Inelastic scattering of neutrons by paramagnetic ions under relaxation conditions

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A general theoretical analysis is made of the inelastic scattering of neutrons by paramagnetic ions interacting with the environment. A situation is considered in which a paramagnetic ion interacts statically with a crystal field and the total angular momentum of a partly filled electron shell of the ion relaxes because of the contact interaction with conduction electrons. A detailed calculation is made of inelastic scattering of neutrons in an intermetallic compound $PrAl_3$ at low temperatures. Analytic expressions are obtained for the profiles of the inelastic scattering peaks and for the temperature dependences of the peak parameters. It is shown that the interaction of the f electrons of Pr with the conduction electrons broadens and shifts the peaks corresponding to transitions between the f-electron states in a crystal field, and also splits the peaks and makes them asymmetric.

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The first systematic experimental investigations of crystal electric fields in metallic systems[1–4] drew the attention of theoreticians to the circumstance that the widths of neutron reflection peaks representing transitions between levels in crystal electric fields can sometimes be considerably greater than the width of the resolution function of a spectrometer. Attention was drawn in Ref. 1 to the dependence of the width of the reflections on the temperature of a sample and on the splitting caused by the crystal electric field. Somewhat later, investigations were made of intermetallic compounds of the $PrAl_3$ type (see, for example, Refs. 5–7) with the hexagonal symmetry of the crystal lattice, corresponding to a higher degree of lifting of the degeneracy of the ground J multiplet than in the case of cubic systems.[1–4]

The interest in crystal fields arises, on the one hand, from the direct influence of the nature of splitting on such macroscopic properties as the specific heat, magnetic susceptibility, etc.; on the other hand, investigations of these fields make it possible to determine the coupling between a paramagnetic ion with the lattice or with conduction electrons in a sample by determination of the spectral characteristics of reflections. Investigations of the mechanisms of broadening of the reflections by crystal electric fields have stimulated a number of theoretical treatments.[8–15]

The mechanism of the dynamic exchange broadening was investigated in Refs. 8–10. The temperature dependence of the broadening due to the spin-spin interaction was obtained in Ref. 11. A calculation of the spin-lattice broadening was made phenomenologically in Ref. 12.

Investigations of the influence of the interaction of the f electrons of a magnetic ion with conduction electrons on the single-ion susceptibility were described in Refs. 13 and 14. A simple expression for the line width was obtained in the case of a two-level system.

An approach developed earlier in Ref. 11 was used in Ref. 15 to obtain the temperature dependence of the broadening of the neutron reflections due to the interaction of the f electrons of a rare-earth ion with conduction electrons, which was in good agreement with the results reported in Ref. 13.

We shall analyze theoretically the inelastic scattering of neutrons by paramagnetic ions under relaxation conditions. We shall develop a general approach for the case when a paramagnetic ion interacts statically with a crystal field of the environment and the total angular momentum of a partly filled electron shell of the ion relaxes because of the contact interaction with conduction electrons. We shall use the superoperator formalism[16] to obtain a general expression for a doubly differential cross section of neutron scattering in which separate summations are carried out over the states of the Hamiltonian of the crystal field and of conduction electrons.

We shall adopt the model of a gas of noninteracting particles for conduction electrons and approximate the density of one-electron states in the conduction band by a constant value. We shall reduce summation over the states in the electron subsystem to integration and obtain an expression for the matrix elements of the relaxation superoperator.

We shall demonstrate the use of the new theory by an analysis of the inelastic scattering of neutrons in an intermetallic compound $PrAl_3$ at low temperatures.

