

## LOCAL SPIN EXCITATIONS AND CURIE TEMPERATURE OF IRON

A.I. Liechtenstein, M.I. Katsnelson\* and V.A. Gubanov

Institute of Chemistry, Ural Science Center, Sverdlovsk, GSP-145, USSR

\*Institute of Metal Physics, Ural Science Center, Sverdlovsk, GSP-170, USSR

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The expression for the Curie temperature of ferromagnetic metals in the mean field approximations is obtained for arbitrary types of exchange interactions. In the framework of local spin density functional approach an exact formula for the effective exchange parameter  $J_0$  is derived. The numerical calculations for ferromagnetic iron illustrate the possibilities of the method.

AS IS KNOWN, ferromagnetism of transition metals is not quantitatively described in the framework of the famous models of exchange interactions. The Stoner model does not take into account the contributions of collective excitations to thermodynamic properties, the Heisenberg model and  $s$ - $d$  exchange model neglect the itinerant nature of metal  $d$ -electrons. A usual approach to describe such systems is to apply the Hubbard model to the description of magnetic properties of  $d$ -metals. However such important features as the  $s$ - $d$  hybridization, the interactions between  $d$ -electrons on different sites and the degeneracy of  $d$ -states are usually not included in the latter model.

In that connection the development of new approaches based on a realistic description of electronic structure of ferromagnetic metals would be strongly desirable. Such calculations of Curie temperature  $T_c$  have been attempted in [1, 2], but the generalization of Slater's magnetic transition state method [3] used in [1] does not have a rigorous justification. In the paper [2] the thermodynamic relations used were obtained essentially in the scope of Heisenberg model. The present paper gives the results of first-principle calculations of  $T_c$  for ferromagnetic metals with arbitrary types of exchange interactions.

We start from a generalized mean field scheme and write the energy  $E$  connected with a given magnetic moment  $\mathbf{M}$  on a certain site 0 in the following form

$$E = -\mathbf{h} \cdot \mathbf{M} \quad (1)$$

here  $\mathbf{h} = \lambda \langle \mathbf{M} \rangle$  and  $\lambda$  is the mean-field parameter.  $T_c$  is determined by the condition of the appearance of non-trivial solutions for the self-consistent equation

$$\langle \mathbf{M} \rangle = \frac{\text{Tr } \mathbf{M} \exp\left(\frac{1}{T} \mathbf{h} \mathbf{M}\right)}{\text{Tr } \exp\left(\frac{1}{T} \mathbf{h} \mathbf{M}\right)} \quad (2)$$

It results in the relations:

$$T_c = \frac{\lambda \langle \mathbf{M}^2 \rangle}{3}, \quad (3)$$

where  $\lambda, \langle \mathbf{M}^2 \rangle$  are calculated at  $T = T_c$ . The parameter  $\lambda$  is connected with the energy of the local spin rotation:

$$E(\theta) = -\lambda M_0^2 \cos \theta \quad (4)$$

$M_0$  is the absolute value of the moment at the site 0 and  $\theta$  is the angle of spin rotations. Therefore one can obtain the relation:

$$\lambda = \frac{2J_0}{M_0^2}; \quad J_0 = \frac{1}{2} \cdot \frac{dE(\theta)}{d(1 - \cos \theta)} \Big|_{\theta=0}. \quad (5)$$

Here  $J_0$  is the effective exchange parameter (In the Heisenberg model with exchange integrals  $J_{ij}$  one has  $J_0 = \sum_j J_{0j}$ ). The substitution of (5) into equation (3) results in:

$$T_c = \frac{2J_0 \langle \mathbf{M}^2 \rangle}{3M_0^2} \quad (6)$$

the  $\langle \mathbf{M}^2 \rangle / M_0^2$  factor (which equals to  $(S + 1)/S$  in the Heisenberg model) takes into account the quantum nature of spin on the site given and has been introduced in [1, 4, 5] without rigorous justification.

