

Paramagnetic labeling as a method for the soft spectroscopy of electronic states

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A self-consistent microscopic theory of the relaxation of the crystal-field levels of an impurity ion in a state with an integer valence implanted in a normal metal is devised. A microscopic approach based on the Coqblin–Schrieffer–Cooper approach, rather than the formal model of the *sf* exchange interaction, makes it possible to take into account the specific details of both the crystal-field states of the impurity ion and the electronic band spectrum of the metal. A new method for the soft spectroscopy of electronic states based on measurements of the temperature dependence of the width $\Gamma_{MM'}(T)$ of transitions between the crystal-field states $|M\rangle$ of a paramagnetic ion implanted in the compound being studied is proposed. To make specific use of this method in neutron and optical spectroscopy, a classification of the types of temperature dependence of the natural relaxation width $\gamma_M(T)$ of the levels is devised, and procedures for possible experimental methods are proposed. A nonzero value of the natural relaxation width $\gamma_G(T)$ of the crystal-field ground state $|G\rangle$ of an impurity ion at zero temperature is obtained within the proposed self-consistent model, but is beyond the scope of perturbation theory. It is shown that the widely accepted estimate of the characteristic temperature of Kondo systems $T^* = \Gamma_G(T=0)/2$ from the quasielastic scattering width at zero temperature $\Gamma_G(T=0)/2$ is incorrect in the case of strong relaxation in a system with soft crystal fields. The proposed model is applied to the quantitative analysis of the relaxation of the crystal-field levels of paramagnetic Pr^{3+} ions implanted in CeAl_3 and LaAl_3 . The results of the calculations are in quantitative agreement with the experimental data. © 1998 American Institute of Physics. [S1063-7761(98)02005-8]

1. INTRODUCTION

The methods that have been developed for studying electronic states in metals (angle-resolved photoemission spectroscopy;¹ quantum oscillations of the magnetic susceptibility,² conductivity,³ magnetostriction,⁴ and elastic moduli⁵ associated with the de Haas–van Alphen effect; infrared spectroscopy;⁶ Raman scattering;⁷ etc.) provide complementary information regarding the structure of electron spectra. A comparison of the experimental data obtained by different methods with the results of band calculations of the electronic structure provides fairly reliable data on the properties of the compounds studied.

The methods for investigating electronic states can be divided into “hard” and “soft” methods. In the case of hard spectroscopy, the influence of the measurement process on the system exceeds the scales W^* of the characteristic interactions forming the electronic spectrum of the system (in Kondo systems W^* is of the order of the Kondo temperature T_K ; in variable-valence systems W^* is of the order of the valence fluctuations). Therefore, compounds with strong electron correlations, which have low-energy modes in the spectrum of elementary excitations, can be investigated most effectively by soft spectroscopic methods, in which the measurement process does not destroy the eigenstates of the system being investigated. The conditions imposed on spectroscopic measurements by the softness of the elementary excitations in variable-valence and Kondo systems greatly

restricts the set of methods that are applicable to the investigation of highly correlated systems. For example, the interpretation of photoemission measurements (because of the large energy transfers in the measurement process) and data from methods based on de Haas–van Alphen oscillations (because of the large magnetic fields, which can destroy the structure of soft excitations) requires a special investigation of the influence of the measurement process on the low-energy properties of the compound being studied. Therefore, the development of new soft spectroscopic methods for highly correlated electronic systems is an important undertaking.

This paper proposes a method for analyzing the electronic structure based on measurements of the temperature dependence of the relaxation of crystal-field levels of an impurity ion which has special properties (a paramagnetic label) and is implanted in the compound being investigated. A similar idea for investigating semiconductor compounds by an electron paramagnetic resonance technique was proposed back in Ref. 8. The method discussed in this paper relies on the technique of measuring the neutron or optical response of the system and is intended for studying metallic compounds. A spectroscopic procedure employing a paramagnetic label can be divided into two stages. In the first stage highly complete information on the energies and wave functions of the paramagnetic label P must be obtained. To this end a combined study (neutron scattering or Raman scattering measurements; magnetic susceptibility and specific heat mea-

