

MULTIPOLAR INTERACTIONS IN METALS AND ALLOYS

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During recent years the experimental evidence was obtained for necessity to take into consideration the multipolar pair interactions to explain the temperature variation of the electric field gradient at the impurity sites in rare-earth metals and alloys [1], the results of measurements of the elastic constant, parastriction and magnetic susceptibility of rare-earth intermetallic compounds [2], the temperature variation of the anisotropy of the magnetic susceptibility of rare-earth metals [3]. Recently, two systems have been identified, TmZn and TmCd where quadrupolar pair interactions dominate and by themselves drive a phase transition [4]. The direct electric quadrupole-quadrupole interaction is small and of opposite sign to explain the experimental results, obtained in [1-4].

The aim of the present work is to investigate the indirect quadrupole-quadrupole interactions between impurity paramagnetic ions as well as between nuclei with spin $I \geq 1$ in metals and alloys, which arises because of the perturbation of the charge density of the conduction electrons by the electric quadrupole moments of the impurity paramagnetic ions and the nuclei. The calculations are performed selfconsistently, having taken into account the exchange and correlation effects in the system of conduction electrons as

well as the Sternheimer's antishielding [5] of the electric field gradient. The influence of these indirect interactions on the magnetic resonance linewidths is studied.

1. We use the dielectric function method [6] to calculate the induced charge density of conduction electrons due to the quadrupole moment of the impurity paramagnetic ion (nucleus) at the origin. According to [6], the expression for the Fourier component of the induced charge density $n(\vec{k})$, in selfconsistent case, can be written in the following form [6]

$$n(\vec{k}) = (4\pi/5)^{1/2} \{ [\epsilon(\vec{k}) - 1] k^2 / 3\epsilon(\vec{k}) \}$$

$$\cdot \sum_{m=-2}^2 Q_{2,m} Y_{2,m}(\theta_k, \Phi_k) \Gamma \quad (1)$$

Here θ_k, Φ_k - the polar angles of the vector \vec{k} ; $Q_{2,m}$ - the component of the electric quadrupole moment of the impurity ion (nucleus); Γ - the antishielding factor [5]: $\Gamma = 1 - R'$ for the impurity paramagnetic ion, $\Gamma = 1 - \chi_\infty$ for the nucleus. Having taken into account the exchange and correlation effects in the system of conduction electrons, the expression for the dielectric function $\epsilon(\vec{k})$ can be expressed in the following form [7]

$$\epsilon(\vec{k}) = 1 + \chi(k) [1 - \chi(k) f(k)]^{-1}, \quad (2)$$

$$f(k) = [(k^2/k^2 + k_F^2 + k_S^2) +$$

$$+ (k^2/k_F^2 + k_s^2)]/4 ,$$

$$\chi(k) = (k_{FT}^2/k^2) \{ (1/2) + (k_F/2k) \cdot$$

$$[(1 - k^2/4k_F^2) \ln |(k+2k_F)/(k-2k_F)|] \},$$

k_F - the wave vector on the Fermi surface; k_s - the inverse screening radius; $k_{FT} = (6\pi N e^2 / E_F)^{1/2}$; N - the concentration of electrons; $-e$ - the electron charge. We perform the inverse Fourier transform of the expression (1) and having taken into consideration the expansion of the plane wave $\exp(-ikR)$ in spherical functions perform integration over the angle variables of the vector \vec{k} . Having taken into account the singularity of $\chi(k)$ at $k = 2k_F$ and asymptotic form of the Fourier transform of the generalized function [8], having limited ourselves to terms inversely proportional to R^4 in the expression for $n(\vec{R})$, where R is the distance from the impurity ion (nucleus) at the origin, finally in the limit of large R we obtain the following expression for the induced charge density of conduction electrons

$$n(\vec{R}) = \{ [-F \cos(2k_F R) / R^3] + [\ln(k_F R) + g] \cdot G \sin(2k_F R) / R^4 \} (4\pi/5)^{1/2} \cdot F \cdot$$

$$\sum_{m=-2}^2 Q_{2,m} Y_{2,m}^*(\theta_R, \phi_R) \} / 6\pi , (3)$$

$$F = 16\pi p k_F^2 / (4+pa)^2 , \quad a = 1 - f(2k_F) ,$$

$$G = 8\pi p^2 a k_F / (4+pa)^3 , \quad p = k_{FT}^2 / 2k_F^2 ,$$

$$g = \gamma - \{ 3(4+pa) / pa \} - 3/2 , \quad \gamma = 0,5772.$$

To calculate the component $B_{2,t^{1j}}$ of the electric field gradient at impurity ion (nucleus) located at the lattice site i , due to the perturbed electronic charge density by the electric quadrupole moment of the j -th impurity paramagnetic ion (nucleus) at origin of coordinates the two-center integral is transformed to the one-center integral (to the center located at the lattice site i) with the help of the relation, proposed in [9]. We suppose that the main contribution to the components of

