

---

<https://doi.org/10.15407/ujpe66.6.503>

YU.G. SEMENOV,<sup>1</sup> S.M. RYABCHENKO<sup>2</sup>

<sup>1</sup> V.E. Lashkaryov Institute of Semiconductor Physics, Nat. Acad. of Sci. of Ukraine  
(41, Prosp. Nauky, Kyiv 03680, Ukraine)

<sup>2</sup> Institute of Physics, Nat. Acad. of Sci. of Ukraine  
(46, Prosp. Nauky, Kyiv 03028, Ukraine)

## MOLECULAR-FIELD APPROXIMATION IN THE THEORY OF FERROMAGNETIC PHASE TRANSITION IN DILUTED MAGNETIC SEMICONDUCTORS

---

*In this pedagogical paper, the comparative analysis of two common approaches describing the ferromagnetic phase transition in diluted magnetic semiconductors (DMS) is expounded in terms of the Weiss field approximation. Assuming a finite spin polarization of the magnetic ions, the treatment of carrier-ion exchange interaction in the first order evokes a homogeneous Weiss molecular field that polarizes the spins of free carriers. In turn, this spin polarization of the free carriers exerts the effective field that may stabilize the DMS spin polarization below a critical temperature  $T_C$ . The treatment of such self-consistent spontaneous DMS magnetization can be done in terms of the spin-spin interaction independent of the inter-ion distance and the infinitesimal in thermodynamic limit. On the other hand, by additionally accounting for the second-order effects of the carrier-ion exchange interaction, we can treat a Weiss field in terms of the Ruderman–Kittel–Kasuya–Yosida indirect spin-spin interaction, which oscillates and does not disappear at finite inter-ion distances in the case of a finite concentration of carriers. These both approaches result in the same Curie temperature  $T_C$  provided a non-correlated homogeneous random distribution of the localized spin moments over the sample volume. We discuss the origin of such coincidence and show when this is not a case in other more realistic models of the conducting DMSs.*

*Keywords:* diluted magnetic semiconductors, ferromagnetic ordering, mean-field approximation, RKKY interaction.

### 1. Introduction

The carrier-ion exchange interaction (CIEI) triggered a train of unusual electronic phenomena in diluted magnetic semiconductors (DMS) like the  $A_{1-x}Mn_xB$  – compounds, where AB denotes II–VI or III–V semiconductors [1, 2]. Soon after the discovery of the giant spin splitting of the exciton spectra in the pioneer paper [1], the ferromagnetic (FM) phase transition accompanied by the mutual spin polarization of

band carriers and localized spin moments (LSMs) in DMS was predicted [3]. That paper had shown how to convert the CIEI of spin polarized LSM to the Weiss molecular field, which polarizes the spins of free carriers (electrons or holes). They, in turn, serve as a source of the exchange field capable to stabilize a finite magnetic moment of LSMs at a certain temperature. The approach of Ref. [3] predicts the FM phase transition with the simultaneous arising of the spontaneous magnetization for subsystems of both the LSMs and the carriers (i.e. electrons and/or

holes). Their mutual directions of spin polarizations depend on the sign of CIEI that is generally different for electrons and holes.

Similarly to works [4, 5], where a modeling of the carriers-induced ferromagnetism through the CIEI was developed for the first time to describe the ferromagnetism of transition metals, the formalism of Ref. [3] involves an additional effect of the ion-ion spin-spin interaction with exchange constants  $J_{mm}(\mathbf{R}_{j1}, \mathbf{R}_{j2})$ , where  $\mathbf{R}_{j1}, \mathbf{R}_{j2}$  are the radii-vectors of the corresponding magnetic ions. In Ref. [3], it was supposed that the effective indirect RKKY [6–8] ion-ion exchange interaction through the carriers could be added to the contributions of  $J_{mm}(\mathbf{R}_{j1}, \mathbf{R}_{j2})$ . This not entirely correct assumption, as well as the discussion presented in the rest of that paper, was not accompanied by a more thorough theoretical analysis [8, 9]. Moreover, all estimations in [3] were carried out in the limit  $J_{mm} \rightarrow 0$ . Consequently, the approach of Ref. [3] allows one to correctly estimate the range of Curie temperatures  $T_C$  for actual magnetically doped semiconductors in the first-order perturbation only.

The formalism developed in Refs. [4, 5] and Ref. [3] treats CIEI in the first order of perturbation theory, which evaluates only corrections to the energy of interacting particles, while it cannot account for the effects of electron (hole) scattering with a changing of their wave vectors. That is why a number of authors use the lexis “direct carrier-ions exchange interaction” to indicate CIEI in the first order of perturbation theory. In this approach, the Weiss field generated by one LSM via free carriers affects another spins regardless the inter-ion distance. At one time, this circumstance caused a lively scientific discussion (see Refs [8] and [9]). Let us also mention that the formalism described above involves no modification of the LSM-LSM exchange interaction due to CIEI.

