MAGNETIC ANISOTROPY OF 3*d*- AND 4*f*-METALS IN THE MODEL OF CRYSTAL FIELD WITH CALCULATION OF COVALENT BONDS AND THEIR FLUCTUATIONS 1. FERMION SPECTRA AND MAGNETIC ORDER

A. I. MITSEK

Institute for Metal Physics, Nat. Acad. of Sci. of Ukraine
(36, Academician Vernadsky Prosp., Kyiv 03142, Ukraine)

UDC 538.1
‰ 2001

Anomalous (in the existing theories of ferromagnetism) temperature dependences of magnetic anisotropy (MA) constants are explained on the basis of calculation of covalent bonds and their fluctuations (CBF). Soft CBF modes cause the strong temperature dependence of exchange parameters of unstable intermetallic compounds such as MnBi up to exchange inversion in MnAs. The varying of a sum of inter- and intraionic interactions in the operator form with respect to polarization of covalent electrons of different types allows us to obtain the Hamiltonian of crystal field (CF) in the form of MA energies. The parameters of the MA Hamiltonian are the functions of CBF correlators. The presence of CBF soft modes in ferrometals and compounds with polymorphism (Co, MnBi, Gd, etc.) defines the strong dependence of MA constants on temperature T, pressure P, etc. The soft modes are caused by the crossing of CBF branches with Fermi surfaces. The small CBF energies in extremal points (minimum) and the strong CBF dispersion in their vicinity lead to a strong (linear) T-dependence of MA constants, magnetization $M_s(T)$, and exchange parameters. The theory explains satisfactorily the MA constants $K_1(T)$ in Co, MnBi, and rare-earth metals (REM), in particular, the change of the $K_1(0)$ sign in the series of heavy REM.

1. Crystal Field and Anisotropic Exchange

The existing theory of magnetic anisotropy (MA) proceeds from the expansion of the MA energy in invariant forms of projections of the local magnetization $\vec{M}(\vec{r})$ operator or operator of angular moment $\vec{J}_r$ of an ion at a site $\vec{r}$ of a ferromagnetic (FM) crystal lattice [1 – 3]. In these limits, the theory can explain the dependence of MA energy on temperature T, pressure P, etc. only for a small number of magnetic materials. It is powerless to explain the MA behaviour in such practically important materials as MnBi, REM and RE intermetallides, to say nothing of alloys, ferrites, etc.

The purpose of this work is to give bases of a more general MA theory of ferrometals, in particular of crystals with polymorphism. Directed (covalent) chemical bonds of ions and their fluctuations (CBF) play the main role in it. Their contribution to exchange energy dominates in bad metals, but good FM materials are often bad metals.

The quasi-classical substantiation of quantum accounts of MA constants uses the potential of a crystal field (CF). Under conditions of electroneutrality, the CF potential submits to the Laplace equation

$$\Delta V = 0, \quad V = \sum C_{nm}\, Y_{nm}(x_j),$$

$$\vec{r} \equiv \{x_j\}, \quad j = (1, 2, 3) = (x, y, z), \tag{1.1}$$

the solution of which has the form of expansion in spherical functions $Y(\vec{r})$ of the coordinate vector $\vec{r}$ [1 – 3]. According to the correspondence principle [4], the vector $\vec{r}$ is replaced by the spin vector $\vec{S}_{\vec{r}}$ (in 3*d*- magnetics) or $\vec{J}_{\vec{r}}$ (for 4*f*-magnetics). So equivalent (to spherical functions $Y(\vec{r})$) operators $O_{nm}(\vec{L}_{\vec{r}})$ in the form of similar polynomials of projections of the orbital moment $\vec{L}_{\vec{r}}$ [3] are introduced into the theory, in particular in (1.1). The parameter of magnetic order is introduced into the theory by expression of the operator $\vec{L}_{\vec{r}}$ through the angular moment $\vec{J}_{\vec{r}}$ for 4*f*-ions [2, 3] as

$$\vec{L}_{\vec{r}} = (2 - g)\, \vec{J}_{\vec{r}}, \quad \vec{S}_{\vec{r}} = (g - 1)\, \vec{J}_{\vec{r}} \tag{1.2}$$

or through $\vec{S}_{\vec{r}}$ for 3*d*-magnetics. Eventually, potential $V(\vec{r})$ (1.1) is replaced by the CF Hamiltonian

$$H^{\mathrm{CF}}(\vec{r}) = \sum C_{nm}\, \hat{O}(\vec{L}_{\vec{r}}),$$

$$H_A^{\mathrm{ex}} = \sum B_{nm}(|\vec{r} - \vec{r}|)\, L_{\vec{r}}^{n} L_{\vec{r}}^{m}, \tag{1.3}$$

to which the Hamiltonian of anisotropic exchange H_A^{ex} is added by analogy, its polynomial form connects orbital moments of different sites.

The previous CF and MA theories were built in the representation of localized magnetic electrons especially for 4*f*-ions), not participating in chemical bonds, or for band electrons participating in isotropic metal bonds [3, 5]. However, the symmetry of crystals, in particular CF anisotropy, is formed by directed bonds. The main of them for metals are homopolar bonds. Therefore, it is necessary in (1.1) and (1.3) first of all to take into account the orbital moments $\vec{l}_{\vec{r}}$ ($\vec{L}_{\vec{r}}$) of covalent electrons. Closed shells with $\vec{L}_{\vec{r}} = 0$ are formed on ionic bonds.

The performed analysis allows us to assume that covalent electrons ($l_{\vec{r}}$) play the essential (and in some cases the main) role in the formation of CF and anisotropic exchange. For example, for hexagonal FM crystals (Co, Gd ...), we have

$$H^{\mathrm{CF}}(\vec{r}) = A_{20}^{dd}(l_{\vec{r}}^{z})^2 + A_{20}^{df}(L_{\vec{r}}^{z} l_{\vec{r}}^{z}) + A_{40}^{dd}(l_{\vec{r}}^{z})^4 + \ldots, \tag{1.4}$$

where 3*d*- (for 3*d*-ions) or 5*d*-electrons (for 4*f*-ions) are considered to be covalent. The index *f* is retained here for magnetic electrons. Similarly,

$$H_A^{\mathrm{ex}} = \sum B_{20}^{dd}(|\vec{r} - \vec{r}'|) l_{\vec{r}}^{z} l_{\vec{r}'}^{z} + \sum B_{20}^{df} l_{\vec{r}}^{z} L_{\vec{r}'}^{z} + \ldots \tag{1.5}$$

It is follows from here that the different signs of MA constants arise from a competition of contributions (1.4) and (1.5) to the MA energy.