the electric field gradient is due to the region with small r , where \vec{r} is the radius-vector of an electron relative to the lattice site i , and restrict ourselves with contribution from the region inside the sphere with radius $R_{ij}/2$ with the center at the lattice site i , where \vec{R}_{ij} is the radius-vector, directed from the lattice site i to the origin of coordinates. We limit ourselves with the terms proportional to $\ln(k_F R_{ij}) / R_{ij}^5$ in calculations. We also suppose that the Z axis is directed along the vector \vec{R}_{ij} . Finally, we get the following expression for the electric field component

$$B_{2,t^{1j}} = R_{ij}^{-3} \cdot \Gamma_1 \cdot \Gamma_j \cdot Q_{2,t^j} \quad (4)$$

$$\cdot [F S_t(2k_F R_{ij}) + G T_t(2k_F R_{ij}) / R_{ij}] ,$$

where

$$S_0(X) = (2 \cos X / 9) -$$

$$- [16 \sin X \sin(X/2) / 3X^2] -$$

$$- [(88 \cos X \cos(X/2)) / 105X^2] ;$$

$$S_{\pm 1}(X) = (4 \sin X / 3X) -$$

$$- [(8 \cos X + 32 \cos X \cos(X/2)) / 105X^2] -$$

$$- [16 \sin X \sin(X/2) / 5X^2] ;$$

$$S_{\pm 2}(X) = (-50 \cos X / 21X^2) -$$

$$- 4 \cos X \cos(X/2) / 35X^2 ;$$

$$T_0(X) = \{ -2 \sin X [\ln(X/2) + -3/2] / 9 \} +$$

$$+ [88 \sin X \ln(X/2) / 35X^2] +$$

$$+ [68 \sin X \cos(X/2) \ln(X/2) / 35X^2] ;$$

$$T_{\pm 1}(X) = \{ -8 \cos X [\ln(X/2) + -3/2] / 3X \} +$$

$$+ 8 \sin X \ln(X/2) / 105X^2 +$$

$$+ 32 \sin X \cos(X/2) \ln(X/2) / 105X^2 ;$$

$$T_{\pm 2}(X) = [248 \sin X \ln(X/2) / 105X^2] +$$

$$+ [4 \sin X \cos(X/2) \ln(X/2) / 35X^2] .$$

2. The Hamiltonian of the indirect quadrupole-quadrupole interaction via the system of conduction electrons between the i -th and

j -th impurity paramagnetic ions (nuclei) for a system of coordinates with Z axis directed along the vector \vec{R}_{1j} has the form

$$H_{Q-Q^{1j}} = \sum_{t=-2}^2 (-1)^t B_{2,-t^{1j}} Q_{2,t^{1j}} = \quad (5)$$

$$= \sum_{t=-2}^2 (-1)^t V_{1j}^{t^1} Q_{2,t^{1j}},$$

$$\text{where } V_{1j}^{t^1} = R_{1j}^{-3} \quad (6)$$

$$\{FS_t(2k_F R_{1j}) + GT_t(2k_F R_{1j})/R_{1j}\} \Gamma_i \Gamma_j.$$

According to [10], the operators of the components of the electric quadrupole moment of the j -th impurity rare-earth ion with the total angular momentum \vec{J}_j can be expressed in the following form

$$Q_{2,0^j} = -e \langle J || \alpha || \rangle \langle r_f^2 \rangle \cdot [3J_{jz}^2 + J(J+1)]/2, \quad (7a)$$

$$Q_{2,\pm 1^j} = \pm e \langle J || \alpha || J \rangle \langle r_f^2 \rangle (3/8)^{1/2} \cdot [J_{jz} J_{j\pm} + J_{j\pm} J_{jz}], \quad (7b)$$

$$Q_{2,\pm 2^j} = -e \langle J || \alpha || J \rangle \langle r_f^2 \rangle \cdot (3/8)^{1/2} J_{j\pm}^2. \quad (7c)$$

Here $\langle r_f^2 \rangle$ - the average square of the $4f$ -electron radius; $\langle J || \alpha || J \rangle$ - the numerical Elliott-Stevens coefficient [10]. The operators of the components of the electric quadrupole moment of the i -th nucleus have the form [10]

$$Q_{2,0^i} = \{eQ/2I(2I-1)\} \cdot \{3I_{1z}^2 - I(I+1)\}, \quad (8a)$$

$$Q_{2,\pm 1^i} = \mp \{eQ/2I(2I-1)\} (3/2)^{1/2} \cdot (I_{1+} I_{1z} + I_{1z} I_{1+}), \quad (8b)$$

$$Q_{2,\pm 2^i} = \{eQ/2I(2I-1)\} (3/2)^{1/2} \cdot I_{1+}^2, \quad (8c)$$

\vec{I}_1 - the nuclear spin moment at the lattice site i ; Q - the nuclear quadrupole moment.