An alternative approach to this problem treats the free carriers as a mediator of the indirect interaction between pairs of localized spins. Such interaction is usually cited as the Ruderman–Kittel–Kasuya–Yosida (RKKY) [6–8] indirect spin-spin interaction. The standard procedure presumes evaluating the energy of the indirect interaction in the second order of perturbation theory that mixes the electronic states with different wave vectors  $\mathbf{k} \neq \mathbf{k}'$ , but excludes the case  $\mathbf{k} = \mathbf{k}'$ . Accordingly, the spin-dependent second-order correction to the energy oscillates with the distance between spin locations. Note, however, that the

actual RKKY-procedure also implicitly involves the contribution of singular points  $\mathbf{k} = \mathbf{k}'$  for the scattering without wave vector changing. That contribution was shown to coincide with first-order effects of the spin-spin interaction [8,9]. Thus, the RKKY indirect spin-spin interaction may lead to FM correlations and phase transition calculated in terms of the first and second orders of perturbation theory.

The FM phase transitions in DMS were first observed in IV-Mn-VI compounds [10] and were explained in terms of the RKKY interactions. Surprisingly, the Weiss molecular field calculated in the first order of perturbation theory [3] and in terms of the sum of RKKY spin-spin interactions results in the same expression in the case of random non-correlated distribution of the magnetic ions. Based on this particular statement, the identity of both approaches became a conventional wisdom [11]. In other words, the Curie temperature evaluated in the first order of CIEI supposes to be not refined with adding the second-order effects of the RKKY interaction. This also means that the second-order effect represented by the sum over scattered electrons/holes with  $\mathbf{k} \neq \mathbf{k}'$  does not contribute to the energy of spins in the Weiss field under a random non-correlated distribution of the magnetic ions.

Nevertheless, in contrast to the common standpoint, the testing of this assumption for the exactly solvable model of flat energy bands reveals the complementary contributions of the “direct” (first order) and “indirect” (second order) interactions to the critical temperature of the FM phase transition [12]. The intrigue of this antinomy was strengthened by the works [13, 14] demonstrated a significant discrepancy of the mean-field [3] and RKKY treatments in the more advanced approximation of random fields. However, the problem how a more realistic approximation of the band structure than the dispersionless one [12] would modify the Weiss molecular field still remains an actual problem of the theory of FM phase transition in disordered magnetic systems. Below, we present the analysis of this problem in terms of the effective fields mediated by CIEI in the first and second orders separately. In particular, we show that the second-order correction to the Weiss field becomes zero provided only a non-correlated equiprobable LSM distribution up to infinitesimal inter-ion distances. Moreover, in contrast to such free gas modeling of the LSM distribution, the irremovable lim-

itation of the minimal inter-ion distance by the lattice constant may visibly correct the estimation of the critical temperature in DMS.

Note that the giant spin splitting observed in the DMS band structure is usually treated in the first order in CIEI. This approach does not involve oscillations of the spin density of charge carriers around the LSM depending on the distance to it. On the other hand, such oscillations may be important in other phenomena. For example, RKKY-like oscillations of the effective spin-spin interaction are responsible for the non-monotonic dependence of the exchange interaction between FM layers on thickness of the non-magnetic spacer between them [15–18].

## 2. Weiss Field in the First-Order Approximation

For the sake of definiteness, let us consider a DMS with the degenerate gas of free carriers, electrons or holes, in a simple energy band accounting for the isotropy dispersion law with an effective mass  $m^*$ . Moreover, to focus only on the effects of CIEI, the direct spin-spin interactions not related to free carriers will be omitted. This simplification merely corresponds to the model developed in Ref. [3] provided nulling the direct spin-spin interaction. The Hamiltonian for the carrier-ion exchange interaction takes the form of a contact interaction between electrons with spin-space coordinates  $\mathbf{s}_i \mathbf{r}_i$  and  $N_m$  magnetic ions with spins  $\mathbf{S}_j$  situated at the lattice sites  $R_j$ :

$$\hat{H}_{L,e} = -\beta \sum_i \sum_j \mathbf{S}_j \mathbf{s}_i \delta(\mathbf{r}_i - \mathbf{R}_j). \quad (1)$$

The constant of CIEI  $\beta N_0$ , where  $N_0$  is the concentration of primitive cells (number of primitive cells divided by the volume), and  $\beta$  is the calculation parameter with dimension of energy multiplied by the volume. The value of  $\beta N_0$  achieves a sufficient magnitude in the valence bands of most DMSs up to 1 eV and even more [19]. The exchange integral, which follows from (1), depends on both crystal and magnetic ion parameters. The correspondent spin-Hamiltonian stems from Eq. (1) after averaging the  $\delta(\mathbf{r}_i - \mathbf{R}_j)$  on the carrier coordinate wave function  $\Psi(\mathbf{r})$ . The latter represents a standard Bloch function normalized to the crystal volume  $V$ , if the CIEI (1) does not sufficiently disturb the electronic states. The necessary condition for this approximation corresponds to the smallness of the parameter  $\varepsilon = \beta N_0/W$ , where  $W$  is a

relevant bandwidth [20]. Below, this parameter is assumed to be small, and the Bloch functions become a good zero-order approximation for the electron/hole states in DMS. One should note that, in such case, the exchange integral for one carrier with one LSM,  $J_{1,1}$ , is

$$J_{1,1} = \beta/V. \quad (1a)$$

If the carrier is localized in some part of the crystal, for instance, the electron of a neutral donor or a carrier in the case of magnetic polaron formation, the exchange integral of one carrier with one LSM may be enhanced sufficiently due to a growth of the carrier density on the LSM in the decreased localization volume.