The calculations of covalent orbital moments $\vec{l}_{\vec{r}}$ as well as their polarization $\vec{s}_{\vec{r}}$ require to take into account spin-orbital (H^{s-o}), Coulomb (Hubbard) (H^{Coul}), and also exchange (Hund, *s*–*d*- exchange, etc.) terms. Covalent bond's energies (H^{ch}) essentially renormalize intraionic parameters in this calculation. Their (*T*, *P*)-dependences require to calculate spectra of band electrons, CBF, their bonds with magnons and, probably, phonons.

The covalent theory of polymorphism influence on MA constants of different orders $K_n(T)$ is advanced in Section 2 by an example of pure ferrometal Co. The important role of soft CBF modes is shown. The application of this theory to intermetallide MnBi, having a sharply anomalous dependence $K_1(T)$, is given in Section 3. The application of the theory for explanation of magnetic properties of REM will be given in part II, as well as conclusions and comparisons with experiments.

2. Ferromagnetic Polymorphous 3*d*-metal. Pure Co

The group of 3*d*-ferrometals (Fe, Co, Ni) in a wide temperature interval forms cubic lattices with strong metal bonds of band electrons. Only the low-temperature hcp Co phase has uniaxial MA, the constants of which $K_1(T)$ and $K_2(T)$ are the strong *T*-functions, up to the change of their signs [6]. Within the limits of the ferromagnon theory, even with account of the maximum for 3*d*-ferrometals magnetostriction constants, it is not possible to explain the change of $K_1(T)$ sign (see [7]). The stability of FM order in Co up to the highest $K_c \approx 1400$ K with practically constant mean spin $S_T(T)$ [6] allows one to construct a simple covalent theory of $K_n(T)$ for hcp Co.

Magnetic (localized) 3*d*-electrons are characterized by spin $S = 1$ and orbital moment $L = 0$ [3, 6]. The contribution to these moments of band electrons is neglected in zero approximation. Therefore, the wave function of 3*d*-electrons

$$\psi_{\vec{r}}^{3d} = (\xi_d \hat{D}_{\vec{r}} + \sum \xi_\sigma f_{\vec{r}\sigma}^{+})\psi_0 \equiv a_{\vec{r}}^{+}\psi_0 \tag{2.1}$$

(where ψ_0 – the function of vacuum, $f_{\vec{r}\sigma}^{+}$ – the Fermi-amplitudes of band electrons) is considered below with constant amplitudes of band (ξ_σ) and covalent (ξ_d) electrons. Variational calculation is spent, assuming $\xi_\sigma = \xi_d = 1$. Multielectronic operator spinor (MEOS) [8] is

$$\hat{D}_{\vec{r}} = \{c_{\vec{r}\sigma}\nu_{\vec{r}L}\, d_{\vec{r}\sigma L}\}, \quad c_{\vec{r}\sigma}^2 = (1 + \vec{\sigma}\vec{s}_{\vec{r}})/2,$$

$$\nu_{\vec{r}L}^2 = (1 + \vec{L}\vec{l}_{\vec{r}})/(2L + 1). \tag{2.2}$$

Fermion MEOS $d_{\vec{r}\sigma L}$ in the coordinate space and MEOS $c_{\vec{r}\sigma}$ in the spin space ($\vec{\sigma}$ – the Pauli matrices) submit to the conditions of locality and normalizing ones:

$$d_{\vec{r}\sigma L}\bar{d}_{\vec{r}\sigma L} = 1 = \mathrm{Sp}_\sigma c_{\vec{r}\sigma}^2 = \mathrm{Sp}_L \nu_{\vec{r}L}^2,$$

$$\bar{d}_{\vec{r}} = (d_{\vec{r}})^{+}, \quad L = 2. \tag{2.3}$$

Formulas, similar to (2.2) – (2.3), can be introduced for magnetic 3*d*-electrons (the Holstein – Primakoff formulas, see [9]). Below at the CBF calculation, the indices of spin (σ) and orbital (*L*) moments are omitted.

The variation parameters of covalent electrons' system $\vec{s}_{\vec{r}}$ and $\vec{l}_{\vec{r}}$ enter into functionals: the Coulomb one in the Hubbard form for charges $N_{\vec{r}} = \hat{D}_{\vec{r}}\hat{D}_{\vec{r}}$

$$H_{\vec{r}}^{\mathrm{Coul}} = U\hat{N}_{\vec{r}}\hat{N}_{\vec{r}} = \frac{U}{2}(1 + \vec{s}_{\vec{r}}^{\,2} + \vec{l}_{\vec{r}}^{\,2} + \ldots), \tag{2.4}$$

spin-orbital and the Hund Hamiltonians

$$H_{\vec{r}}^{s-o} = \lambda_0(\vec{s}_{\vec{r}}\vec{l}_{\vec{r}}) + \lambda_1(\vec{S}_{\vec{r}}\vec{l}_{\vec{r}}), \quad H_{\vec{r}}^{H} = -A(\vec{S}_{\vec{r}}\vec{s}_{\vec{r}}) \tag{2.5}$$

for intraionic interactions. The Hamiltonian of covalent bond

$$H^{\mathrm{ch}} = -\sum \Gamma(|\vec{\rho}|)\,\hat{D}_{\vec{r}}\hat{\bar{D}}_{\vec{r}} =$$

$$= -\sum \Gamma(|\vec{\rho}|)\,d_{\vec{r}}\bar{d}_{\vec{r}}\,(1 + \vec{s}_{\vec{r}}\vec{s}_{\vec{r}} + \vec{l}_{\vec{r}}\vec{l}_{\vec{r}} + \ldots) \qquad (2.6)$$

has operator coefficient

$$\hat{\Gamma} = \sum_{\vec{\rho}} \Gamma\, d_{\vec{r}}\bar{d}_{\vec{r}}, \quad \vec{\rho} = \vec{r} - \vec{r}'. \qquad (2.7)$$

It is possible to consider it as a constant ($\hat{\Gamma} \approx \Gamma$) at low $T << 10^3$ K under conditions of a stable lattice and also in the nearest neighbours' approximation. However, Co polymorphism (the transition hcp $\rightarrow$ fcc at an increase of $T \geq T_0 \approx 600$ K) requires the direct account of soft CBF.

