AN APPLICATION OF THE MODIFIED ZENER MODEL FOR THE FERROMAGNETIC TRANSITION METALS

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The molecular field approximation is applied to the effective spin Hamiltonian previously derived from the modified Zener model. The spontaneous magnetization is calculated and a comparison of the obtained results with the observed properties of Fe, Co and Ni is made.

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1. Introduction

For the explanation of the magnetic properties of the transition metals (TM) and their alloys two types of models are currently applied, itinerant electron models (band theories) [1] and those which contain localized spins interacting with the band electrons [2, 3]. The modified Zener model (MZM) [3, 4] is of second type of models. Originally this model was proposed by Zener to describe the mixed-valence oxides. This model can also be applied to describe the magnetic properties of the 3*d* transition metals.

On the grounds of phenomenological considerations Goodenough [2] proposed that in a crystal of TM and compounds both localized and itinerant 3*d* electrons can coexist. Starting from Goodenough's hypothesis we assume x electrons at each atom site coupled according to Hund's rule, to yield the spin S and the remaining $n-x$ electrons (n is the number of d electrons per atom) are itinerant and can hop from site to site. Within the MZM the itinerant 3*d* electrons are described by the Hubbard Hamiltonian and they couple to the localized spin $\boldsymbol{S}$ by the term $-2J\boldsymbol{S}_i\boldsymbol{\sigma}_i$ where $\boldsymbol{\sigma}_i$ is the itinerant electron spin operator. Such a formulation of the problem is probably a reasonable simplification accounting for orbital degeneracy and intra-atomic exchange interaction (Hund's rule

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coupling). Starting from this model Hamiltonian we want to explain some of the magnetic properties of the 3*d* TM and their alloys. In this paper we calculate the temperature variation of the spontaneous magnetization M. A comparison of the obtained results with the observed properties of Fe, Co, Ni and with the previously published results is made in Section 3. A short discussion is given in Section 4.

2. *The formulation of the problem and approximations*

The MZM Hamiltonian extended for the fifth-fold degenerated 3*d* band is given by

$$\mathscr{H} = \sum_{k,\sigma,\lambda} \varepsilon_{k\sigma,\lambda} n_{k\sigma,\lambda} - 2J \sum_{i,\lambda} \boldsymbol{S}_i \boldsymbol{\sigma}_{i\lambda} + U \sum_{i,\lambda} n_{i\uparrow,\lambda} n_{i\downarrow,\lambda} - \mu \sum_{i,\sigma,\lambda} n_{i\sigma,\lambda}$$
$$- g_l \mu_B H \sum_i S_i^z - g_i \mu_B H \sum_{i,\sigma,\lambda} \sigma n_{i\sigma,\lambda}, \tag{1}$$

where standard notation is used. For details about the notation see e.g. [3].

The thermodynamic properties of the model Hamiltonian can be calculated using Green functions (GF) technique [3]. Recently Kozarzewski [5] studied the properties of the MZM with the help of the GF method and he obtained from (1) an effective Hamiltonian of localized spins (see [5] for details). The generalizations of his results for the fifth-fold degenerated *d* band can be written as follows

$$\mathscr{H} \cong \mathscr{H}_i + \mathscr{H}_l,$$

where $\mathscr{H}_i$ and $\mathscr{H}_l$ are the effective Hamiltonians for the itinerant and localized 3*d* electrons respectively. The operators $\mathscr{H}_i$ and $\mathscr{H}_l$ are of the form

$$\mathscr{H}_i = \sum_{k,\sigma,\lambda} \varepsilon_{k\sigma} n_{k\sigma,\lambda}$$

$$\varepsilon_{k\sigma} = \varepsilon_k - 2J\sigma \langle S_i^z \rangle + U \langle n_{i-\sigma,\lambda} \rangle - g_i \mu_B H \sigma$$

$$\mathscr{H}_l = - \sum_i h_{\text{eff}} S_i^z$$

$$h_{\text{eff}} = g_l \mu_B H + 5J \langle n_{i\uparrow,\lambda} - n_{i\downarrow,\lambda} \rangle + 5J^2 \langle S_i^z \rangle \chi^{zz}$$

$$\chi^{zz} = \frac{N_\uparrow + N_\downarrow + 2UN_\uparrow N_\downarrow}{1 - U^2 N_\uparrow N_\downarrow}$$

$$N_\sigma = N_\sigma(\mu - \tfrac{1}{2} U \langle n_{i\uparrow,\lambda} + n_{i\downarrow,\lambda} \rangle), \qquad \sigma = (\uparrow, \downarrow) \equiv (+1, -1). \tag{2}$$

$N_\sigma(\varepsilon)$ is the density of the band states. The last part of the molecular field h_{eff} corresponds to the higher order with respect to J/U in the contribution to the real part of the self-energy operator for the Green function $\langle\langle S_i^+ | S_j^- \rangle\rangle$ [3]. A similar form for the real part of the self-energy was used in [7]. The simplified effective Hamiltonian (2) will be used to obtain the temperature dependence of the spontaneous magnetization of pure transition metals.