If one will neglect spin fluctuations of LSM, Eq. (1) represents the Zeeman energy of electrons in the homogeneous Weiss field of magnetic ions ( $m$ ) acting on the carrier (let it be an electron ( $e$ )) spins:

$$\mathbf{B}_{e/m} = \frac{\beta n_m \langle \mathbf{S}_m \rangle}{g_e \mu_B}, \quad (2)$$

where  $n_m$ ,  $g_e$  and  $\mu_B$  are the LSM concentration, electron g-factor and Bohr magneton, respectively.

On the other hand, CIEI (1) can be transformed to the Zeeman energy of the magnetic ions affected by the exchange field of the electrons with the mean value  $\langle \mathbf{s}_e \rangle$  of the spin polarization,

$$\mathbf{B}_{m/e} = \frac{\beta n_e \langle \mathbf{s}_e \rangle}{g_m \mu_B}, \quad (3)$$

where  $g_m$  is the LSM g-factor, and  $n_e$  is the electron concentration.

Equations (2) and (3) look like the complete system of equations with respect to effective fields, if one takes the following relations into account:

$$\langle \mathbf{S}_m \rangle = -\chi_m^{(1)} \frac{\mathbf{B}_{m/e}}{g_m \mu_B} \quad (4)$$

and

$$\langle \mathbf{S}_e \rangle = -\chi_e^{(1)} \frac{\mathbf{B}_{e/m}}{g_e \mu_B}, \quad (5)$$

where the LSM susceptibility  $\chi_m^{(1)}(\mathbf{B}_{m/e})$  per one LSM is a function of  $\mathbf{B}_{m/e}$  and the temperature  $T$ , and  $\chi_e^{(1)} = (3/8)g_e^2 \mu_B^2 / \varepsilon_F$  is the susceptibility per one particle of degenerate electrons with the Fermi energy  $\varepsilon_F$ .

The equation for the critical temperature  $T_C$  of the appearance of a spontaneous magnetization represents the case of infinitesimal exchange fields  $\mathbf{B}_{m/e}$

and  $\mathbf{B}_{e/m}$  in Eqs (4) and (5). Thus, to find  $T_C$ , we should replace the  $\chi_m^{(1)}(\mathbf{B}_{m/h})$  by the zero-field susceptibility  $\chi_m^{(1)}(0)$ . In the simplest case of magnetic ions interacting only via band carriers, a solution of the correspondent equation takes the form [12]:

$$T_C = \frac{S(S+1)}{3} \beta^2 n_m n_e \frac{\chi_e^{(1)}}{g_e^2 \mu_B^2} = \frac{S(S+1)}{8} \frac{\beta^2 n_m n_e}{\varepsilon_F}. \quad (6)$$

Hereinafter, the temperature  $T$  is expressed in energy units.

This equation can be derived in different manners useful for the following analysis. Let us write down the Hamiltonian with the Zeeman energy  $\hat{H}_{\text{Zeem}}^{\text{eff}} = g_m \mu_B \mathbf{B}_{m/e} \sum_j \mathbf{S}_j$  of the magnetic ions in the effective magnetic field [Eq. (3)] of conducting electrons. Then the substitution of Eq. (5) to Eq. (3) transforms the Zeeman Hamiltonian to

$$\hat{H}_{\text{Zeem}}^{\text{eff}} = -\beta^2 n_m n_e \frac{\chi_e^{(1)}}{g_e^2 \mu_B^2} \langle \mathbf{S}_m \rangle \sum_j \mathbf{S}_j. \quad (7)$$

The last equation clearly shows that the Hamiltonian  $\hat{H}_{\text{Zeem}}^{\text{eff}}$  is nothing but the Weiss-field approximation of the Hamiltonian of the pair spin-spin interaction of  $N_m$  LSMs diluted in a sample of volume  $V$ :

$$\hat{H}_{SS}^{(1)} = -\frac{1}{V} \frac{\beta^2 n_e \chi_e^{(1)}}{2g_e^2 \mu_B^2} \sum_{j,j' (j \neq j')} \mathbf{S}_j \mathbf{S}_{j'}. \quad (8)$$

These equations define the Weiss (or molecular) field

$$\mathbf{B}_W^{(1)} = -\beta^2 \frac{n_m n_e}{g_m \mu_B} \frac{\chi_e^{(1)}}{g_e^2 \mu_B^2} \langle \mathbf{S}_m \rangle, \quad (9)$$

that uniformly affects each LSM. Superscript “(1)” on the left-hand sides of Eqs. (8) and (9) indicate that these values are valid in the first order of perturbation theory in terms of the unperturbed electron eigenfunctions. The factor 1/2 in Eq. (8) reflects the fact that each pair of spins in the sum over  $j$  and  $j'$  is twice accounted.