1. USE OF THE SUPEROPERATOR FORMALISM IN THE DESCRIPTION OF INELASTIC NEUTRON SCATTERING

Let us assume that a monochromatic beam of unpolarized neutrons with a wave vector $\mathbf{k}_0$ is scattered magnetically by electrons of a paramagnetic ion in a sample and that such scattering transfers a neutron from a state $\mathbf{k}_0$ to a state $\mathbf{k}_1$, and the sample from a state $|i\rangle$ of energy E_i to a state $|f\rangle$ with an energy E_f. In the first Born approximation the doubly differential cross section of this process is described by the formula[9]

$$\frac{d^2\sigma}{d\omega d\Omega_{\mathbf{k}_1}}=F(\mathbf{k}_0,\mathbf{k}_1)\sum_{if}\rho_i|\langle i|\mathbf{J}_\perp|f\rangle|^2\delta(\omega-E_f+E_i). \qquad (1)$$

Here, $F(\mathbf{k}_0\mathbf{k}_1)$ is a factor unimportant in the subsequent analysis,

$$\hbar\omega=(\hbar^2/2m)(k_0^2-k_1^2)$$

is the energy transferred from a neutron to the sample,

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$$J_\perp = k^{-2}[\mathbf{k}\times[\mathbf{J}\times\mathbf{k}]] \quad (2)$$

is the component of the total angular momentum $\mathbf{J}$ of the investigated paramagnetic ion in a direction perpendicular to the momentum $\mathbf{k} = \mathbf{k}_0 - \mathbf{k}_1$ transferred to the sample, and

$$\rho = \exp(-H/T)/\mathrm{Sp}[\exp(-H/T)] \quad (3)$$

is the density matrix at a temperature T.

We shall represent the total Hamiltonian H of the sample in the form

$$H = H_A + H_B + H_I, \quad (4)$$

where H_A is the static part of the Hamiltonian of the paramagnetic ion, H_B is the Hamiltonian of the subsystem with which the paramagnetic ion is interacting (for example, the conduction electron system) and which we shall call—for brevity—the thermostat, and H_I is the Hamiltonian of the interaction between the paramagnetic ion and the thermostat.

Using next the δ-function representation

$$\delta(\omega - E_f + E_i) = -\pi^{-1}\,\mathrm{Im}\,(\omega - E_f + E_i + i\delta)^{-1} \quad (5)$$

and introducing the Liouville operator $\hat{L}$ in accordance with the definition

$$\hat{L}A = HA - AH, \quad (6)$$

where H is the Hamiltonian of the system and A is an arbitrary quantum-mechanical operator, we can transform Eq. (1) into (see Ref. 16):

$$\frac{d^2\sigma}{d\omega d\Omega_{\mathbf{k}_1}} = -\frac{1}{\pi}F(\mathbf{k}_0, \mathbf{k}_1)\,\mathrm{Im}\,\mathrm{Sp}\{\rho \mathbf{J}_\perp^+ (\omega - L + i\delta)^{-1}\mathbf{J}_\perp\}. \quad (7)$$

Here, δ is an infinitesimally small width of a paramagnetic ion state.

The problem now is to transform Eq. (7) so that it contains explicitly only summation over the paramagnetic ion states. We shall assume that the rate of relaxation due to the interaction H_I is low compared with temperature so that the density matrix of Eq. (3) can approximately be assumed to be factorized:

$$\rho \approx \rho_A \rho_B, \quad (8)$$

where ρ_A is the density matrix of the paramagnetic ion corresponding to the Hamiltonian H_A and ρ_B is the density matrix of the thermostat. In the slow relaxation case, we can follow the treatment of Ref. 16 so that the Eq. (7) is transformed identically to the form

$$\frac{d^2\sigma}{d\omega d\Omega_{\mathbf{k}_1}} = -\frac{1}{\pi}F(\mathbf{k}_0\mathbf{k}_1)\,\mathrm{Im}\,\mathrm{Sp}_A\{\rho_A \mathbf{J}_\perp^+ \hat{G}(\omega + i\delta)\mathbf{J}_\perp\}, \quad (9)$$

where

$$\hat{G}(\omega + i\delta) = (\omega - \hat{L}_A - \hat{M} + i\delta)^{-1}, \quad (10)$$

the relaxation superoperator $\hat{M}$ being of the form

$$\hat{M}(\omega + i\delta) = P\hat{L}_I Q(\omega - \hat{L}_A - \hat{L}_B - Q\hat{L}_I Q + i\delta)^{-1} Q\hat{L}_I P, \quad (11)$$

whereas the action of the projection operator P reduces to summation over the thermostat variables, i.e., $PA = \mathrm{Sp}_B(\rho_B A)$. The operator Q is defined by $Q = 1 - P$.