3. Results and numerical calculations

The magnetic moment per atom is defined as follows

$$M = g_l\mu_B\langle S_i^z\rangle + g_i\mu_B\langle\sigma_i^z\rangle 5, \tag{3}$$

where g_i and g_l are the gyromagnetic factors for localized spins and itinerant electrons respectively. The factor 5 is due to the orbital degeneracy of the $3d$ band. The mean values $\langle S_i^z\rangle$, $\langle\sigma_i^z\rangle \equiv \langle n_{i\uparrow,\lambda} - n_{i\downarrow,\lambda}\rangle$ have to be calculated from a set of two self-cosistent equations

$$\langle S_i^z\rangle = SB_S(Sh_{\text{eff}}/k_BT) \tag{4}$$

$$\langle n_{i\sigma,\lambda}\rangle = \frac{1}{N}\sum_k f_0(\varepsilon_{k\sigma,\lambda}) \tag{5}$$

$$n = \sum_\sigma \langle n_{i\sigma,\lambda}\rangle. \tag{6}$$

The chemical potential can be determined with the use of Eq. (6). In equations (4), (5), (6) the standard notation (see [3]) is used. For simplicity of numerical calculations we describe the band states by the density of states in the form

$$N(\varepsilon) = \begin{cases} 0 & |\varepsilon| > W \\ \dfrac{2}{\pi W}\sqrt{1-\left(\dfrac{\varepsilon}{W}\right)^2} & |\varepsilon| \leqslant W. \end{cases} \tag{7}$$

It is seen from Eqs. (2) to (6) that the model described above has three undefined parameters U, J, S which can be varied. Due to the fact that the comparison of the results with the experimental data for Fe, Co, Ni will be made, we have to determine these parameters from the conditions imposed upon spontaneous magnetization M at $T = 0$, Curie temperature T_c and the whole number of itinerant $3d$ electrons n.

TABLE I

	Units	Fe	Co	Ni
$M(T=0)$	μ_B	2.22	1.6	0.55
T_c	K	1040	1390	630
n	—	7.2	8.4	9.45
W	eV	3.22	2.64	2.25
S	—	3/2	1/2	1/2
n_i	—	4.2	7.4	8.45
U	eV	3.87	3.34	3.89
J	eV	−0.066	0.168	−0.121

where: T_c — Curie temperature, n — number of d electrons per atom, W — half width of the d band, S — size of the localized spin, n_i — number of the itinerant d electrons per atom, U, J — relevant coupling constants.