It would be instructive to show another derivation of Eq. (8). It originates from the definition of a homogeneous mean field induced by the ensemble of LSMs in the operator representation  $\hat{\mathbf{B}}_{e/m} = \frac{\beta}{g_e \mu_B} \frac{1}{V} \sum_j \mathbf{S}_j$ . This field reduces the magnetic energy of the free carriers to the standard form

$$\hat{H}_{SS}^{(1)} = -\frac{1}{2} V \chi_{\text{Pauli}} \hat{\mathbf{B}}_{e/m}^2, \quad (10)$$

that is, just Eq. (8) provided the Pauli susceptibility of an electron gas is  $\chi_{\text{Pauli}} = n_e \chi_e^{(1)}$ .

Equation (10) establishes an effective spin-spin interaction independent of the inter-ion distance. Moreover, it becomes infinitesimal in the thermodynamic limit  $V \rightarrow \infty$  for any pair of spins that keeps a finite value of the Weiss field in the thermodynamic limit  $N_m \rightarrow \infty$  under  $n_m = \text{const}$ , as mentioned above. This result arises in the first order of perturbation theory that treats CIEI (1) in terms of the undisturbed electron wave functions. Nevertheless, the finite critical temperature (6) follows from the Weiss field approximation of Eq. (8) provided the finite LSM concentration  $n_m = N_m/V$ .

### 3. RKKY Interaction

An alternative approach to the FM phase transition stems from the CIEI transforming to an indirect LSM spin-spin interaction mediated by free carriers in the second order of perturbation theory:

$$\hat{H}_{SS}^{(2)} = \frac{\beta^2}{V^2} \sum_{\sigma, \sigma'} \sum_{\mathbf{k}, \mathbf{k}' = (k' \neq k)} \frac{f(\varepsilon_{\mathbf{k}})(1 - f(\varepsilon_{\mathbf{k}'}))}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}} \times \sum_{j, j' (j \neq j')} \mathbf{e}^{i(\mathbf{k} - \mathbf{k}')(\mathbf{R}_j - \mathbf{R}_{j'})} (\sigma | \mathbf{S}_j \mathbf{s}_e | \sigma') (\sigma' | \mathbf{S}_{j'} \mathbf{s}_e | \sigma), \quad (11)$$

where  $f(\varepsilon_{\mathbf{k}})$  is the Fermi–Dirac distribution function, and the normalizing factor  $V^{-2}$  appears in the calculation of a matrix element with Bloch functions of the band electrons.

Accounting for the identity for the trace over the spin variable  $\sigma$ ,  $\text{Tr}_{\sigma}(\mathbf{S}_j \mathbf{s}_e)(\mathbf{S}_{j'} \mathbf{s}_e) = 1/2 \mathbf{S}_j \mathbf{S}_{j'}$  and rearranging the  $\mathbf{k}$  and  $\mathbf{k}'$  in Eq. (11), we obtain:

$$\hat{H}_{SS}^{(2)} = \frac{\beta^2}{4V^2} \sum_{\mathbf{k}, \mathbf{k}' = (k' \neq k)} \frac{f(\varepsilon_{\mathbf{k}}) - f(\varepsilon_{\mathbf{k}'})}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}} \times \sum_{j, j' (j \neq j')} \mathbf{e}^{i(\mathbf{k} - \mathbf{k}')(\mathbf{R}_j - \mathbf{R}_{j'})} \mathbf{S}_j \mathbf{S}_{j'}. \quad (12)$$

The procedure in the second order of perturbation theory implies to eliminate the points  $\mathbf{k}' = \mathbf{k}$  from the sum in Eq. (12)<sup>1</sup>. Nevertheless, to restore the analyticity of the integrand arising as a result of the integral representation of the sums over  $\mathbf{k}'$ , expression (12) should be supplemented with the limit  $\mathbf{k}' \rightarrow \mathbf{k}$ , as it

<sup>1</sup> Other exclusive points  $\mathbf{k}' \neq \mathbf{k}$  at  $|k'| = |k|$  are not actual, since the exponent  $\exp[i(\mathbf{k} - \mathbf{k}')\mathbf{R}_j]$  nullifies their contribution.

was stressed in the original work by Yosida [8]. Being applied to the fraction in Eq. (12), this limit produces  $-\delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\text{F}})$ , where  $\varepsilon_{\text{F}}$  is Fermi energy. Then the straightforward calculations yield the expression of the additive to Eq. (12) due to such treatment of  $\mathbf{k} \neq \mathbf{k}'$  in sum (12) in the form:

$$\delta \hat{H}_{SS}^{(2)} = \frac{\beta^2}{4V} D(\varepsilon_{\text{F}}) \sum_{j,j'(\neq j)} \mathbf{S}_j \mathbf{S}_{j'} = \frac{\beta^2 n_e \chi_e^{(1)}}{2V g_e^2 \mu_{\text{B}}^2} \sum_{j,j'(\neq j)} \mathbf{S}_j \mathbf{S}_{j'}, \quad (13)$$