We shall assume also that the rate of relaxation is low compared with the characteristic separations between the energy levels of the paramagnetic ion. Then, the relaxation superoperator can be represented in an approximation which is quadratic in respect of the relaxation interaction:

$$\hat{M}(\omega + i\delta) \approx P\hat{L}_I Q(\omega - \hat{L}_A - \hat{L}_B + i\delta)^{-1} Q\hat{L}_I P. \quad (12)$$

We can therefore see that the problem reduces to a calculation of the relaxation superoperator matrix that depends both on the model of the thermostat itself, governed by the Hamiltonian H_B, and on the interaction H_I between the thermostat and the paramagnetic ion.

2. RELAXATION DUE TO THE INTERACTION WITH CONDUCTION ELECTRONS

The matrix of the relaxation superoperator in the space of the states of the paramagnetic ion Hamiltonian H_A can be obtained by assuming a specific model for the description of conduction electrons. We shall use the simplest model of a gas of noninteracting electrons with the Hamiltonian

$$H_B = \sum_{\mathbf{k}\sigma} \xi_{\mathbf{k}} C^+_{\mathbf{k}\sigma} C_{\mathbf{k}\sigma}, \quad (13)$$

where $\xi_{\mathbf{k}} = \hbar^2 k^2/2m - \varepsilon_F$ is the energy of a free electron measured from the Fermi energy; $C^+_{\mathbf{k}\sigma}$ and $C_{\mathbf{k}\sigma}$ are the creation and annihilation operators of a conduction electron with a wave vector $\mathbf{k}$ and a spin projection σ. Moreover, we shall assume that the interaction of the total angular momentum of the partly filled f shell of the paramagnetic ion with conduction electrons is of the exchange type:

$$H_I = -(g-1)J_{sf}(\mathbf{JS}), \quad (14)$$

where g is the gyromagnetic Landé factor, J_{sf} is the s–f exchange integral, and S^q are the components of the effective spin operator of conduction electrons, which can be introduced conveniently as follows:

$$S^z = \frac{1}{2N}\sum_{\mathbf{kk}'}(C_{\mathbf{k}\uparrow}^+ C_{\mathbf{k}'\uparrow} - C_{\mathbf{k}\downarrow}^+ C_{\mathbf{k}'\downarrow}),$$

$$S^+ = \frac{1}{N}\sum_{\mathbf{kk}'} C_{\mathbf{k}\uparrow}^+ C_{\mathbf{k}'\downarrow}, \qquad S^- = \frac{1}{N}\sum_{\mathbf{kk}'} C_{\mathbf{k}\downarrow}^+ C_{\mathbf{k}'\uparrow}; \quad (15)$$

here, N is the total number of conduction electrons.

Let us assume that $(|m\rangle, E_m)$, $(|n\rangle, E_n)$, ... are the eigenfunctions and the corresponding eigenvalues of the paramagnetic ion Hamiltonian H_A (the ion may be subject to, for example, a crystal field), whereas $(|\alpha\rangle, E_\alpha)$, $(|\beta\rangle, E_\beta)$, ... are the eigenfunctions and the eigenvalues of H_B. Then, the matrix element of the relaxation superoperator can be represented in the form

$$M_{n,m;n'm'} = \sum_{\substack{n_1 m_1 \\ \alpha\beta_1\beta_2\gamma}} (\rho_B)_\alpha (L_I)^{\alpha\alpha;\beta_1\beta_2}_{nm;n_1m_1} \times \frac{1}{\omega - E_{n_1} + E_{m_1} - E_{\beta_1} + E_{\beta_2} + i\delta}(L_I)^{\beta_1\beta_2;\gamma\gamma}_{n_1m_1;n'm'}. \quad (16)$$