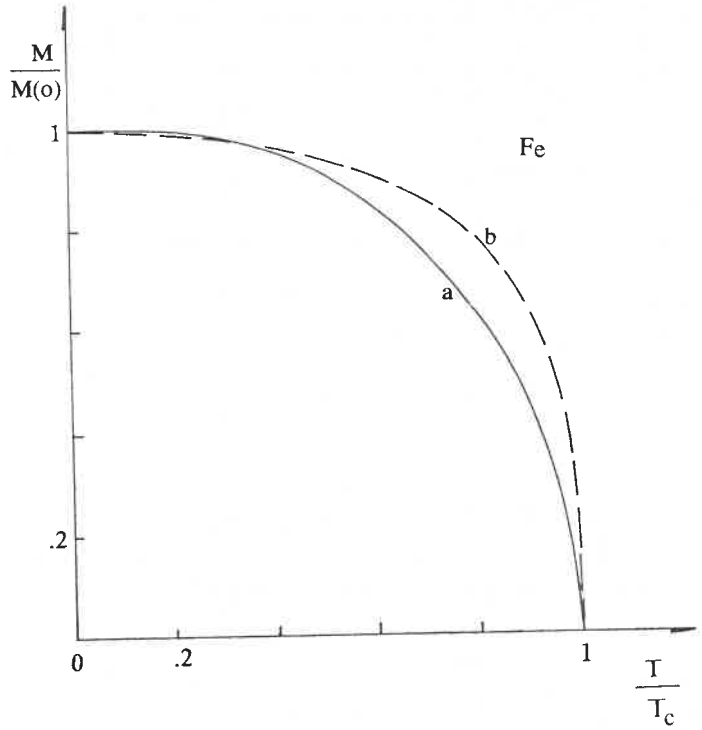

Fig. 1

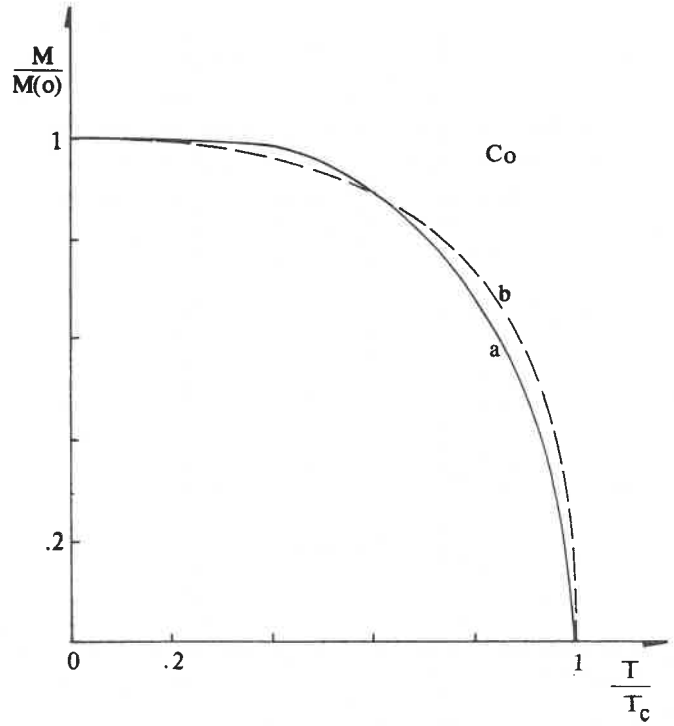

Fig. 2

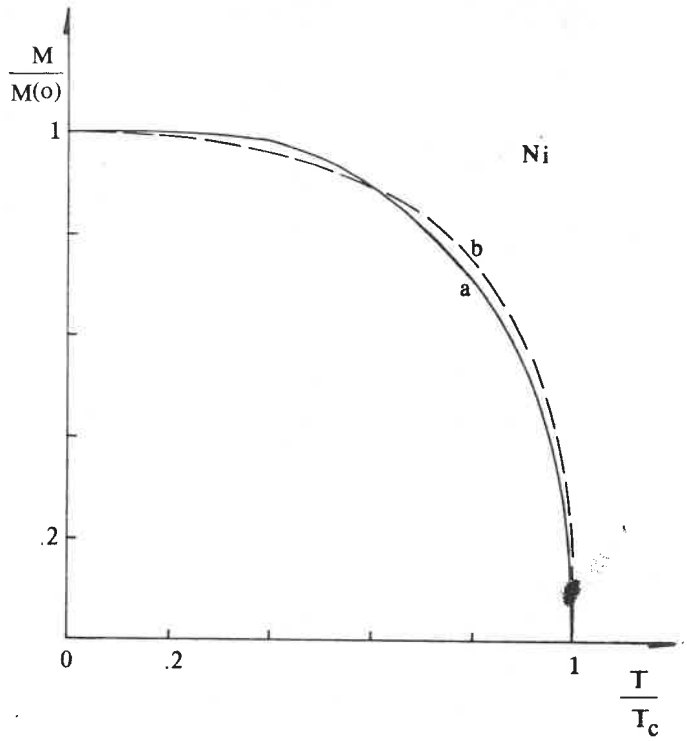

Fig. 3

Figs 1, 2, 3. The spontaneous magnetization vs. temperature for ferromagnetic 3*d* metals Fe, Co, Ni respectively, *a* — calculated, *b* — experimental results taken from [10] for Fe, [8] for Co and [9] for Ni

The quantities $M(T = 0)$, T_c, n, W, g_i, g_1 are well known for Fe, Co, Ni and for our calculations suitable values are taken from [4, 6]. The explicit form of the above mentioned three conditions used in the determination of U, J, S is simple (for the density of states (7)) and will not be presented. Using the values 1/2, 1, 3/2 for S one can easily see that only for some values of S the solutions of these equations are reasonable. The calculated coupling constants are collected in Table I. Numerical calculation of the magnetization M for Fe, Co, Ni, with U, J, S taken from Table I, is presented in Figs. 1, 2, 3. For comparison the experimental data are also depicted.

4. Discussion

We conclude that the model discussed here gives a reasonable description for iron, cobalt and nickel. This model may be treated as a sequel to paper [4] for understanding of MZM model for the 3*d* transition metals. The obtained results are unfortunately more qualitative than quantitative. The great difference between experimental results and the calculations given here appears for the magnetization for iron. In all cases the decrease of magnetization $M(T)$ in the range of T $(0, 1/2T_c)$ is too small. This fact is well known and is caused by the kind of molecular field approximation scheme used in calculations.

There are also some ambiguities concerning the number of itinerant $3d$ electrons and the role of $4s$ electrons in determining of the details of the magnetization curve. One can obtain a satisfactory fit for $M(T = 0)$, T_c, μ_{eff} above T_c and exchange splitting in Fe and Ni by assuming the number of the itinerant $3d$ electrons to be less than one per atom. In Fe for example we have assumed $S = 1$ and a free electron like density of states. Then the experimental values of $M(T = 0)$, T_c and μ_{eff} are obtained if $J = 0.27$ eV and depending on the number of itinerant electrons per atom in the range 0.2 to 0.25, if U changes from 1.3 to 7.5 eV, the effective mass of an electron — from 4.8 to 1.6 and exchange splitting at $T = 0$ varies from 0.8 to 2.0 eV. This is in striking agreement with what was suggested by Stearns [11]. However, for these parameters the spontaneous magnetization is substantially lower in the middle of the $(0, T_c)$ range than the observed one. The proposed model and approximation used are probably too simple for quantitative results and a more sophisticated theory is needed. The correct theory must consider some aspects of localized moments which appear due to the correlation effects [4].

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