where  $D(\varepsilon_{\text{F}}) = 3n_e/4\varepsilon_{\text{F}}$  is the electron density of states of each spin branch at the Fermi surface. The comparison of  $\delta \hat{H}_{SS}$  with Eq. (8) shows that the integrand in the integral approximation of the sums on  $\mathbf{k}$  and  $\mathbf{k}'$  in Eq. (12) is transformed to a smooth analytic function by adding the first-order Hamiltonian  $\hat{H}_{SS}^{(1)} = \delta \hat{H}_{SS}$  to the effective Hamiltonian representing the spin-spin interaction in the second order  $\hat{H}_{SS}^{(2)}$ . The calculation of these integrals in the usual manner reproduces the common expression for the RKKY interactions:

$$\hat{H}_{\text{RKKY}} = \hat{H}_{SS}^{(1)} + \hat{H}_{SS}^{(2)} = \frac{1}{2} \sum_{j,j'(\neq j)} J_{\text{RKKY}}(\mathbf{R}_{j,j'}) \mathbf{S}_j \mathbf{S}_{j'}, \quad (14)$$

where the effective constant of the indirect interaction between the ions distanced on  $\mathbf{R}^{j,j'}$  is

$$J_{\text{RKKY}}(\mathbf{R}^{j,j'}) = \frac{2\beta^2 k_{\text{F}}^{(3)} \chi_{\text{Pauli}}}{\pi g_e^2 \mu_{\text{B}}^2} F_{\text{RKKY}}(2k_{\text{F}} R_{j,j'}) \quad (15)$$

and

$$F_{\text{RKKY}}(x) = \frac{x \cos x - \sin x}{x^4}. \quad (16)$$

Equation (14) along with definitions (15) and (16) is usually called ‘‘indirect RKKY exchange interaction’’. Each term  $J_{\text{RKKY}}(\mathbf{R}_{j,j'}) \mathbf{S}_j \mathbf{S}_{j'}$  in sums (14) corresponds to a finite pair spin-spin interaction. For this reason, coefficient 1/2 guarantees that each pair is accounted for once.

Expression (15) is obtained for degenerate electrons or holes and is not applicable to the single carrier case. However, Eq. (1a) reflects the dependence of the CIEI exchange constant on the density of carriers at a single LSM. The actual dependence of  $k_{\text{F}}$  and  $\chi_{\text{Pauli}}$  on carriers’ concentration  $n_e$  establishes the inverse proportionality of the prefactor of  $F_{\text{RKKY}}(x)$  in (15) to carriers’ density in power 4/3. Therefore, the enlargement of the crystal volume  $V$  at a fixed number

of carriers diminishes the  $J_{\text{RKKY}}$  as  $1/V^{4/3}$  that resembles Eq. (1a).

It should be emphasized that the second order for the indirect interaction in the form of Eq. (14) provides a finite strength of the effective exchange interaction (15) for any finite inter-ion distance  $|R_{j,j'}|$  in the case of finite carriers’ concentration. From this standpoint, addition (13) to Hamiltonian (12) in the first-order form (8) does not modify this interaction in the limit  $V \rightarrow \infty$  at  $n_e = \text{const}$ , because  $\hat{H}_{SS}^{(1)} \xrightarrow{V \rightarrow \infty} 0$ . Nevertheless, this conclusion fails, if we turn from the local (intensive) individual LSM magnetic property to thermodynamic (extensive) properties that characterize the phase state in the entire system. As has been shown, the thermodynamic limit does not nullify the molecular field stemmed from the Hamiltonian  $H_{SS}^{(1)}$  (5) provided a finite concentration  $n_m$ . Therefore, we should expect additive contributions to thermodynamic potentials stemmed from the first and second orders of the Hamiltonians  $\hat{H}_{SS}^{(1)}$  and  $\hat{H}_{SS}^{(2)}$ <sup>2</sup>. In particular, the exactly solvable model for a spin cluster [12] confirms this general result.

#### 4. RKKY Modeling of the Phase Transition

Let us consider the critical temperature of the FM phase transition calculated for the RKKY interaction in the Weiss field approximation. The latter imposes the equal mean values  $\langle \mathbf{S}_j \rangle = \langle \mathbf{S}_{j'} \rangle$  for all LSMs so that Weiss field

$$\mathbf{B}_{\text{W}} = \frac{1}{g_m \mu_{\text{B}}} \sum_{j'} J_{\text{RKKY}}(\mathbf{R}_{j,j'}) \langle \mathbf{S}_{j'} \rangle \quad (17)$$

evenly polarizes each magnetic ion. The resulting spin polarization can be found in terms of the Brillouin function  $B_S$  as  $\langle S \rangle = -SB_s(g_m \mu_{\text{B}} B_{\text{W}} B/T)$ . The last equation evaluates the critical temperature of the FM phase transition: as

$$T_{\text{C}} = \frac{1}{3} S(S+1) \sum_{j'} J_{\text{RKKY}}(\mathbf{R}_{j,j'}). \quad (18)$$

Assuming a random LSM distribution with constant density  $n_m$ , the integral representation of the sum over  $j'$  reads

$$\sum_{j'} J_{\text{RKKY}}(\mathbf{R}_{j,j'}) \rightarrow n_m \int_0^{\infty} J_{\text{RKKY}}(r) 4\pi r^2 dr. \quad (19)$$

<sup>2</sup> We recall that RKKY in the integral form just involves the contributions of both first and second orders of perturbation theory.