Using the defintion of the Liouville operator (6), we obtain

$$(L_I)^{\alpha\alpha;\beta_1\beta_2}_{nm;n_1m_1} = -(g-1)J_{sf}[(\mathbf{J}_{nn_1}\mathbf{S}_{\alpha\beta_1})\delta_{mm_1}\delta_{\alpha\beta_2} - (\mathbf{J}_{m_1m}\mathbf{S}_{\beta_2\alpha})\delta_{nn_1}\delta_{\alpha\beta_1}],$$

$$(L_I)^{\beta_1\beta_2;\gamma\gamma}_{n_1m_1;n'm'} = -(g-1)J_{sf} \times [(\mathbf{J}_{n_1n'}\mathbf{S}_{\beta_1\gamma})\delta_{m_1m'}\delta_{\beta_2\gamma} - (\mathbf{J}_{m'm_1}\mathbf{S}_{\gamma\beta_2})\delta_{n_1n'}\delta_{\beta_1\gamma}].$$

Substituting these relations in Eq. (16), we find that the matrix elements of the relaxation superoperator are described by the following expression:

$$M_{nm;n'm'}=\delta_{mm'}\sum_p J_{np}{}^i J_{pn'}{}^j S^{ij}(\omega-E_p+E_m)$$
$$-\delta_{nn'}\sum_p J_{m'p}{}^i J_{pm}{}^j S^{ij*}(-\omega-E_p+E_n)$$
$$-J_{nn'}{}^i J_{m'm}{}^j[S^{ij}(\omega-E_{n'}+E_m)-S^{ij*}(-\omega-E_{m'}+E_n)], \quad (17)$$

where

$$S^{ij}(\Omega)=(g-1)^2J_{sf}{}^2\sum_{\alpha\beta}(\rho_B)_\alpha\frac{S_{\alpha\beta}{}^iS_{\beta\alpha}{}^j}{\Omega-E_\beta+E_\alpha+i\delta}. \quad (18)$$

Using the definitions of Eq. (15) and the well-known commutation relations for the operators $C^+_{k\sigma}$ and $C_{k\sigma}$, we can show that only the diagonal components of the tensor $S^{ij}(\Omega)$ differ from zero, namely

$$S^{xx}(\Omega)=S^{yy}(\Omega)=S^{zz}(\Omega)=S(\Omega). \quad (19)$$

We have introduced here the function

$$S(\Omega)=\frac{1}{2}(g-1)^2J_{sf}{}^2\sum_{\mathbf{kk'}}\frac{\bar{n}_\mathbf{k}(1-\bar{n}_\mathbf{k'})}{\Omega-\xi_\mathbf{k'}+\xi_\mathbf{k}+i\delta}, \quad (20)$$

which contains the average occupation numbers of one-electron states at a given temperature

$$\bar{n}_\mathbf{k}=[\exp(-\xi_\mathbf{k}/T)+1]^{-1}. \quad (21)$$

We can thus see that the matrix elements of the relaxation operator are governed by the function $S(\Omega)$ alone and the expression (17) becomes

$$M_{nm;n'm'}=\delta_{mm'}\sum_p(\mathbf{J}_{np}+\mathbf{J}_{pn'})S(\omega-E_p+E_m)$$
$$-\delta_{nn'}\sum_p(\mathbf{J}_{m'p}+\mathbf{J}_{pm})$$
$$\times S^*(-\omega-E_p+E_n)-(\mathbf{J}_{nn'}+\mathbf{J}_{m'm})[S(\omega-E_{n'}+E_m)$$
$$-S^*(-\omega-E_{m'}+E_n)]. \quad (22)$$

We can find the explicit form of the function $S(\Omega)$ by approximating the density of one-electron states in the conduction band by a constant quantity

$$\rho(\xi)=\begin{cases}\rho_F, & \text{if } -D\leqslant\xi\leqslant D,\\ 0, & \text{if } |\xi|>D,\end{cases} \quad (23)$$

where the limiting energy is $D\approx\varepsilon_F$, and ρ_F is the density of one-electron states on the Fermi surface. In the case of this simple density-of-states function the double sum in Eq. (20) reduces to the following integral:

$$S(\Omega)=\frac{1}{2}(g-1)^2J_{sf}{}^2\rho_F{}^2\int_{-D}^{D}d\xi\int_{-D}^{D}d\xi'\frac{\bar{n}_\mathbf{k}(1-\bar{n}_\mathbf{k'})}{\Omega-\xi'+\xi+i\delta}. \quad (24)$$