We simplify the variation of sum (2.4) – (2.6) assuming

$$\vec{s}_{\vec{r}} = \vec{\alpha}_{\vec{r}} s, \quad \vec{l}_{\vec{r}} = \vec{\gamma}_{\vec{r}} l, \quad |\alpha_{\vec{r}}| \approx |\gamma_{\vec{r}}| \approx 1,$$

$$(A, \lambda_0, \lambda_1) < 0, \qquad (2.7')$$

that results in the operator system of equations

$$\begin{pmatrix} (U - \hat{\Gamma}) & \lambda_0 \\ \lambda_0 & (U - \hat{\Gamma}) \end{pmatrix} \begin{pmatrix} \hat{l} \\ \hat{s} \end{pmatrix} = \begin{pmatrix} -\lambda_1 \\ A \end{pmatrix} S, \quad \hat{S} \rightarrow \hat{S}_{\vec{r}}. \qquad (2.8)$$

The operator solutions are obtained as

$$\hat{\vec{s}}_{\vec{r}} = [(U - \hat{\Gamma})^2 - \lambda_0^2]^{-1} \{A\,(U - \hat{\Gamma}) + \lambda_0\,\lambda_1\}\,\vec{S}_{\vec{r}},$$

$$\hat{\vec{l}}_{\vec{r}} = \hat{Q}_{\vec{r}}\vec{S}_{\vec{r}}, \qquad (2.9)$$

where

$$\hat{Q}_{\vec{r}} = -[(U - \hat{\Gamma})^2 - \lambda_0^2]^{-1} \{\lambda_1\,(U - \hat{\Gamma}) + A\,\lambda_0\}. \qquad (2.9')$$

We substitute solution (2.9) to the Hamiltonians of CF (1.4) and of anisotropic exchange (1.5) and receive the MA Hamiltonian

$$H^{\mathrm{MA}} = \hat{k}_1^{\,i} \sum (S_{\vec{r}}^{\,z})^2 + \sum \hat{k}_1^{\,\mathrm{ex}}(|\vec{\rho}|)\, S_{\vec{r}}^{\,z} S_{\vec{r}}^{\,z}. \qquad (2.10)$$

The parameter of one-ionic MA

$$k_1^{\,i} = A_{20}^{dd} \langle [(U - \hat{\Gamma})^2 - \lambda_0^2]^{-2} \{(U - \hat{\Gamma})\,\lambda_1 + A\,\lambda_0\}^2 \rangle \qquad (2.11)$$

depends on T and P, that is found out after the averaging of the function of the operator Γ (2.7) on CBF. However, the sign of (2.11) is determined by A_{20} sign.

The change of the sign of $K_1(T)$ in Co becomes possible after the account of anisotropic exchange, whose parameter

$$\hat{k}_1^{\,\mathrm{ex}} = B_{20}^{dd}(|\vec{\rho}|)\,\hat{Q}_{\vec{r}}\hat{Q}_{\vec{r}} \qquad (2.12)$$

also depends on T, but this dependence differs from (2.11). The similar formulas are received for MA constants of higher orders. For example, for the 4th order,

$$k_2^i = A_{40}^{dd} \langle Q_{\vec{r}}^4 \rangle, \quad \text{`} \quad , \qquad (2.13)$$

that also results in strong T-dependence because of averaging on CBF. The CBF influence on MA is defined by the ratio (Γ / U). Some estimations of the effects can be made by assuming $S = 1$, $s \approx -0.15$. Under the condition $|A| >> |\lambda_1|$, we receive

$$A / U \approx -0.1, \quad |\hat{Q}_{\vec{r}}| \sim |\lambda_1 - 0.1\lambda_0| / U, \qquad (2.13')$$

for Co (at $\Gamma \leq U$). Temperature dependence of MA constants is found by calculating CBF correlators.

We suppose that there are 2 magnetic holes and one delocalized hole (represented by a fermion $a_{\vec{r}\sigma}^{+}$) from three holes in the $3d$-shell of a Co ion, according to (2.1). In zero approximation, spin and orbital effects (indices σ and L) are neglected. The Hamiltonian of $3d$-holes is

$$H^d = E_d \sum a_{\vec{r}}^{+} a_{\vec{r}} - \sum V(|\vec{\rho}|)\, a_{\vec{r}}^{+} a_{\vec{r}},$$

$$V \xi_d^2 = \Gamma(|\vec{\rho}|), \quad d_{\vec{r}} f_{\vec{r}} = 0, \qquad (2.14)$$

where we use the condition of orthogonality of localized covalent and band states.

On the basis of (2.1), the Green functions [10]

$$G_{\vec{k}}^{f} = \langle\langle f_{\vec{k}} | f_{\vec{k}}^{+} \rangle\rangle, \quad G_{\vec{k}}^{d} = \langle\langle \bar{d}_{\vec{k}} | f_{\vec{k}}^{+} \rangle\rangle,$$

$$V_{\vec{k}} = V(0) - V(\vec{k}) \qquad (2.15)$$

and Fourier-image of the integral $V(\vec{\rho})$ for the electron jumping between sites $\vec{r}$ and $\vec{r}'$ are introduced. The motion equations are

$$\begin{pmatrix} E - \tilde{\varepsilon}_{\vec{k}} & (\xi_f \xi_d / \sqrt{N})\, V_{\vec{k}} \\ (\xi_f \xi_d / \sqrt{N})\, V_{\vec{k}} & E - \xi_d^{\,2} V_{\vec{k}} \end{pmatrix} \begin{pmatrix} G_{\vec{k}}^{f} \\ G_{\vec{k}}^{d} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad (2.16)$$

where

$$\tilde{\varepsilon}_{\vec{k}} = \xi_f^2 (E_d + V_{\vec{k}}) - \tilde{\varepsilon}_F, \quad E_d < 0,$$

$$\tilde{\varepsilon}_F = \varepsilon_F - E_d \xi_f^2. \qquad (2.16')$$

For a good ferrometal such as Co ($|\xi_f| >> |\xi_d|$), the solutions of the secular equation for system (2.16) are

$$E_{\vec{k}}^{\pm} = \{V_{\vec{k}} - \varepsilon_F \pm [(V_{\vec{k}} - \varepsilon_F)^2 + 4\varepsilon_F V_{\vec{k}} \xi_d^2]^{1/2}\}/2, \qquad (2.17)$$

see Fig. 1,*a*. The essential role, especially in the fcc phase, is played by a part of the CBF branch at small $|\vec{k}| << 1$

$$E_{\vec{k}}^{+} \approx \xi_d^2 V_{\vec{k}} \approx (V_1 \xi_d^2) \vec{k}^2, \quad V_1 \approx V(0),$$

$$\hat{\Gamma}_{\vec{r}} \approx \sum_{\vec{\rho}} \Gamma(|\vec{\rho}|)\, d_{\vec{r}} \bar{d}_{\vec{r}}, \qquad (2.18)$$

where the operator of covalent energy $\hat{\Gamma}_{\vec{r}}$ is introduced as

$$\langle \hat{\Gamma}_{\vec{r}} \rangle \approx \xi_d^2 V(0)(1 - \alpha_{5/2}^F \tau_\Gamma^{5/2}),$$

$$\tau_\Gamma = k_B T / V_1 \xi_d^2, \quad T > T_0. \qquad (2.18')$$

The band energy

$$E_{\vec{k}}^{f} \approx E_{\vec{k}} \approx V_{\vec{k}} \xi_f^2 - \varepsilon_F, \quad |\vec{k}| << 1 \qquad (2.18'')$$

gives a small contribution to the temperature dependence of MA constants (2.11) – (2.13).