The substitution of this approximation into Eq. (18) reproduces expression (6) for the Curie temperature obtained in the first order of perturbation theory. Obviously, applying another approximation for LSM distribution (such as a lattice gas or correlated LSM dispensation) will violate the identity of Eqs (18) and (6).

To clarify such coincidence, let us go back to Eq. (11) and treat it as the energy of spin  $\mathbf{S}_j$  in the Weiss effective field

$$\mathbf{B}_W^{(2)} = \frac{\beta^2}{2g_m\mu_B V^2} \sum_{\mathbf{k}, \mathbf{k}' (\neq \mathbf{k})} \frac{f(\varepsilon_{\mathbf{k}}) - f(\varepsilon'_{\mathbf{k}'})}{\varepsilon_{\mathbf{k}} - \varepsilon'_{\mathbf{k}'}} \times \sum_{j, j' (\neq j)} e^{i(\mathbf{k}-\mathbf{k}')(\mathbf{R}_j - \mathbf{R}_{j'})} \langle \mathbf{S}_{j'} \rangle. \quad (20)$$

The independence of  $\langle \mathbf{S}_j \rangle = \langle \mathbf{S} \rangle$  of the specific spin location immediately simplifies the summation over  $j'$ . If the ideal gas models the magnetic ion distribution over the crystal, the sum over  $j'$  yields a non-zero result only for  $\mathbf{k} = \mathbf{k}'$  that, in turn, nullifies  $\mathbf{B}_W^{(2)}$ . This result demonstrates that the conventional utilization of a homogeneous distribution of magnetic ions results in the exclusion of the second order of perturbation theory. On the other hand, supplementing the singularity at  $\mathbf{k} = \mathbf{k}'$  with the limit  $\mathbf{k} \rightarrow \mathbf{k}'$  reproduces the  $\mathbf{B}_W^{(1)}$  (12) that is virtually included to  $\mathbf{B}_W^{(2)}$ . This means that  $\mathbf{B}_W^{(1)}$  (12) should be not taken into account once again as an independent contribution to the Weiss field (19). Thus, a simple evaluation of  $T_C$  in the first approximation (8) turns out equivalent to a more complicated summation of the spin-spin RKKY interactions over the locations of magnetic ions in the crystal.

However, our approach can be applicable to a more realistic LSM distribution, which is not equivalent to a constant probability independent of the lattice structure. As the first obvious generalization, let us consider the lattice gas approximation rather than the free gas model. The simplest way to estimate the effect of a lattice gas distribution consists in the explicit limitation of the minimal inter-ion distance  $d$ . At larger distances, the constant probability, proportional to the concentration  $n_m$  still approximates the discrete distribution function over the lattice sites. Such elaboration diminishes the strength of the molecular field by the factor  $\delta = \frac{4\pi}{3} n_m d^3$  provided  $k_F d \ll 1$ . This correction may be not too small compared with 1. For example, in DMS with the zinc

blende lattice, the short-range space correlation modifies expression (8) for the Curie temperature by the factor  $1 - \frac{\sqrt{2\pi}}{3} x$  that reduces  $T_C$  by 15% at the LSM substitution level  $n_m \Omega = x = 10\%$  ( $\Omega$  is the volume of a semiconductor primitive cell). Apparently, the same result is produced by the RKKY approach, Eq. (14), provided the integration over the reduced domain  $(d, \infty)$  takes the space correlations in Eq. (20) into account.

Another non-trivial example discloses the case of approximate estimation of  $T_C$  based on decreasing RKKY's interaction strength (15) for the remote LSMs. This diminishing interaction also results in decreasing the collective effect of the remote LSMs to the Weiss field. The latter can be evaluated using the RKKY interaction of some LSM located at the  $\mathbf{R}_j$  site with a finite number of LSMs surrounding  $\mathbf{R}_j$  [10]. In such case, the contribution of the first order (8), (13) vanishes assuming a large crystal volume and a finite number  $N_{m'}$  of LSMs located at lattice sites  $\mathbf{R}_{j'}$  inside an allotted volume  $V'$  which maintains the concentration  $n_m = N_{m'}/V'$ . Thus, the account for the finite number of LSMs might approximately evaluate the Weiss field in terms of Eq. (20) derived in the second order in CIEI. The appearance of a non-zero effect of Eq. (20) looks not surprising, since the summation over the limited numbers  $\mathbf{R}_j$  in a finite volume  $V'$  admits the finite contributions of the wave vectors that lie beyond the specific electronic states with  $k = k'$ . Then the estimation of  $T_C$  assumes applying  $\mathbf{B}_W^{(2)}$  to all LSMs in the whole crystal. The detailed analysis of the Weiss field  $\mathbf{B}_W^{(2)}$  in an LSM cluster embedded into a large crystal is beyond the scope of this paper. Note, however, that a cluster with  $N_{m'}$  LSMs in a volume  $V'$  mimics the actual DMS with a fixed LSM concentration  $n_m$ , where the Weiss field is  $\mathbf{B}_W^{(1)}$ . Such intuitive approach supposes that  $\mathbf{B}_W^{(2)}$  well approximates  $\mathbf{B}_W^{(1)}$  at large enough  $V'$ . The correctness of such approximation is estimated by a deviation of the integral in Eq. (19) from that calculated for the finite upper limit  $2k_F(V')^{1/3}$ . As seen, either consideration does not assume the interference of  $\mathbf{B}_W^{(2)}$  and  $\mathbf{B}_W^{(1)}$  for the Weiss field evaluation.