The exchange parameter  $J_0$  can be determined directly from the results of electronic structure calculations by the Green function method. According to equation (5) one should calculate the variation of the total energy of a crystal during the small rotations of spin moment at the site 0. As a consequence of the "local force" theorem in the local spin density functional methods [6] the first variation of the total energy equals to variation of sum of one-electron energies derived from the fixed potential. In the scope of multiple-scattering Green-function method one obtain the following formula [2, 7]

$$\delta E = \frac{1}{\pi} \int_{-\infty}^{\epsilon_F} d\epsilon \text{Im Tr } \ln (1 - \Delta \cdot T) \quad (7)$$

where  $\epsilon_F$  — is the Fermi energy,  $\Delta = t^{-1} - \tilde{t}^{-1}$ , and  $t$ ,  $\tilde{t}$  — are the initial and final one-site scattering  $t$ -matrix.  $T$  is the scattering path operator, defined by the equation:

$$(T^{-1})_{LL'}^{ij} = t_{iL}^{-1} \delta_{ij} \delta_{LL'} - G_{LL'}^{ij} \quad (8)$$

here  $G$  is structure Green-function matrix. The single-site  $t$ -matrix has the following spinor structure form [2, 8]:

$$t_i = \frac{1}{2}(t_{\uparrow} + t_{\downarrow}) \cdot \hat{I} + \frac{1}{2}(t_{\uparrow} - t_{\downarrow})(\mathbf{e}_i \cdot \boldsymbol{\sigma}), \quad (9)$$

where  $\boldsymbol{\sigma}$ ,  $I$  — are Pauli and unit matrices,  $\mathbf{e}_i$  is the unit vector in the direction of magnetic moment at the site  $i$ . Under the conditions considered  $\mathbf{e}_0 = (\sin \theta, 0, \cos \theta)$ , and

$$\Delta_{ij} = \frac{1}{2} \delta_{i0} \delta_{j0} (t_{\uparrow}^{-1} - t_{\downarrow}^{-1}) \begin{pmatrix} 1 - \cos \theta & -\sin \theta \\ -\sin \theta & -1 + \cos \theta \end{pmatrix} \quad (10)$$

The insertion of the expression (10) into equation (7), (5) leads to the formula:

$$J_0 = -\frac{1}{4\pi} \int_{-\infty}^{\epsilon_F} d\epsilon \operatorname{Im} \operatorname{Tr}_L \{ t_{\uparrow}^{-1} - t_{\downarrow}^{-1} \} (T_{\uparrow}^{00} - T_{\downarrow}^{00}) + (t_{\uparrow}^{-1} - t_{\downarrow}^{-1})^2 T_{\uparrow}^{00} \cdot T_{\downarrow}^{00} \} \quad (11)$$

where  $\operatorname{Tr}_L$  — means the trace over the orbital variables. It is worth noting that  $J_0 = 0$  in the one-site case ( $T^{00} = t$ ).

It's worth mentioning that the method suggested is rather close to that proposed by Hubbard [9]. But in the difference from the latter we start from the LSDF approach take into account the peculiarities of the real electronic structure and use essentially the "local force" theorem which allows to obtain the rigorous expression for  $J_0$  parameter (11). In the paper [9] the dependence of  $E$  on  $\theta$  has been calculated numerically basing on the Hubbard model, but the closed expression for  $J_0$  has not been found.

In the Slater's magnetic transition state method [3] generalised for the metal case in [1] it is necessary to calculate the spin flip energy at the site given, which is reduced only approximately to the sum of one-electron energy differences in transition state, in contrast to the rigorous expression (11), which includes the characteristics of the ground state only. Besides, the consideration given above is applicable even for the case when the exchange parameter itself depends on the spin configuration, that is rather probable in the itinerant electron magnetism. In this case  $J_0$  should be calculated for the magnetically disordered state with the  $T^{00}$  found in the KKR-CPA treatment of paramagnetic state [2, 8]. Then the expression

$$T_{\sigma}^{00} = T^{00} [1 - (t^{-1} - t_{\sigma}^{-1}) T^{00}]^{-1}, \quad (12)$$

where  $\sigma = (\uparrow, \downarrow)$ , should be substituted into equation (11).