surements) must be made of a reference single crystal of $P_I\{B\}$ ($\{B\}$ is the chemical formula without the paramagnetic label). In the second stage small quantities of the A ions in the compound $A_I\{B\}$ under investigation are replaced by the paramagnetic label P. Scrutiny of the temperature dependence of the relaxation of crystal-field levels of the paramagnetic label P in the compound $(A_{1-x}P_x)_I\{B\}$ can provide unique information regarding the electronic structure of the compound under investigation when several conditions are fulfilled. First, the inequality $x \ll 1$ is a necessary condition, which allows us to treat the relaxation of the crystal field at the paramagnetic label as a purely single-ion effect. Second, it must be shown that the structure of the crystal field of the paramagnetic label P in $(A_{1-x}P_x)_I\{B\}$ does not differ significantly from the structure of the crystal field in the pure reference crystal of $P_I\{B\}$. Fulfillment of the second condition has already been demonstrated for several compounds, in which the main contribution to the formation of the crystal field is made by the nearest neighbors from a formula unit of $\{B\}$, and hence the structures of the crystal fields of the paramagnetic label P in $P_I\{B\}$ and $(A_{1-x}P_x)_I\{B\}$ are practically identical. Examples of such compounds include RAI_3 ,^{9–11} RNi_5 ,^{12–14} and RNi ^{14–16} (R is a rare-earth ion).

It should be noted that the existing methods for calculating the temperature dependence of the relaxation of crystal-field states cannot be applied to the analysis of specific, highly correlated systems. Some of the methods employ the formal Hamiltonian, i.e., one which is not related in any way to the electronic structure, of the sf model.^{17–19} Another deficiency of the previously developed methods is the use of nonself-consistent second-order perturbation theory,^{17,18,20,21} which is inapplicable in the case of the large relaxation widths characteristic of highly correlated systems.

The goal of the present work is to devise a self-consistent theory for the relaxation of crystal-field levels, which can serve as a tool for studying the electronic structure of particular, highly correlated electronic systems with strong relaxation broadening. Section 2 presents the derivation of a microscopic interaction Hamiltonian, an analysis of the differences between it and the formal Hamiltonian of the sf model, and a discussion of the Coqblin–Schrieffer model. In Sec. 3 self-consistent equations are obtained for the natural relaxation widths of the crystal-field levels, and their influence on the cross section for magnetic inelastic neutron scattering is analyzed. In Sec. 4 qualitatively different types of temperature dependence of the relaxation width are classified. The effects associated with departure from the weak-relaxation approximation are analyzed in Sec. 5. In Sec. 6 the conditions which must be satisfied by the paramagnetic label are analyzed in detail, and experimental procedures which provide the most easily interpreted information are presented. The results of measurements of the relaxation widths of the crystal-field states of the paramagnetic label Pr^{3+} in the compounds $LaAl_3$ and $CeAl_3$ are considered in Sec. 7. The conclusions are presented in Sec. 8.

2. SPECIFIC DETAILS OF THE INTERACTION OF CRYSTAL-FIELD STATES WITH CONDUCTION ELECTRONS IN THE COQBLIN–SCHRIEFFER MODEL

The interpretation of the relaxation of a real paramagnetic label in a particular compound requires the formulation of a problem which takes into account both the specific details of the state of the impurity and the features of the electronic structure of the metal. Therefore, the sf exchange Hamiltonian, which is often employed to analyze the relaxation of crystal-field levels,^{17–19}

$$\mathcal{H}_{sf} = \sum_{MM'} (f_M^\dagger \hat{\mathbf{J}}_{MM'} f_{M'}) (c_\alpha^\dagger \boldsymbol{\sigma}_{\alpha\beta} c_\beta) \quad (1)$$

(where M and M' are the indices of the crystal-field states, α and β are the spin indices of the conduction electrons, $\hat{\mathbf{J}}$ is the total momentum operator, and $\boldsymbol{\sigma}$ denotes a Pauli matrix) is unsuitable for analyzing relaxation in a particular system, since it is a purely formal object, which is not related in any way to the features of the electronic structure of the metal or to the real character of the interaction of an impurity with conduction electrons.