A more accurate estimation of the  $T_C$  supposes incorporating an inter-ion exchange interaction not related to band carriers to the formalism developed above. This interaction of the antiferromagnetic (AFM) type inside of the nearest neighboring pairs

of LSMs may exceed the effect of the carrier-induced exchange field, and thermal energy  $T$  (as it was mentioned earlier,  $T$  is expressed in energy units) and establishes their total zero spin moments. As a result, such nearest neighboring LSMs are omitted that appears as the effective LSM density  $x' < x$  [21]. Introducing the phenomenological parameter  $x'$  improves the matching of experimental data and calculations for the spin splitting of exciton spectra. Such approximation of the AFM inter-ion interaction is also clearly applicable to the consideration of the magnetic (including FM) properties of DMS in terms of the Weiss field calculated in the first order. Nevertheless, the exclusion of AFM pairs from consideration enhances a deviation of the actual LSM distribution from the ideal gas model along with a consequent difference of the results obtained in the second-order approximation with ones, where the mean field is treated in the first order [3–5].

## 5. Conclusions

This paper clearly demonstrates that the molecular field approximation applied to the second-order expression of the LSM indirect interaction in the form of the sum of exponentials (12) reveals the nulling of this contribution for all electronic states with wave vectors  $\mathbf{k} \neq \mathbf{k}'$  provided a free gas modeling of the LSM distribution. The points  $\mathbf{k} = \mathbf{k}'$  must be excluded in the formalism of the second order of perturbation theory. On default, however, these exclusive states commonly append to the formalism presuming the limit  $\mathbf{k} \rightarrow \mathbf{k}'$  evaluates the effect that does not depend on the locations of magnetic ions. From this standpoint, the space averaging of the RKKY interaction (16) results in its homogeneous part, which appears as a supplement to the indirect interaction in the limit  $\mathbf{k} \rightarrow \mathbf{k}'$  coinciding with the effective Hamiltonian (8) of the first-order interaction. In other words, the molecular field treatment of the RKKY interaction produces the same result that can be obtained by considering only the first order in CIEI. However, this is not the case for more advanced theories that involve a randomizing of the local exchange fields at particular LSM locations [14, 15] or utilize a dispersionless band structure [13], which violates the smallness of the exchange constant  $\beta N_0$  compared to the bandwidth  $W \rightarrow 0$ .

In addition, the present paper appends the previous analyzes with particular second-order effects

stemmed from the difference of the lattice gas and ideal gas distributions for LSM in DMS.

*The participation of SMR in this work was partly supported by project II-05-20. No. 11 of the Physics & Astronomy Department of the NAS of Ukraine for the support of the researches priority for the state.*