Allowing during integration in Eq. (24) that $T\ll D$ and $\Omega\ll D$, we obtain the result

$$S(\Omega)=S'(\Omega)+iS''(\Omega), \quad (25)$$

$$S'(\Omega)-S'(0)=\frac{\gamma}{\pi}\Omega\left\{-1-c-\ln\frac{D}{4\pi T}+\left(\frac{\Omega}{2\pi T}\right)^2\times\sum_{n=1}^{\infty}\frac{1}{n}\left[\left(\frac{\Omega}{2\pi T}\right)^2+n^2\right]^{-1}\right\}, \quad (26)$$

$$S''(\Omega)=-\gamma\Omega[1-\exp(-\Omega/T)]^{-1}, \quad (27)$$

where $c = 0.577\,215\,664\,9\ldots$ is the Euler constant and

$$\gamma=\tfrac{1}{2}\pi[(g-1)J_{sf}\rho_F]^2 \quad (28)$$

is a small parameter of the theory.

A simple analysis of Eq. (22) shows that any constant (independent of Ω) correction to the real part of $S'(\Omega)$ makes no contribution to the matrix elements of the relaxation superoperator. This is why the difference $S'(\Omega)-S'(0)$ is calculated.

At high temperatures when $T\gg\Omega$, the function $S(\Omega)$ has the simple form

$$S(\Omega)=-\gamma\left\{\frac{\Omega}{\pi}\ln\left(0.386\frac{D}{T}\right)+iT\right\}. \quad (29)$$

We can thus see that the matrix elements for the inverse Green superoperator are

$$[G^{-1}(\omega+i\delta)]_{nm;n'm'}=(\omega-E_n+E_m+i\delta)\delta_{nn'}\delta_{mm'}$$
$$-[M(\omega+i\delta)]_{nm;n'm'}. \quad (30)$$

The real part of the relaxation supermatrix determines the shifts of the peaks representing inelastic neutron scattering, whereas its imaginary part gives the broadening of these peaks.

The restrictions imposed on the rate of relaxation by the temperature of a sample and transition energies remain valid right down to the lowest temperatures because the relaxation broadening and shifts are proportional to the small parameter γ.

3. NEUTRON SCATTERING IN AN INTERMETALLIC COMPOUND $PrAl_3$

In an intermetallic compound $PrAl_3$ the paramagnetic Pr^{3+} ions have a partly filled $4f$ shell containing two f electrons. In accordance with the Hund rules this electron configuration has the ground state with $S=1$ and $L=5$. Since the $4f$ shell is less than half-filled, the spin-orbit interaction produces a ground state $^3H_4$ with the total momentum $J=4$. Since the Pr^{3+} ions are in an electric field of an environment of the hexagonal symmetry, the splitting of the $^3H_4$ nonet is described by a Hamiltonian which is invariant under the transformation group of the coordinates D_{3h} (Ref. 7):

$$H_A=B_2{}^0O_2{}^0+B_4{}^0O_4{}^0+B_6{}^0O_6{}^0+B_6{}^6O_6{}^6, \quad (31)$$

where O^m_n are the equivalent operators. According to Ref. 7, we have $B^0_2=2.37\pm0.15$, $B^0_4=-(2.21\pm0.2)\cdot10^{-2}$, $B^0_6=(1.25\pm0.1)\cdot10^{-3}$, $B^6_6=(18.2\pm0.8)\cdot10^{-3}$ K. The interaction (31) splits the nonet into three singlets Γ_1, Γ_3, and Γ_4 and three doublets Γ^1_5, Γ^2_5, and Γ_6.