The specific features of the relaxation occurring as a consequence of the interaction of an impurity with conduction electrons can be taken into account in the approaches^{22–25} based on the Schrieffer–Wolff and Cornut–Coqblin formalisms.^{26–28} A scheme permitting a first-principles calculation of the relaxation of a paramagnetic label can be devised within the method proposed in Refs. 22–25. The Anderson Hamiltonian describing an impurity ion¹⁾ with one f electron implanted in a metal is represented in the form of the sum

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1. \quad (2)$$

Here the first term

$$\begin{aligned} \mathcal{H}_0 = & \sum_{\theta\mathbf{k}\sigma} \epsilon_{\theta\mathbf{k}} c_{\theta\mathbf{k}\sigma}^\dagger c_{\theta\mathbf{k}\sigma} + \sum_M E_M f_M^\dagger f_M \\ & + \frac{U}{2} \sum_{MM'}^{M \neq M'} f_M^\dagger f_M f_{M'}^\dagger f_{M'} \end{aligned} \quad (3)$$

describes the subsystem of delocalized conduction electrons with consideration of the single-particle potential of the f subshell (which is treated as a core state) and the subsystem of the crystal field of the f subshell in the single-particle potential created by the conduction electrons. The operator $c_{\theta\mathbf{k}\sigma}^\dagger$ ($c_{\theta\mathbf{k}\sigma}$) describes the creation (annihilation) of a conduction electron with the energy $\epsilon_{\theta\mathbf{k}}$, whose state is characterized by the Bloch wave

$$|\theta\mathbf{k}\sigma\rangle = u_{\theta\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} |\sigma\rangle \quad (4)$$

with the wave vector \mathbf{k} , the band index θ , and the spin projection σ . The operator f_M^\dagger (f_M) describes the creation (annihilation) of the crystal-field state $|M\rangle$ with the energy E_M . The wave functions $|M\rangle$ of the states of an f electron transform in accordance with the irreducible representation Υ_M of the point group of the site of the rare-earth impurity ion \mathcal{S}_{imp} :

$$|M\rangle = \sum_{m=-J_{\text{imp}}}^{J_{\text{imp}}} \Lambda_{m,J_{\text{imp}}}^M |m\rangle. \quad (5)$$

Here the $|m\rangle$ are spherical harmonics, which describe the projections m of the total angular momentum of the impurity J_{imp} , and U is the on-site Coulomb repulsion constant.

For a microscopic calculation procedure we must represent the many-particle interaction of the localized and delocalized subsystems in terms of the nomenclature for the band states of conduction electrons, rather than in the approximation of symmetrized partial waves.^{27,28} In this nomenclature the interaction Hamiltonian

$$\mathcal{H}_1 = \sum_{\theta\mathbf{k}\sigma M} V_{\theta\mathbf{k}\sigma}^M f_M^\dagger c_{\theta\mathbf{k}\sigma} + \text{H.c.} \quad (6)$$

describes the mixing of the localized state $|M\rangle$ with the Bloch wave $|\theta\mathbf{k}\sigma\rangle$, and the hybridization parameter

$$V_{\theta\mathbf{k}\sigma}^M = \langle \theta\mathbf{k}\sigma | V_{\text{mix}}(\mathbf{r}) | M \rangle \quad (7)$$

can be calculated by a band-calculation procedure. In the case of an impurity state with a nearly integer valence (the hybridization scale $|V_{\theta\mathbf{k}\sigma}^M|$ is considerably smaller than the distance from the E_M and $E_M + U$ levels to the Fermi energy ϵ_F), the Coqblin–Schrieffer transformation,^{26,27} which eliminates the first order with respect to the hybridization from the Hamiltonian, is applicable. As a result, the interaction of the localized and delocalized subsystems is described by elastic and inelastic scattering processes of the conduction electrons on localized crystal-field states of the impurity:

$$\mathcal{H}_{\text{ex}} = \sum_{MM'} \sum_{\theta\mathbf{k}\sigma} \sum_{\theta'\mathbf{k}'\sigma'} J_{\theta\mathbf{k}\sigma, \theta'\mathbf{k}'\sigma'}^{MM'} f_M^\dagger f_{M'} c_{\theta\mathbf{k}\sigma}^\dagger c_{\theta'\mathbf{k}'\sigma'}. \quad (8)$$