1. A.V. Komarov, S.M. Ryabchenko, O.V. Terletsii, I.I. Zheru, R.D. Ivanchuk. Magneto-optical studies and the double opticomagnetic resonance of the exciton band in  $\text{Mn}^{2+}$ -doped CdTe. *JETP* **46**, 318 (1977), [translate from *Zh. Exp. Teor. Fiz.* **73**, 608 (1977)].
2. *Introduction to the Physics of Diluted Magnetic Semiconductors*. Edited by J. Kossut, J.A. Gaj (Springer, 2010).
3. E.A. Pashitskii, S.M. Ryabchenko. Magnetic ordering in semiconductor with magnetic impurities. *Sov. Phys. Solid State* **21**, 322 (1979).
4. C. Zener. Interaction between the  $d$ -shells in the transition metals. *Phys. Rev.* **81**, 440 (1951).
5. C. Zener. Interaction between the  $d$ -shells in the transition metals. III. Calculation of the Weiss factors in Fe, Co, and Ni. *Phys. Rev.* **83**, 299 (1951).
6. M.A. Ruderman, C. Kittel. Indirect exchange coupling of nuclear magnetic moments by conduction electrons. *Phys. Rev.* **96**, 99 (1954).
7. T. Kasuya. A theory of metallic ferro- and antiferromagnetism on Zener's model. *Progress of Theoretical Physics* **16**, 45 (1956).
8. K. Yosida. Magnetic properties of Cu–Mn alloys. *Phys. Rev.* **106**, 893 (1957).
9. J.H. Van Vleck. Note on the interactions between the spins of magnetic ions or nuclei in metals. *Rev. Mod. Phys.* **34**, 681 (1962).
10. T. Story, G. Karczewski, L. Swierkowski, R.R. Galazka. Magnetism and band structure of the semimagnetic semiconductor Pb–Sn–Mn–Te. *Phys. Rev. B* **42**, 10477 (1990).
11. T. Dietl, H. Ohno. Dilute ferromagnetic semiconductors: Physics and spintronic structures. *Rev. Mod. Phys.* **86**, 187 (2014).
12. Y.G. Semenov, S.M. Ryabchenko. Exactly solvable model for carrier-induced paramagnetic-ferromagnetic phase transition in diluted magnetic semiconductors. *Physica E* **10**, 165 (2001).
13. Y.G. Semenov, V.A. Stephanovich. Suppression of carrier-induced ferromagnetism by composition and spin fluctuations in diluted magnetic semiconductors. *Phys. Rev. B* **66**, 075202 (2002).
14. Y.G. Semenov, V.A. Stephanovich. Enhancement of ferromagnetism in uniaxially stressed dilute magnetic semiconductors. *Phys. Rev. B* **67**, 195203 (2003).
15. P. Grunberg, R. Schreiber, Y. Pang, U. Walz, M.B. Brodsky, H. Sowers. Layered magnetic structures: Evidence for antiferromagnetic coupling of Fe layers across Cr interlayers. *J. Appl. Phys.* **61**, 3750 (1987).
16. M. Getzlaff. *Fundamentals of Magnetism* (Section 15.1 Interlayer Exchange Coupling (IEC) Across a Non-Magnetic Spacer Layer) (Springer, 2008) [ISBN: 978-3-540-31152-2].

17. P.J.H. Bloemen. Interlayer exchange coupling and giant magnetoresistance in magnetic multilayers. *Acta Physica Polonica A*, **89**, 277 (1996).
18. F. Stobiecki, T. Lucicski, R. Gontarz, M. Urbaniak. Influence of the annealing process on the gmr effect in permalloy/copper multilayers. *Materials Science Forum* **287–288**, 513 (1998).
19. Y.G. Semenov, V.G. Abramishvili, A.V. Komarov, S.M. Ryabchenko. Magneto-optical investigations of diluted  $Cd_{1-x}Mn_xS$  magnetic semiconductors in the B-excitation region. *Phys. Rev. B* **56**, 1868 (1997).
20. S.M. Ryabchenko, Yu.G. Semenov, O.V. Terletski. Exchange-scattering effects on band energies in magnetically mixed semiconductors. *Phys. Stat. Sol. (b)* **144**, 661 (1987).
21. J. Cibert, D. Scalbert. Diluted magnetic semiconductors: Basic physics and optical properties. In: *Spin Physics in Semiconductors*. Edited by M.I. Dyakonov (Springer, 2008), **157**, p. 389.

Received 11.11.20

Ю.Г. Семенов С.М. Рябченко

#### НАБЛИЖЕННЯ МОЛЕКУЛЯРНОГО ПОЛЯ В ТЕОРІЇ ФЕРОМАГНІТНОГО ФАЗОВОГО ПЕРЕХОДУ В РОЗБАВЛЕНИХ МАГНІТНИХ НАПІВПРОВІДНИКАХ

У цій роботі педагогічного характеру викладено порівняльний аналіз двох загальних підходів, що описують феромагнітний фазовий перехід у розбавлених магнітних напів-

провідниках (DMS), з точки зору наближення поля Вейсса. Припускаючи скінчену спінову поляризацію домішкових магнітних іонів, ми розглядаємо обмінну взаємодію цих магнітних іонів і вільних носіїв заряду напівпровідника в першому порядку теорії збурень і отримуємо однорідне молекулярне поле Вейсса, яке поляризує спіни носіїв. У свою чергу, ця спінова поляризація вільних носіїв створює ефективне поле, яке може стабілізувати спінову поляризацію DMS нижче критичної температури  $T_C$ . Трактуювання такої самоузгодженої спонтанної намагніченості DMS може здійснюватися з точки зору спін-спінової взаємодії між магнітними іонами, незалежної від відстані між ними і нескінченно малої в термодинамічній границі. З іншого боку, врахування додатково ефектів обмінної взаємодії магнітних іонів і вільних носіїв заряду у другому порядку теорії збурень описує поле Вейсса в термінах непрямої спін-спінової взаємодії Рудермана-Кіттеля-Касуя-Йосиди, яка осцилює і не зникає при скінчених міжіонних відстанях при скінченій концентрації носіїв. Обидва підходи приводять до однакової температури Кюрі  $T_C$  у випадку некорельованого однорідного випадкового розподілу локалізованих спінових моментів по об'єму зразка. Ми обговорюємо походження такого збігу та показуємо, коли це не так у інших більш реалістичних моделях DMS зі скінченною електропровідністю (концентрацією носіїв струму).

*Ключові слова:* розбавлені магнітні напівпровідники, феромагнітне впорядкування, наближення середнього поля, РККІ взаємодія.