More important is the crossing of branches near the Fermi level (see Fig. 1,*a*):

$$E_{\vec{k}}^{\pm} \approx \pm |\xi_d| \sqrt{\varepsilon_F V_{\vec{k}}} + (V_{\vec{k}} - \varepsilon_F)/2. \qquad (2.19)$$

A significant value of the nondiagonal matrix elements (2.16) results in a maximum on the band branch ($k \approx k_0 > k_F$ – the Fermi momentum) and a minimum on the CBF branch. So, good metal ($\varepsilon_F > \Gamma(0) = \xi_d^2 V(0)$) differs from semiconductor, or semimetal ($\varepsilon_F < \Gamma(0)$), in which the band branch (f) is more flat than the CBF branch (Fig. 1,*b* for semiconductor). Solution (2.18) becomes complicated with regard for $s\bar{d}$ -hybridization [10]. Therefore, in general case, using general reasons for singularities of the band isoenergetic surfaces of metal [11], we suppose

$$E_{\vec{k}}^{d} \approx E_d(\vec{k}_0) + \omega |\vec{k} - \vec{k}_0|, \quad \vec{k}_0 = \vec{k}_{\min},$$

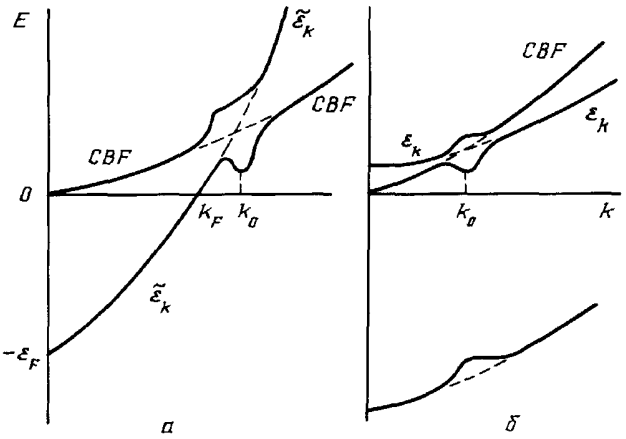

Fig. 1. Electronic spectra $E(k)$ of: a – one-band metal, b – two-band semiconductor. The crossing of conduction band's branch $\varepsilon(k)$ and covalent bond fluctuations' (CBF) branch is shown, when the minimum point $k = k_0$ is near the Fermi momentum k_F

$$|\vec{k} - \vec{k}_0| \le \Delta_{\vec{k}}, \quad \Gamma = \xi_d^2 V. \qquad (2.20)$$

The linear term's coefficient is $\omega > 0$ for the CBF branch (minimum) or $\omega < 0$ for the band branch, and ω values for different branches should differ. Below we shall be interested only by the CBF branch ($\omega > 0$).

The CBF correlator in a vicinity of the extremum ($\varepsilon_{\vec{k}} >> E_{\vec{k}}^{d}$) is

$$\langle d_{\vec{k}} \bar{d}_{\vec{k}} \rangle = N_{\vec{k}} \approx [\exp(\beta E_{\vec{k}}^{d}) + 1]^{-1} / N, \quad \beta = 1/k_B T. \qquad (2.21)$$

The integral number of CBF (ρ^2 – the stability parameter of a chemical lattice [6, 10]) is, according to (2.20),

$$1 - \rho^2 = \Sigma N_{\vec{k}} \approx e^{-\beta E_d(\vec{k}_0)} \alpha_1 k_0^2 (k_B T/\omega)$$

$$\text{at } (\Delta_{\vec{k}} \omega \beta) >> 1. \qquad (2.22)$$

If the minimum CBF energy is small enough,

$$E_d(\vec{k}_0) << k_B T_0,$$

$$\Phi^{ch} \approx \Gamma(0)\{1 - \chi_F e^{-\beta E_d(\vec{k}_0)} (\vec{k}_B T/\omega)\}, \quad T < T_0, \qquad (2.23)$$

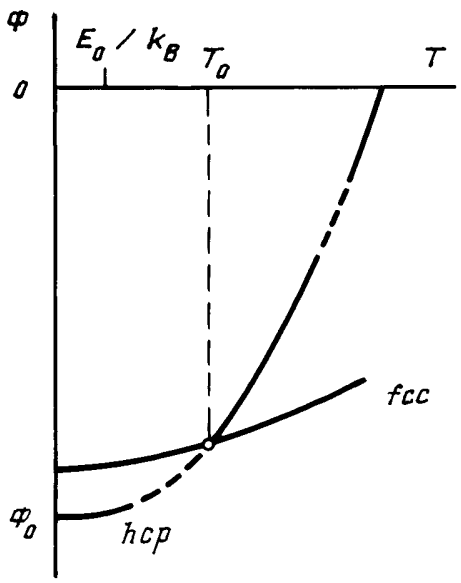

Fig. 2. T-dependences of thermodynamical potentials $\Phi(T)$ for the fcc and hcp Co phases, the point $T = T_0$ of the fcc – hcp transition is shown

the thermodynamic potential (t.d.p.) of covalent bond $\Phi^{ch}(T < T_0)$ depends on T much stronger than the t.d.p. of the fcc phase (2.18′), see Fig. 2. There is the point of equality of phases' t.d.p. $T = T_0$ for Co polymorphism.

Let's estimate the values included in (2.23). We suppose $\xi_d^2 = 0.1$, $k_0 \sim 1$, $\omega \sim 10\, E_d(\vec{k_0})$. We receive the strong (linear) dependences on T for MA constants, for example, taking into account the magnon contribution [12]

$$K_1^i(T)/K_1^i(0) \approx [1 - \chi_1 (T/T_0)\, e^{-R/T}]\, S_T^3,$$

$$R = E_d(\vec{k_0}) / k_B. \qquad (2.24)$$

The coefficient is

$$\chi_1 = \chi_2 (k_B T_0 / \omega)\, \chi_F,$$

$$\chi_2 = 2\,|\lambda_1|\, \Gamma / [\,|\lambda_0 A| - |\lambda_1|\,(U - \Gamma)]. \qquad (2.24')$$

Anisotropic exchange renormalizes coefficient (2.24). Thus, it can be $\chi_1 > 1$, that can change the $K_1(T)$ sign and lead to the orientational magnetic transition, which is observed in fcc Co, at $T_1 < T_0$.