Application of the above theory to the scattering of neutrons by the paramagnetic Pr^{3+} ions under conditions of relaxation of the total momentum of an ion due to the interaction with conduction electrons can be demonstrated most clearly at low temperatures $T\lesssim1$ meV, when in practice only the singlet Γ_1 and the doublet Γ_6 are populated and when the momentum projections are $m_J=0$ and $m_J=\pm1$. In this case we can assume that the effective momentum of an ion is $J=1$ and consider a simplified system of the ion levels in a crystal field which contains the singlet Γ_1 and the doublet

Γ_6. Then, the dimensions of the supermatrices are not very large and the difficulties associated with inversion of a matrix in the calculation of the Green superoperator (10) can be overcome relatively easily. Summation in Eq. (9) over the f-shell states of the ion in a polycrystalline sample gives the simple result:

$$\frac{d^2\sigma}{d\omega\, d\Omega_k} \propto -\frac{2}{3\pi}\,\mathrm{Im\,Sp}\{\rho_A \mathbf{J}^+\hat{G}(\omega+i\delta)\mathbf{J}\}$$
$$=-\frac{2}{3\pi}\,\mathrm{Im}\{\rho_1[G_{11;11}+G_{-1-1;-1-1}-G_{11;-1-1}-G_{-1-1;11}]+\rho_1[G_{01;01}+G_{0-1;0-1}+G_{01;-10}+G_{0-1;10}]+\rho_0[G_{10;10}+G_{-10;-10}+G_{10;0-1}+G_{-10;01}]\}. \quad (32)$$

Here, the factor $F(\mathbf{k}_0\mathbf{k}_1)$ is omitted and we have

$$\rho_0=[1+2\exp(-\Delta/T)]^{-1}, \quad (33)$$

$$\rho_1=\rho_0\exp(-\Delta/T), \quad (34)$$

where Δ is the energy of the doublet state (relative to the singlet state).

The matrix elements in the first brackets of Eq. (32) describe elastic neutron scattering by the f shell of the investigated ion, which is in the doublet state. The second and third brackets contain the matrix elements describing inelastic neutron scattering which is accompanied by a transition of the f shell from the doublet to the singlet state and by the reverse transition. The matrix elements of the Green superoperator have the following symmetry:

$$G_{11;11}=G_{-1-1;-1-1},\quad G_{11;-1-1}=G_{-1-1;11},\quad G_{01;01}=G_{0-1;0-1},$$
$$G_{10;10}=G_{-10;-10},\quad G_{01;-10}=G_{01;10}=G_{10;0-1}=G_{-10;01},$$

which can reduce the number of the required calculations. Since only inelastic scattering is of interest to us, it is permissible to limit calculations to just three matrix elements of the Green superoperator: $G_{01;01}$, $G_{10;10}$, and $G_{01;-10}$. The contribution to the scattering cross section near $\omega=-\Delta$ is made by the matrix elements

$$G_{01;01}=\frac{\omega+\Delta-M_{01;01}}{(\omega+\Delta-M_{01;01})^2-M^2_{01;0-1}} \quad (35)$$

and

$$G_{01;-10}=-\frac{1}{2\Delta}\frac{M_{01;10}}{\omega+\Delta-M_{01;01}-M_{01;0-1}}, \quad (36)$$

where the matrix elements of the relaxation superoperator $\hat{M}$ are calculated for $\omega=-\Delta$. The form of the scattering cross section near $\omega=\Delta$ is governed by the matrix elements

$$G_{10;10}=\frac{\omega-\Delta-M_{10;10}}{(\omega-\Delta-M_{10;10})^2-M_{10;-10}} \quad (37)$$

and

$$G_{10;0-1}=\frac{1}{2\Delta}\frac{M_{10;01}}{\omega-\Delta-M_{10;10}-M_{10;-10}}, \quad (38)$$

where the matrix elements of the relaxation superoperator $\hat{M}$ are calculated for $\omega=\Delta$.