In the real calculations it is not difficult to include also the Fermi-distribution function [8], but in the case of iron the corresponding effects appear to be quite small [2].

We have applied the approach given to the ground state of the ferromagnetic iron and used the real-space Green-function method [10], where scattering path operator is obtained by means of direct inversion of equation (8) for the finite cluster of atoms. We have considered the  $\text{Fe}_{15}$  cluster, which includes the central atom and two coordination sphere atoms in bcc-lattice. The calculations were carried out using the Gunnarsson - Lundqvist [11] exchange-correlation potential.

Due to  $O_h$ -symmetry of cluster  $\text{Fe}_{15}$ , the trace over the orbital variables reduces to the sum over four irreducible representations:  $t_{2g}$  and  $e_g$  for  $d$ -states, and  $a_{1g}$ ,  $t_{1u}$  for  $s$ - and  $p$ -states of the central atom. The exchange parameter  $J_0$  from equation (11) contains the following contributions:  $J_{t_{2g}} = 27.53$  meV,  $J_{e_g} = 43.99$  meV,  $J_{a_{1g}} = -8.83$  meV,  $J_{t_{1u}} = -2.01$  meV (these values are not multiplied by the degeneration factors). It's worth noting, that  $t_{2g}$ - and  $e_g$ -electrons give approximately the same contributions to  $J_0$ , which is reasonable for the metallic bond;  $s$ - and  $p$ -contributions are rather small and have antiferromagnetic sign. The total exchange parameter for iron appears to be:  $J_0 = 155.71$  meV.

Unfortunately, the quantum factor  $\langle \mathbf{M}^2 \rangle / M_0^2$  in the formula (6) for  $T_c$  can't be rigorously calculated. As an estimate, we use the following expression [4]:

$$\langle \mathbf{M}^2 \rangle = \frac{g_s^2 \sum_{l=1}^5 W_l S_l (S_l + 1)}{\sum_{l=1}^5 W_l}, \quad (13)$$

where  $W_l$  is the probability to find  $l$  electrons from different  $d$ -subbands on a given site, which are not compensated by the electron spins from the same subbands [4],  $S = l/2$ . We have:

$$\begin{aligned} W_1 &= 3w_{t_{2g}} + 2w_{e_g} \\ W_2 &= 3w_{t_{2g}^2} + 6w_{t_{2g}} w_{e_g} + w_{e_g^2} \\ W_3 &= w_{t_{2g}^3} + 6w_{t_{2g}^2} w_{e_g} + 3w_{t_{2g}} w_{e_g^2} \\ W_4 &= 2w_{t_{2g}^3} w_{e_g} + 3w_{t_{2g}^2} w_{e_g^2} \\ W_5 &= w_{t_{2g}^3} w_{e_g^2}. \end{aligned} \quad (14)$$

Here  $w_{\alpha} = n_{\alpha\uparrow} + n_{\alpha\downarrow} - 2n_{\alpha\uparrow}n_{\alpha\downarrow}$ ,  $n_{\alpha\sigma}$  — is the average occupation number of the state  $\alpha = (t_{2g}, e_g)$ .

Using the results of our  $\text{Fe}_{15}$ -cluster calculation we have  $\langle \mathbf{M}^2 \rangle / M_0^2 = 1.77$ , which is rather close to the value

$(S + 1)/S$  for  $S = 1$ . Then the Curie temperature as calculated from equation (6) appears to be  $T_c = 2130$  K (the experimental value is  $T_c(\text{Fe}) = 1043$  K). The agreement is reasonable but not impressive. To improve such an agreement between the theoretical and experimental  $T_c$  values one should carry out KKR-CPA calculations for paramagnetic iron [2, 8] and use the equation (12) for  $T^{00}$ . Such calculations are in progress.

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