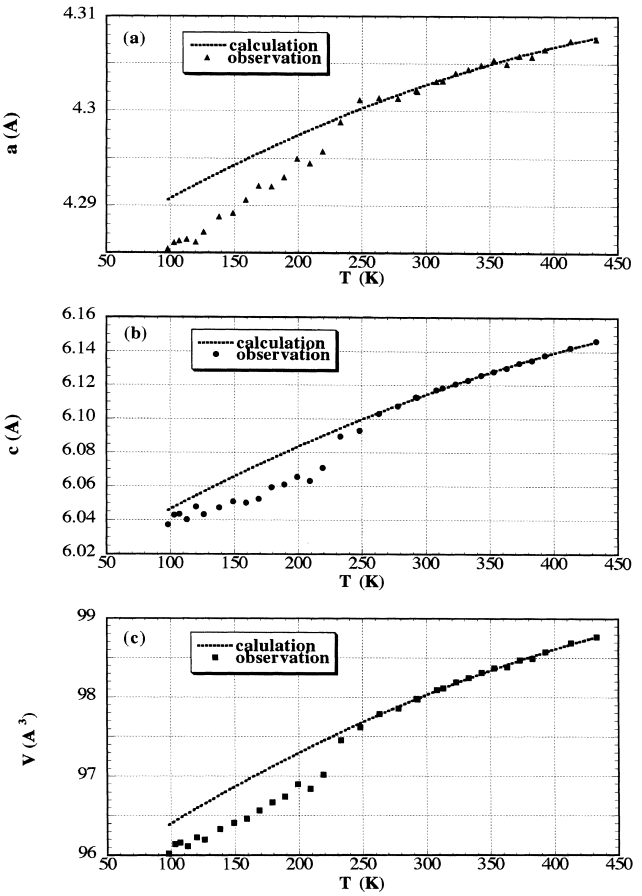

Fig. 8. Variations of lattice parameters *a* and *c*, and the volume of MnBi as a function of temperature. The calculated curves were determined to fit the high temperature part of the data.

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References

[1] C. Guillaud, J. Phys. Radium 12 (1951) 223.
[2] H. Yoshida, T. Shima, T. Takahashi, H. Fujimori, Mater. Trans. JIM 40 (1999) 455.
[3] T. Chen, J. Appl. Phys. 45 (1974) 2358.
[4] B.W. Roberts, Phys. Rev. 104 (1956) 607.
[5] C. Guillaud, J. Phys. Radium 12 (1951) 143.
[6] P.A. Albert, W.J. Carr Jr., J. Appl. Phys. 32 (1961) 201S.
[7] T. Hihara, Y. Koi, J. Phys. Soc. Japan 29 (1970) 343.
[8] A.F. Andresen, W. Halg, P. Fischer, E. Stol, Acta Chem. Scand. 21 (1967) 1543.
[9] G.A. Samara, A.A. Giardini, Bull. Am. Phys. Soc. 9 (1964) 635.
[10] E. Adams, W.M. Hubbard, A.M. Syeles, J. Appl. Phys. 23 (1952) 1207.
[11] Ya.S. Shur, E.V. Shtol'TS, V.I. Margolina, Sov. Phis. JETP 11 (1960) 33.
[12] I.S. Shur, Ye.V. Shtol'TS, G.S. Kandaurova, L.V. Rebneva, Fiz. Metal. Metalloved. 8 (1959) 38.
[13] H. Yoshida, J. Chiba, T. Kaneko, H. Fujimori, S. Abe, Physica B 237–238 (1997) 525.
[14] T. Tonegawa, J. Phys. Soc. Japan B 17 (1962) 1398.