We note that a practically linear dependence $K_1(T)$ observed in Co in a wide temperature interval was interpreted repeatedly, see [7, 13, 14]. The Carr assumption [14] about a decisive role of thermal expansion was refuted [7] by direct account of the magnetoelastic contributions to $K_1(T)$. The calculation [13] on the basis of a two-lewel model of Co electronic structure is closer to our interpretation. The difference is that, in our theory, a continuous CBF spectrum is calculated directly, instead of the model hypothesis [13] about fluctuational transitions between levels.

3. Unstable FM Intermetallide. Tetragonal MnBi

Equiatomic compound Mn($[\mathrm{Ar}]\,3d^5\,4s^2$) and Bi($[\mathrm{Xe}]\,4f^{14}\,5d^{10}\,6s^2\,6p^3$) forms a complex lattice [6, 9]. Its instability relative to heating up to ≈ 600 K [15, 16], and also to formation of antistructural defects indicates a weakness of chemical bonds. The metal bond does not play a determining role, as MnBi is a bad metal with large electroresistance [9, 17]. Uniaxial, low for good metals, symmetry and complexity of a chemical lattice points to domination of covalent bonds, and its instability allows one to assume the existence of soft CBF modes.

We take into account the covalent bonds Mn – Mn(Γ^{dd}), MnBi(Γ^{dp}), and Bi – Bi(Γ^{pp}). The wave functions are in the MEOS form for 3d- and 6p-ions

$$\hat{D}_{\vec{r}} = \{c_{\vec{r}\sigma}(\vec{s}_{\vec{r}})\, \nu_{\vec{r}L}\, d_{\vec{r}L\sigma}\}, \quad c_{\vec{r}\sigma} = [(1 + \vec{\sigma}\vec{s}_{\vec{r}})/2]^{1/2},$$

$$\nu_{\vec{r}L} = [(1 + \vec{L}\vec{L}_r)/(2L + 1)]^{1/2} \qquad (3.1)$$

for Mn ions ($L = 2$) with covalent 3d-electron and spin $S = 2$, where σ – the Pauli matrix, L – the matrix of orbital moment in the appropriate discrete spaces. MEOS of Bi ions ($L = 1$)

$$\hat{P}_{\vec{r}} = \{c_{\vec{r}\sigma}(\vec{\pi}_{\vec{r}})\, \nu_{\vec{r}L}(\vec{l}_{\vec{r}})\, p_{\vec{r}L\sigma}\},$$

$$d_{\vec{r}L\sigma}\bar{d}_{\vec{r}L\sigma} = 1 = p_{\vec{r}L\sigma}\bar{p}_{\vec{r}L\sigma}, \quad d_{\vec{R}}\bar{p}_{\vec{R}} = 0 \qquad (3.2)$$

are also local and orthogonal to 3d-states. Metric definiteness of functional fermion spaces is a consequence of conditions (3.2).

A weak (in comparison with chemical bonds) spin-orbital bond

$$H^{s}_{\vec{r}} = \lambda_0 (\vec{L}_{\vec{r}}\vec{S}_{\vec{r}}) + \lambda_1 (\vec{L}_{\vec{r}}\vec{s}_{\vec{r}}) + \lambda_2 (\vec{l}_{\vec{r}}\vec{\pi}_{\vec{r}}) \qquad (3.3)$$

inside ions causes a nontrivial solution of the problem of crystal field in the form

$$H^{CF}_{\vec{r}} = A_{20}^{dd} (L^z_{\vec{r}})^2 + \Sigma A_{20}^{dp} (|\vec{\rho}|)(L^z_{\vec{r}} J^z_{\vec{r}+\vec{\rho}}) + \ldots \qquad (3.4)$$

The first term (3.4) is considered as one-ionic MA (Mn ions), the second – as anisotropic exchange. The operators of orbital moments included in them are expressed by a variational procedure through one

parameter of magnetic order, the local spin $\vec{S}_{\vec{r}}$ of an ion Mn^{3+}. Covalent electrons are described by the intraionic Hamiltonians (after spur operations on $\vec{\sigma}$ and $\vec{L}$) [8, 10]

$$H^{d}_{\vec{r}} = U_d\,(1 + \vec{s}^{\,2}_{\vec{r}} + \vec{L}^{\,2}_{\vec{r}})/2 - A_d\,(\vec{S}_{\vec{r}}\vec{s}_{\vec{r}}),$$

$$H^{p}_{\vec{r}} = U_p\,(1 + \vec{l}^{\,2}_{\vec{r}} + \pi^{2}_{\vec{r}})/2 \qquad (3.5)$$

and by covalent bond

$$H^{\rm ch} = -\sum \Gamma^{dd}\,\hat{D}_{\vec{r}}\hat{\bar{D}}_{\vec{r}} - \sum \Gamma^{pp}\,\hat{P}_{\vec{r}}\hat{\bar{P}}_{\vec{r}} -$$

$$- \sum (\Gamma^{dp}\,\hat{D}_{\vec{r}}\hat{\bar{P}}_{\vec{r}} + \text{h.c.}). \qquad (3.6)$$

The Hamiltonian of band electrons and their hybridization with covalent electrons

$$H^{\rm el} = \sum \tilde{\varepsilon}_{\vec{k}} f^{+}_{\vec{k}} f_{\vec{k}} + \sum [(g_{d\vec{k}} d_{\vec{k}} + g_{p\,\vec{k}} p_{\vec{k}}) f_{\vec{k}} + \text{h.c.}],$$

$$d_{\vec{r}} f_{\vec{r}} = 0 = p_{\vec{r}} f_{\vec{r}}, \qquad (3.7)$$

with the account of orthogonality of band and covalent states defines the form of dispersion of hybridization coefficients

$$g_{j\,\vec{k}} = \sum g_j\,(|\vec{\rho}|)(1 - e^{i\,\vec{k}\vec{\rho}}), \quad \tilde{\varepsilon}_{\vec{k}} = \varepsilon_{\vec{k}} - \varepsilon_{\rm F}. \qquad (3.7')$$

The Fermi energy $\varepsilon_{\rm F}$ is defined by dispersion of a band spectrum $\varepsilon_{\vec{k}}$ (integrals of electron jumping V between ions of different types) and the number N_e of conduction electrons. Spin and orbital indices at the spectra calculation (as well as in Section 2) are omitted, not considering (for brevity) appropriate effects that influence kinetic, optical, and other properties.