The expressions (35)–(38) for the matrix elements of the Green superoperator near $\omega=\pm\Delta$ are obtained within the framework of the above approximation of slow relaxation corresponding to $\gamma\ll 1$. After calculation of the relevant matrix elements of the relaxation superoperator from Eq. (22) and substitution of the matrix elements of the Green superoperator of Eqs. (35)–(38) in the expression for the scattering cross section (32), we obtain the following energy dependences:

$$\frac{d^2\sigma}{d\omega\, d\Omega}\propto\frac{\alpha_1\Gamma_d/2+\beta(\omega+\Delta-\Delta_d)}{(\omega+\Delta-\Delta_d)^2+\Gamma_d^2/4}+\frac{\rho_1\Gamma_u/2}{(\omega+\Delta-\Delta_u)^2+\Gamma_u^2/4} \quad (39)$$

near $\omega=-\Delta$ and

$$\frac{d^2\sigma}{d\omega\, d\Omega}\propto\frac{\alpha_0\Gamma_d/2-\beta(\omega-\Delta+\Delta_d)}{(\omega-\Delta+\Delta_d)^2+\Gamma_d^2/4}+\frac{\rho_0\Gamma_u/2}{(\omega-\Delta+\Delta_u)^2+\Gamma_u^2/4} \quad (40)$$

near $\omega=\Delta$. The width $\Gamma_{d,u}$ and the shifts $\Delta_{d,u}$ are given below.

The above expressions (39) and (40) demonstrate clearly all the effects described by the theory developed above. In addition to the already known relaxation broadening and shift of the inelastic scattering peaks, our theory predicts splitting of the peaks because of the interaction of the f electrons with conduction electrons, as well as asymmetry of these peaks. The interaction between the f and conduction electrons results in a relaxation shift and broadening of each component of a doublet by a different amount. Therefore, a doublet splits into lower (d) and upper (u) states. The inelastic scattering peaks shift toward lower energies ω transferred to a neutron because the f electron energy decreases due to the interaction with conduction electrons.

The asymmetry of the peaks corresponding to transitions to the lower state of a doublet is due to interference between the scattering of neutrons by the f and conduction electrons. The second scattering channel is strongly suppressed because of the quadratic dependence of the process on the s-f exchange interaction, so that the interference effects are small. Similar coherent relaxation effects appear also in the determination of the Mössbauer emission spectrum.[17,18]

The Breit-Wigner parametrization of the inelastic scattering cross section near a resonance under relaxation conditions is an approximate process but this approximation is fully justified in the case of slow relaxation when the relaxation rate is a slowly varying function of ω, compared with the cross section itself in the region of a resonance.

The temperature dependences of the parameters of the peaks are

$$\Delta_u(T)=-4S'(\Delta)$$
$$=\frac{4\gamma}{\pi}\Delta\left\{1+c+\ln\frac{D}{4\pi T}-\left(\frac{\Delta}{2\pi T}\right)^2\sum_{n=1}^{\infty}\frac{1}{n}\left[\left(\frac{\Delta}{2\pi T}\right)^2+n^2\right]^{-1}\right\}, \quad (41)$$

$$^1/_2\Gamma_u(T)=\gamma[T+2\Delta(\mathrm{cth}(\Delta/2T)-1)], \quad (42)$$

$$^1/_2\Gamma_d(T)=\gamma[T+4\Delta\,\mathrm{cth}(\Delta/2T)], \quad (43)$$

$$\alpha_0(T)=\rho_0+(\rho_1+\rho_0)(\Delta_u/\Delta), \quad (44)$$

$$\alpha_1(T)=\rho_1+(\rho_1+\rho_0)(\Delta_u/\Delta), \quad (45)$$

$$\beta(T)=2(\rho_1+\rho_0)\gamma\,\mathrm{cth}(\Delta/2T). \quad (46)$$

The shift of the lower doublet state is $\Delta_d=2\Delta_u$. It follows that the doublet splitting is $\Delta_d-\Delta_u=\Delta_u$.