In the coordinate system $\tilde{X}, \tilde{Y}, \tilde{Z}$, in which the angle between the \tilde{Z}

axis and the vector \vec{R}_{1j} is equal to θ_{1j} , the Hamiltonian of the indirect quadrupole-quadrupole interaction can be written in the following form [11]

$$H_{Q-Q} = \sum_{i < j} \sum_{t=-2}^2 W_{1j}^{t^1} \tilde{Q}_{2,t^{1j}} \tilde{Q}_{2,-t^j}; \quad (9)$$

$$W_{1j}^0 = (1 - 3\sin^2\theta_{1j}/2) V_{1j}^0 - (3\sin^2 2\theta_{1j} V_{1j}^1 - 3\sin^4\theta_{1j}^2)/4;$$

$$W_{1j}^1 = -(3\sin^2 2\theta_{1j} V_{1j}^0/8) + [1 - (5\sin^2\theta_{1j}/2) + 2\sin^4\theta_{1j}] V_{1j}^1 - \sin^2\theta_{1j} (1 - \sin^2\theta_{1j}/2) V_{1j}^2;$$

$$W_{1j}^2 = (3\sin^4\theta_{1j} V_{1j}^0/8) - \sin^2\theta_{1j} (1 - \sin^2\theta_{1j}/2) V_{1j}^1 + (1 - \sin^2\theta_{1j} + \sin^4\theta_{1j}/8) V_{1j}^2.$$

Here $\tilde{Q}_{2,t^{1j}}, \tilde{Q}_{2,-t^j}$ - the operators of the components of the electric quadrupole moments of the j -th and i -th ions (nuclei), respectively, defined relative to the coordinate system $\tilde{X}, \tilde{Y}, \tilde{Z}$; the summation in (9) is carried over all pairs of ions (nuclei).

The expressions (5), (6), (9) describe also the indirect quadrupole-quadrupole interactions of paramagnetic ion-nuclei via conduction electrons the ground state of which in electric crystal field is electronic spin singlet. But the operator $Q_{2,t^j}(Q_{2,-t^i})$ in (5), (9) should be changed to the operator of the effective nuclear electric quadrupole moment $Q_{2,t^j}(Q_{2,-t^i})$ [12].

3. According to (5), (6), (9), the indirect quadrupole-quadrupole interaction of the impurity paramagnetic ions and the nuclei in metals and alloys is more long-range than the direct quadrupole-quadrupole interaction of the ions and nuclei. The energy of this indirect multipolar interaction decreases with the distance R_{1j} between the j -th and i -th impurity ions (nuclei) as R_{1j}^{-3} , oscillating with the period, which is determined by the value of the wave vector on the Fermi surface and R_{1j} .

Contrary to the indirect spin-spin exchange interaction via conduction electrons between impurity paramagnetic ions and identical nuclei, which induces narrowing of the magnetic resonance linewidth, the indirect quadrupole-quadrupole interactions, due to nonisotropic spin part of the Hamiltonian, can be considered as an additional source of broadening of the resonance lines. Let us consider the dilute magnetic alloys Au:Er, Ag:Er, Ag:Dy. According to [13], the ground state of the ions Er^{3+} in Au, Ag and Dy^{3+} in Ag is the doublet Γ_7 with the isotropic g-factor, which is equal to $6,80 \pm 0,05$ for Er^{3+} in Au, to $6,85 \pm 0,04$ for Er^{3+} in Ag, $7,63 \pm 0,08$ for Dy^{3+} in Ag. The first excited state for these ions is the quartet $\Gamma_8(1)$. The magnitudes of the splitting between the ground and first excited states Δ and the cubic crystal field parameters X are equal, respectively, to 16 K, -0,36 for Er^{3+} in Au; 35 K, -0,35 for Er^{3+} in Ag; 10 K, -0,56 for Dy^{3+} in Ag [13]. The indirect spin-spin interaction between impurity paramagnetic ions in dilute magnetic alloys appears in the second order of the perturbation theory in H_Q-Q . The width of the Lorentz line is equal to