A solution of the variation problem in the operator form is

$$\vec{s}_{\vec{r}} = \hat{\Delta}_3^{-1}\hat{\Delta}_s\,\vec{S}_{\vec{r}}, \quad \hat{\Delta}_s = A_d\,(\hat{U}_d\,\hat{U}_p - \hat{\Gamma}^{dp}_{\vec{r}}\hat{\Gamma}^{pd}_{\vec{r}}) +$$

$$+ \lambda_0\,\lambda_i\,\hat{U}_p, \quad \hat{U}_j = U_j - \hat{\Gamma}^{jj}_{\vec{r}},$$

$$\vec{L}_{\vec{r}} = \hat{\Delta}_3^{-1}\hat{\Delta}_L\,\vec{S}_{\vec{r}}, \quad \hat{\Delta}_L = -\hat{U}_p\,(\lambda_0\,\hat{U}_d + \lambda_1\,U_p),$$

$$\hat{\Gamma}^{dd}_{\vec{r}} = \sum \Gamma^{dd}\,(|\vec{\rho}|)\,d_{\vec{r}}\bar{d}_{\vec{r}},$$

$$\vec{l}_{\vec{r}} = \hat{\Delta}_3^{-1}\hat{\Delta}_l\,\vec{S}_{\vec{r}}, \quad \hat{\Delta}_l = \Gamma^{pd}_{\vec{r}}\,(\lambda_0\,\hat{U}_d + \lambda_1\,A_d),$$

$$\hat{\Gamma}^{pd} = (\Gamma^{dp})^{+}. \qquad (3.8)$$

The operator (denominator (3.8))

$$\hat{\Delta}_3 = \hat{U}_d\,(\hat{U}_d\,\hat{U}_p - \hat{\Gamma}^{dp}\,\hat{\Gamma}^{pd}) - \lambda_1^2\,\hat{U}_p, \quad \langle\hat{\Delta}_3\rangle > 0, \qquad (3.9)$$

is positively determined. Spin polarization of Bi ions

$$\hat{\vec{\pi}}_{\vec{r}} = A_d\,\hat{\Gamma}^{pd}\,(\hat{U}_d\,\hat{U}_p)^{-1}\,\vec{S}_{\vec{r}} \qquad (3.10)$$

is defined by the parameter of covalent bond Mn–Bi, which is not small ($|\langle\Gamma^{dp}\rangle| \sim U_p$). Contribution (3.10) to magnetization is significant. The spin-orbital contribution $\sim \lambda^2\,|\,\Gamma^{dp}\,|^{\,2}/\,A_d\,U_d\,U_p$ is considered to be small, in comparison with (3.10), and $\vec{\pi}_{\vec{r}}$ is not taken into account.

We substitute (3.8) in (3.3) and receive the MA Hamiltonians. One-ionic MA is

$$\hat{H}^{\rm CF}_i\,(\vec{r}) = \hat{k}^{\,i}_1\,(S^{\,z}_{\vec{r}})^2, \quad \hat{k}^{i}_1 = \hat{\Delta}_3^{-2}\,\hat{\Delta}_L^2\,A^{dd}_{20}. \qquad (3.11)$$

Anisotropic exchange is

$$H^{\rm ex}_{\rm MA} = \sum A^{\,dp}_{20}\,(|\vec{\rho}|) \times$$

$$\times \langle \hat{\Delta}_3^{-1}\,(\vec{r})\,\hat{\Delta}_3^{-1}\,(\vec{r}')\,\hat{\Delta}_L\,(\vec{r})\,\hat{\Delta}_L\,(\vec{r}')\rangle\,S^{\,z}_{\vec{r}}S^{\,z}_{\vec{r}'}, \qquad (3.12)$$

where the averaging $\langle\ \rangle$ of products of coordinate MEOS is supposed. The parameter of one-ionic MA ($K^{\,i}_1$) is found by the same averaging, the sign of which is simply determined by the sign of A^{dd}_{20}. The MEOS correlator in (3.11) is positively determined. The sign of the MEOS correlator in (3.12) depends on CBF spectra and will be determined below.

3.1. Connected Electronic (Covalent-band) Spectra

We consider intermetallides as a limiting case of ordering alloys [12]. We assume weak bonds of the identical ions in a lattice MnBi ($|\,\Gamma^{jj}\,| << |\,\Gamma^{dp}\,|$) and weak hybridization of the band 3*d*- and 6*p*-electrons ($g_p \to 0$). By the method of the two-time Bogolyubov – Green functions (similar to Section 2), the secular equation

$$\Delta_e = (E - \tilde{\varepsilon}_{\vec{k}})(E^2 - |\,\Gamma^{dp}_{\vec{k}}\,|^{\,2}) - g^{\,2}_{d\vec{k}}(E - \Gamma^{pp}_{\vec{k}}) \approx 0 \qquad (3.13)$$

is received. In the center of the Brillouin zone, two CBF branches are square-law functions of the quasi-momentum

$$E^{\rm CBF}_{\vec{k}} \approx E^{\pm}_{dp}\,\vec{k}^{\,2},$$

$$E^{\pm}_{dp} = \pm\,[\,|\,\Gamma^{dp}\,|^{\,2} + (g_d^2 / 2\varepsilon_{\rm F})^2]^{1/2} + g_d^2 / 2\varepsilon_{\rm F}, \quad (3.14)$$

that gives the constant contribution to the t.d.p. of a covalent bond

$$\Phi_0^{\rm CBF} \sim -\,E^{dp} < 0, \quad |\,g_{d\vec{k}}\,| \approx g_d\,k^2 << |\,\Gamma^{dp}\,|\,. \quad (3.15)$$

In a vicinity of the Fermi surfaces of band electrons, CBF branches, crossing them, (similar to Fig. 1,*a*) form extrema $E^{\rm CBF}(\vec{k})$. There are the soft CBF modes, giving the basic thermal contribution in $\Phi^{\rm CBF}$, which causes destabilization of a lattice MnBi at $T \to T_0 - 0$.