The interaction constants of the effective Hamiltonian are expressed in terms of quantities which can be determined by band-calculation methods:^{22–25}

$$J_{\theta\mathbf{k}\sigma, \theta'\mathbf{k}'\sigma'}^{MM'} = \frac{V_{\theta\mathbf{k}\sigma}^{M'} (V_{\theta'\mathbf{k}'\sigma'}^M)^*}{2} \left[\frac{1}{\epsilon_{\theta\mathbf{k}} - E_M} + \frac{1}{\epsilon_{\theta'\mathbf{k}'} - E_{M'}} \right]. \quad (9)$$

Although the nomenclature of the band states of conduction electrons is adequate in cases where the problem is a first-principles calculation of the parameters, the nomenclature of symmetrized partial waves, which permits the use of symmetry arguments, is more convenient for qualitative analysis. As a result of the standard transformation into the representations $|\theta k M\rangle$ of the partial waves^{27,28}

$$c_{\theta\mathbf{k}\sigma}^\dagger = \sum_{kM''} \langle \theta\mathbf{k}\sigma | \theta k M'' \rangle c_{\theta k M''}^\dagger \quad (10)$$

(here $c_{\theta k M''}^\dagger$ is the annihilation operator of a conduction electron in the state centered on the impurity ion with the wave number k , the total angular momentum J_{imp} , and the angular dependence described by the irreducible representation $Y_{M''}$), the Hamiltonian of the exchange interaction can be represented in the form

$$\begin{aligned} \mathcal{H}_{\text{ex}} = & \sum_{MM'} f_M^\dagger f_{M'} \sum_{M''M'''} \sum_{kk'} \sum_{\theta\theta'} \Theta_{\theta k M''}^{\theta' k' M'''}(M, M') \\ & \times c_{\theta k M''}^\dagger c_{\theta' k' M'''} \end{aligned} \quad (11)$$

where

$$\begin{aligned} \Theta_{\theta k M''}^{\theta' k' M'''}(M, M') = & \sum_{\mathbf{k}\mathbf{k}'} \sum_{\sigma\sigma'} \langle \theta\mathbf{k}\sigma | \theta k M'' \rangle \\ & \times \langle \theta' k' M''' | \theta' \mathbf{k}' \sigma' \rangle J_{\theta\mathbf{k}\sigma, \theta' \mathbf{k}' \sigma'}^{MM'}. \end{aligned} \quad (12)$$

The only restriction which is imposed on the symmetry of the exchange interaction is the condition that the interaction (11) have the symmetry of the point group of the impurity site.³¹ Generally speaking, the seed basis of crystal-field states $\{|M\rangle\}$ obtained with consideration of only the single-particle crystal potential is not diagonal when the perturbation (11) is taken into account. In low-symmetry systems this perturbation can mix seed states of the crystal-field basis.³² Therefore, in the general case the relation

$$\Theta_{\theta k M''}^{\theta' k' M'''}(M, M') = \tilde{J}_{\theta k, \theta' k'}^{MM'} \delta_{M''M} \delta_{M'''M'}, \quad (13)$$

which reduces the exchange Hamiltonian to the standard Coqblin–Schrieffer expression in the partial-wave representation

$$\mathcal{H}_{\text{ex}} = \sum_{MM'} f_M^\dagger f_{M'} \sum_{kk'} \sum_{\theta\theta'} \tilde{J}_{\theta k, \theta' k'}^{MM'} c_{\theta k M}^\dagger c_{\theta' k' M'}, \quad (14)$$

is an artefact of the simplifying assumption that the mixing potential has spherical symmetry in the vicinity of the impurity. Nevertheless, even in the simplest approximation, in which the band index θ and the dependence on the wave number k are neglected (i.e., the band system of the conduction electrons is replaced by an effective density of states), the approximate Hamiltonian

$$\mathcal{H}_{\text{ex}} = \sum_{MM'} \bar{I}^{MM'} f_M^\dagger f_{M'} c_M^\dagger c_M, \quad (15)$$