$$\Delta H = \pi M_2^3/2 / (3M_4)^{1/2}, \quad (10)$$

where M_2 and M_4 are the second and the fourth moments of the resonant line. Using the wave functions of the ground and excited states from [14], the following values of the parameters: $\langle r^2 \rangle = 0,666 a_0^2$ (a_0 - the Bohr radius), $\langle J || \alpha || J \rangle = -4/9 \cdot 25 \cdot 7$ for Er^{3+} ; $\langle r^2 \rangle = 0,727 \cdot a_0^2$, $\langle J || \alpha || J \rangle = -2/9 \cdot 35$ for Dy^{3+} [10]; $E_f = 5,49$ eV $a = 4,07 \cdot 10^{-8}$ cm for Au; $a = 4,08 \cdot 10^{-8}$ cm for Ag [14], where a - the lattice constant; $k_s = k_{FT}$; summing only over the nearest neighbours, after averaging over the directions of the magnetic field for crystalline powder we obtain: $\Delta H(Q-Q) = 29,3 \cdot 10^3$ C Oe for Au:Er; $\Delta H(Q-Q) = 13,4 \cdot 10^3$ C Oe for Ag:Er; $\Delta H(Q-Q) = 106 \cdot 10^3$ C Oe for Ag:Dy, where C - the concentration of paramagnetic ions, $\Delta H(Q-Q)$ - the contribution of H_Q-Q to the linewidth. According to [10], the contribution to the

linewidth due to the magnetic dipole-dipole interaction for the case, when the effective spin $S=1/2$, and for powder is equal to: $\Delta H(d-d) = 34,4 \cdot 10^3$ C Oe for Au:Er; $\Delta H(d-d) = 34,6 \cdot 10^3$ C Oe for Ag:Er; $\Delta H(d-d) = 38,9 \cdot 10^3$ C Oe for Ag:Dy. Comparing $\Delta H(Q-Q)$ and $\Delta H(d-d)$ for the dilute magnetic alloys Au:Er, Ag:Er, Ag:Dy, we may conclude that the contribution of the indirect quadrupole-quadrupole interactions to the resonance linewidth may be of the same order and exceed the contribution of the magnetic dipole-dipole interactions to the linewidth. Let us consider the contribution of the indirect nuclear quadrupole-quadrupole interaction via conduction electrons in metals to the NMR linewidth. For the Gauss form of the resonant line the conclusions about the linewidth can be made, knowing only its second moment. The second moment M_2 , caused by the indirect quadrupole interaction, is given by [15]

$$h^2 M_2 = [eQ/I(2I-1)]^4 [I(I+1)-3/4]^2 16 \cdot I(I+1) \sum_{J \neq 1} \{ [2(W_{1J}^0 + 9W_{1J}^1/2)^2/3] + \quad (11)$$

$$+ 9(W_{1J}^1 + 2W_{1J}^2)^2 + 135(W_{1J}^1)^2/2 \} / 105.$$

The second moment M_2' caused by the nuclear magnetic dipolar interaction is given by [10]

$$h^2 M_2' = (3/5) (\gamma_N \hbar)^4 I(I+1) \sum_{J \neq 1} R_{J1}^{-6}. \quad (12)$$

where γ_N is the gyromagnetic ratio for the nuclear spins, the average over the angles has been taken. For the NMR linewidth in the crystalline powder of Au^{197} ($I=3/2$, $Q = 6 \cdot 10^{-24}$ cm² [16]; $k_F = 1,21 \cdot 10^8$ cm⁻¹, $k_{FT} = 1,73 \cdot 10^8$ cm [14]; $k_s = k_{FT}$ [7]; $\mu = 0,1439 \mu_N$ [17], $\gamma_\infty = -72$ [5]) we obtain $M_2/M_2' = 3,74$. Thus we may conclude that for the crystalline powder of Au^{197} the indirect quadrupole-quadrupole interactions between nuclei make a contribution to the NMR linewidth comparable with the contribution from the magnetic dipolar interaction between nuclei. The influence of the indirect quadrupole-quadrupole interactions of the rare-earth ion - nuclei on

shape and width of the lines for magnetic resonance on the electron-nuclear levels should increase in the case, when the ground state of the ion is the electron spin singlet. The expressions for the components of the effective nuclear electric quadrupole moments contain the terms, which depend on the excited states of the paramagnetic ion and reflect the symmetry of the electric crystal field, acting on the ion [12]. Due to large values of the electron magnetic moment of the paramagnetic ion in the excited state compared to the nuclear magnetic moment, the effective nuclear quadrupole moment substantially exceeds the nuclear quadrupole moment. Besides, the antishielding factors in the rare-earth ions are large [5].

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