Near a minimum point $\vec{k} = \vec{k}_0$ of the upper CBF branch (3.13), (3.14), its ascending parts are approximated by linear functions. However, in contrast to good metal Co with greater hybridization energy $|\,V\,| >> |\,g_d\,|$,the minimum $E(\vec{k})$ of the CBF branches (3.13) should be less sharp. Therefore, we take into account the asymmetry of parts $E^{\pm}(\vec{k})$, higher and below k_0, relatively to the sphere $|\,\vec{k}\,| = k_0$

$$E^{\pm}(k_0 \pm q) \approx E_0(k_0) \pm G_{\pm}\,q, \quad \text{for } |\,\vec{q}\,| = q \le k_{\pm}\,. \quad (3.16)$$

The general form of the t.d.p. of covalent bonds (including zero (negative) energy (3.15)) is

$$\Phi \approx \Phi_0 + \sum_{\vec{k}j} E^{j}_{\vec{k}}\, n_{\rm F}(E^{j}_{\vec{k}}), \quad j = +\,,-\,, \quad (3.17)$$

where $n_{\rm F}$ the Fermi function of form (2.21).

The contribution of the extreme spectrum part (3.16) to t.d.p. (3.17) is

$$\Delta\Phi(T) \approx \sum (E_0 + G_{\pm}\,q)\exp\{-\,\beta(E_0 + G_{\pm}\,q)\},$$

$$\beta = 1/k_{\rm B}\,T, \quad (3.18)$$

or

$$\Delta\Phi \approx C_+\,k_0^2\,e^{-\beta E_0}\,\{(E_0/\beta)\,G_1 + (G_2/\beta^2)\}, \quad (3.18')$$

where

$$C_+ \sim 0.1, \quad G_1 = \sum_j G_j^{-1}, \quad G_2 = \sum_j G_j^{-2}. \quad (3.18'')$$

The general form of covalent t.d.p. is given in Fig. 2. At low $T << T_0$, the weak temperature dependence of t.d.p. is defined by a square-law part of CBF branches (3.14) and by the exponentially small contribution (3.18). A growth in $T \ge (E_0 / k_{\rm B})$ results in a strong linear dependence $\Phi(T)$ with the square-law amendment (the second term in (3.18′)). Reduction of covalent bond's energy destabilizes MnBi lattices and facilitates the creation of antistructural defects.

In the vicinity of k_0, there are also the extreme parts of band spectra. Their influence on electron (hole) mobility is defined by despersion of isoenergetic (band) surfaces, in particular, the anisotropy of Fermi surfaces, which we do not discuss here.

3.2. Parameters of MA and Exchange. MA Constants

Covalent energy, its spin part, is responsible for the exchange bond of local spins $\vec{S}_{\vec{r}}$ of Mn ions and for polarization of covalent electrons ($\vec{s}_{\vec{r}}$ and $\vec{\pi}_{\vec{r}}$). Comparison of experimental data on MnBi [6, 9, 15] with the theory of ideal ferromagnons [9, 12, 17–19] shows that, at $T < T_c/2$, the magnon contribution to MA constants plays a secondary role. The main role is played by the soft CBF modes (3.16). They define the CBF correlators in expressions (3.11) (3.12) for the MA parameters $(k_1^i, k_1^{\rm ex})$.

In approximation (3.13), we have

$$k_1^{\rm ex} \approx -\,A_{20}^{dp}(|\,\vec{\rho}\,|)\,\langle\hat{\Delta}_3^{-2}\rangle\langle\Gamma_{\vec{r}}^{dp}\rangle(\lambda_0 U_d + \\ + A_d\,\lambda_1)\,U_p\,(\lambda_0 U_d + \lambda_1 U_p) \quad (3.19)$$

for anisotropic exchange (3.12), where

$$\langle\hat{\Delta}_3^{-2}\rangle \approx [\,U_d\,(U_d U_p - \langle\Gamma_{\vec{r}}^{dp}\,\Gamma_{\vec{r}}^{pd}\rangle) - \\ - \lambda_1^2\,U_p]^{-2} > 0, \quad T < T_0. \quad (3.20)$$

Experimental data for the MA constants (K_1, K_2) in MnBi [6, 9], in particular, the small value $K_1(0) < 0$, indicate compensation of contributions (3.11) and (3.12) in MA at $T = 0$. At $U_p >> |\,\Gamma^{dp}\,|$, it means

$$0 < A_{20}^{dd} << |\,A_{20}^{dp}\,|\,, \quad A_{20}^{dp} < 0 \quad (3.20')$$

owing to $k_1^i > 0$.

We substitute the operator

$$\hat{\Gamma}_{\vec{r}}^{dp} = \sum_{\vec{\rho}} \Gamma^{dp}(|\,\vec{\rho}\,|)\,d_{\vec{r}}\,\bar{p}_{\vec{r}\mp\vec{\rho}} \to \\ \to \sum_{\vec{\rho}} \Gamma^{dp}(|\,\vec{\rho}\,|)\,\sum_{\vec{k}} d_{\vec{k}}\,\bar{p}_{\vec{k}}\,(e^{\,i\vec{k}\vec{\rho}} - 1) \quad (3.21)$$

in (3.19) and receive

$$\langle\Gamma_r^{dp}\,\Gamma_r^{pd}\rangle = |\,\Gamma^{dp}(0)|^{\,2}\,[\,1 - \sum_k N_k^{pp}\,(1 - e^{ika})],$$

$$N_{\vec{k}}^{pp(d)} = \langle p_k \bar{p}_k (\bar{d}_k)\rangle, \qquad (3.22)$$

where a is the distance Bi^{-} Bi. Averaging of operator (3.21) is reduced to the account of the correlator $N_{\vec{k}}^{dp}$ (3.22). The Green function is equal to

$$G_{\vec{k}}^{pd} = \langle\langle \bar{p}_{\vec{k}} | d_{\vec{k}} \rangle\rangle = (E - \tilde{\varepsilon}_{\vec{k}})\, \Gamma_{\vec{k}}^{pd} / N\Delta_e (E, \vec{k}). \qquad (3.23)$$

Three roots of the secular equation (3.13) $E_k^{\pm}$ and E_k^f (3.16) allows us to write down the correlator

$$\langle d_{\vec{k}} \bar{p}_{\vec{k}} \rangle = \Gamma_{\vec{k}}^{pd} R_{\vec{k}}^{t} / N,$$

$$R_{\vec{k}}^{t} = \sum_j (E_{\vec{k}}^{j} - \tilde{\varepsilon}_{\vec{k}}) R_{\vec{k}}^{j} n_F (E_{\vec{k}}^{j}), \quad j = +, -, f, \qquad (3.23')$$

where the main term is

$$R_{\vec{k}}^{+} = (E_{\vec{k}}^{f} - E_{\vec{k}}^{+}) / (E_{\vec{k}}^{+} - E_{\vec{k}}^{-}) [E_{\vec{k}}^{+} E_{\vec{k}}^{-} - (E_{\vec{k}}^{f})^2]. \qquad (3.23'')$$