An analysis of Eqs. (42) and (43) for the peak widths shows that at low temperatures $T\ll\Delta$ the scattering of neu-

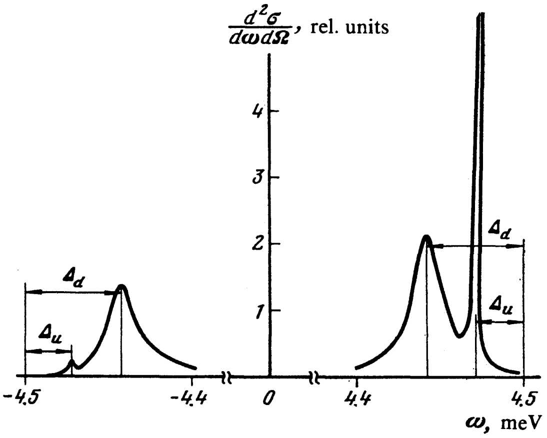

FIG. 1. Profiles of peaks due to inelastic neutron scattering. The curves are calculated using the formulas (39) and (40) describing the profiles of peaks due to inelastic neutron scattering accompanied by a transition of the f shell from a doublet to a singlet state (on the left) and with a reverse transition (on the right). The scale for the left-hand part is 100 times greater than for the right-hand part. The parameters of the curves are calculated from Eqs. (41)–(46) and (33)–(34) assuming that $\gamma = 0.63\times 10^{-3}$, $\Delta = 4.5$ meV, $D = 10$ eV, and $T = 0.5$ meV.

trons is only on the lower doublet state which relaxes at a finite rate $\frac{1}{2}\Gamma_d(0) = 4\Delta\gamma$, whereas the rate of relaxation of the upper state is $\frac{1}{2}\Gamma_u(0) = 0$. When temperature is increased, the splitting between the upper and lower doublet states decreases and the widths of the corresponding peaks increase proportionally to temperature.

The asymmetry coefficient β of a peak corresponding to the lower doublet state is governed only by the value of the parameter γ at low temperatures, i.e., $\beta(0) = 2\gamma$. In this model the peak asymmetry increases on cooling. The model predicts a particularly strong asymmetry of the peak corresponding to ineleastic scattering and accompanied by a transition of the f shell from the lower doublet state to a singlet. An interesting property of the model is that the intensity of the peak corresponding to this transition has a minimum at a temperature $T \approx 0.3$ meV and it increases on further cooling. This model effect is associated with an increase in the relaxation shift as a result of cooling. The change in the shift is governed by the ratio between the positions of the doublet Δ and the effective width of the conduction band D.

The magnitudes of all the effects are proportional to the relaxation parameter γ which can be estimated for the Pr^{3+} ion using the gyromagnetic Landé factor $g = 0.8$, the exchange integral $J_{sf} = 0.2$ eV (Ref. 10), and the density of states $\rho_F = 0.5\ \text{eV}^{-1}$. The substitution of these values into Eq. (28) gives $\gamma = 0.63\cdot 10^{-3}$.

Figure 1 shows curves calculated using Eqs. (39) and (40) for $\gamma = 0.63\cdot 10^{-3}$, $\Delta = 4.5$ meV, $D = 10$ eV, and $T = 0.5$ meV. Since the scale for the left-hand side is 100 times greater than for the right-hand side, it is clear that the areas under the peaks corresponding to transitions to the lower doublet state differ by just two orders of magnitude, whereas the population of the doublet represents only $\sim 10^{-4}$ of the singlet population.

It should be pointed out that in an analysis of the cross section for the scattering of neutrons by the Pr^{3+} ions at temperatures above 1 meV we must calculate the populations ρ_0 and ρ_1 allowing for all the nonet states Γ_1, Γ_3, Γ_4, $\Gamma_5^{(1)}$, $\Gamma_5^{(2)}$, and Γ_6. It should be pointed out that at temperatures $T < 0.1$ meV we can no longer use our theory because at $T = 0.1$ meV the relaxation shift is $\Delta_u = 0.03$ meV.

An analysis of high-resolution experimental data on neutron scattering can give the temperature dependences of the peak parameters in accordance with the parametrization of Eqs. (39) and (40). Then, a comparison of these dependences with those given by Eqs. (41)–(46) will demonstrate to what extent the proposed model describes the process of neutron scattering by paramagnetic ions under relaxation conditions. Low-resolution experimental data can be used to check the model by comparison of the experimental dependences of the areas under the peaks.

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