As the CBF chemical potential is equal to zero, a part of the interionic (exchange) MA parameter, dependent from T (3.19), at $|A_d| << U_d$, looks like

$$Q_1 (T) = \Delta k_1^{\text{ex}} (T) / k_1 (0) \approx A_{20}^{dp} e^{-\beta E_0} (\chi_1 T + \chi_2 T^2) /$$

$$/ |A_{20}^{dd} U_p - A_{20}^{dp} \Gamma^{dp} (0)| . \qquad (3.24)$$

For comparison with experiment, we write down (3.24) in the form (see Fig. 3):

$$Q_1 (T) = Q_0 e^{-\beta E_0} (\chi_1 T + \chi_2 T^2), \quad Q_0 < 0. \qquad (3.24')$$

A relatively small quantity of the priming total value of the MA parameter ($k_1(0) << |k_1 (300\ \text{K})|$)

$$k_1 (0) \approx [A_{20}^{dd} (\lambda_0 U_d + \lambda_1 U_p) U_p - \Gamma_0^{dp} (\lambda_0 U_d +$$

$$+ \lambda_1 A_d) A_{20}^{dp}] U_p (\lambda_0 U_d + \lambda_1 U_p) / \Delta_3^2 \qquad (3.25)$$

indicates, probably, compensation of the one-ionic and interionic contributions to the MA energy. In Fig. 3, the experimental data (crosses) are rather well interpreted by dependence (3.24) at $Q_0 = -7.5 \times 10^6$ erg/cm^3, $\chi_1 = 0.9 \cdot 10^{-2}\ \text{K}^{-1}$, $\chi_2 = 0$.

3.3. Anomalies of MnBi Spontaneous Magnetization

In contrast to ferrometal (Co), the temperature instability of covalent bonds strongly influences the exchange energy and spontaneous magnetization $M_s (T)$ of intermetallides. We substitute (3.8) in (3.6) and receive the parameter of Heisenberg exchange

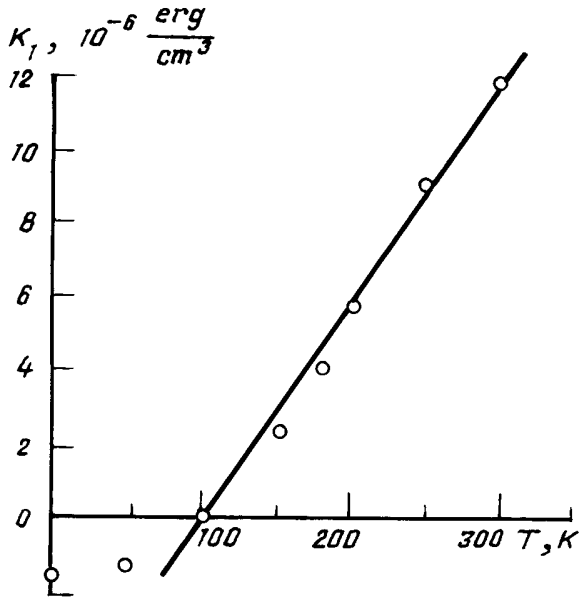

Fig. 3. Interpretation of experimental data (crosses) by the theoretical dependence (solid line) (3.24) for the magnetic anisotropy constant $K_1 (T)$ of tetragonal MnBi

$$H^{\text{ex}} = -\sum A (|\rho|) \vec{S}_{\vec{r}} \vec{S}_{\vec{r}} \qquad (3.26)$$

in the form

$$A (|\vec{\rho}|, T) \approx (A_d / U_d)^2 \{\Gamma^{dd} (|\rho|) + (\langle \Gamma_{\vec{r}}^{dp} \Gamma_{\vec{r}}^{pd} \rangle / U_p)\} \approx$$

$$\approx A_s (|\vec{\rho}|)(1 - a_1 T + a_2 T^2). \qquad (3.26')$$

The negative sign of the first temperature term in a bracket in (3.26′) is caused by the negative sign of correlator (3.22) ($a_1 > 0$, the sign of a_2 is defined by the fine structure of spectrum branches).

Reduction of U_p and increase of the covalent bond $|\Gamma^{dp}|$ in a series of Mn pniktides can result in inversion of the exchange and a transition in the antiferromagnetic state, that, probably, defines the MnAs phase diagram (see [9, 12]). We consider that the covalent nature of such a transition is preferable, in comparison with the models of Kittel, Bean – Rodbell and others (see a review of these models in [9, 12]).

The contribution of covalent electrons' polarization (3.8) to magnetization M_s should strongly depend on T, similarly to (3.26) and (3.24). Comparison of the

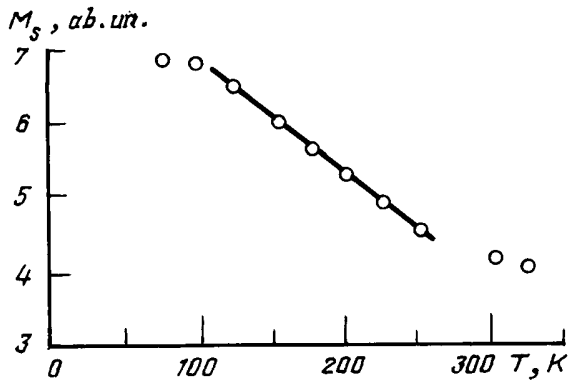

Fig. 4. Approximation of MnBi spontaneous magnetization (crosses) by the theoretical solid curve (3.28)

$s\bar{d}$ -model with experiment (see [9]) allows us to assume an usual negative sign $A_d < 0$, whence $\langle s_{\vec{r}} \rangle < 0$. If $\mathrm{Re}\,\langle \Gamma^{dp} \rangle < 0$, the contribution of Bi ions to magnetization, according to (3.10), is

$$\Delta \vec{M}_s\,[\mathrm{Bi}] = N \langle \vec{\pi}_{\vec{r}} \rangle \uparrow\uparrow \vec{M}_s. \tag{3.27}$$

The calculation, similar to (3.24), gives a strong T-dependence of contribution (3.27):

$$\Delta M_s\,[\mathrm{Bi}] = \Delta M_s\,(T = 0)\{1 - b_1 Q_1\,(T)\}. \tag{3.28}$$

From here, we find $b_1 = 2.2 \cdot 10^{-3}\,\mathrm{K}^{-1}$ and $\Delta M_s\,[\mathrm{Bi}] = 0.33\,M_s$ on comparison with experiment (Fig. 4) by receiving χ_1 from Fig. 3. The last result confirmst strong polarization of covalent electrons that does not contradict experimental data. We have $\pi \approx 1/2$ at $S = 2$ and $s = -1/2$.