which faithfully takes into account the principal features of the symmetry of the states of the delocalized electrons, differs significantly from the formal sf exchange Hamiltonian (1). When the relaxation width is calculated, the sf exchange Hamiltonian (1) induces only transitions with a change in the projection of the total angular momentum of the impurity by unity or without any change in its projection. The relative values of the matrix elements specifying the transitions $|M'\rangle \rightarrow |M\rangle$ do not depend on the features of the electronic structure and are determined only by the properties of the Pauli matrices and the structure of the wave functions $|M\rangle$ of the localized states. Conversely, all the quantities appearing in the Hamiltonian (11) can be calculated for a specific impurity in a specific crystal, and the parameters of the approximate Hamiltonian (15) are obtained by averaging (11). Thus, in the general case the Hamiltonian (15) has nonzero matrix elements for the transition between any local states $|M\rangle$ and $|M'\rangle$, and the relations between the different matrix elements $\bar{I}^{MM'}$ are determined by the localized states of both the crystal field of the impurity and the band structure of the conduction electrons.

The calculation of the averaged parameters $\bar{I}^{MM'}$ can be performed by the methods described in Refs. 22–25 and is

beyond the scope of the present work. In this paper we wish to analyze which features of the temperature dependence of the relaxation widths of the crystal-field levels can be observed for various relations between the symmetrized exchange constants $\bar{T}^{MM'}$ of the Hamiltonian (15).

3. RELAXATION WIDTHS OF CRYSTAL-FIELD LEVELS AND THEIR INFLUENCE ON THE WIDTHS OF THE PEAKS FOR NEUTRON TRANSITIONS

The relaxation width Γ_{if} associated with the transition $|i\rangle \rightarrow |f\rangle$ is determined by the natural widths γ_i and γ_f of the initial $|i\rangle$ and final $|f\rangle$ states. It should be noted that the natural widths are determined not only by the mutual relaxation processes of the initial and final states $|i\rangle \leftrightarrow |f\rangle$, but also by the processes $|i\rangle \leftrightarrow |M\rangle$ ($|f\rangle \leftrightarrow |M\rangle$), which are associated with the interaction of the initial (final) states with all the other crystal-field states $\{|M\rangle\}$. In this case the natural width of the initial (final) state is determined by the set of parameters $\{\bar{T}^{iM}\}$ ($\{\bar{T}^{fM}\}$) of the Hamiltonian (15).

Let us consider the process responsible for the inelastic neutron transition $|i\rangle \rightarrow |f\rangle$ from the initial state $|i\rangle$ with the energy E_i to the final state with the energy $E_f = E_i + \Delta_{fi}$. We introduce the Matsubara Green's functions describing the crystal-field states of the impurity center j and the Green's functions of similar nature for Abrikosov pseudofermions,³³

$$\mathcal{G}_\lambda = -\langle T_\pi f_{j,M}(\tau) f_{j,M}^\dagger(0) \rangle, \quad (16)$$

which have the following forms in the zeroth approximation (i.e., in the absence of relaxation):

$$\mathcal{G}_i^{(0)} = (i\omega - E_i + \mu)^{-1}, \quad (17)$$

$$\mathcal{G}_f^{(0)} = (i\omega - E_i - \Delta_{fi} + \mu)^{-1} \quad (18)$$

(in the notation adopted μ is the chemical potential of the pseudofermions, and in the final formulas it must be assumed that $\mu \rightarrow -\infty$).

The retarded Green's functions, which specify the spectral response of the system, can be obtained using the analytic continuation of the Matsubara Green's functions from the upper semiaxis onto the entire complex plane of ω . Passage to the retarded Green's functions in the zeroth-order Green's functions requires the replacement $i\omega \rightarrow \omega + i\delta$. The interactions of the crystal-field states with other subsystems of elementary excitations of the crystal lead to renormalization of the crystal-field energy and to the appearance of a frequency-dependent imaginary part in the denominator of the Green's function. The renormalizations of the crystal-field splittings can be included in the definition of the Green's functions (17) and (18) and will not be considered further. Let us next concentrate our attention on the temperature dependence of the relaxation width and take into account that the retarded Green's functions of the crystal-field levels can be written in the pole approximation in the form

$$\mathcal{G}_i^R(\omega) = [\omega - E_i + \mu + i\gamma_i(\omega)]^{-1}, \quad (19)$$

$$\mathcal{G}_f^R(\omega) = [\omega - E_i - \Delta_{fi} + \mu + i\gamma_f(\omega)]^{-1}. \quad (20)$$

The on-site susceptibility, which determines the magnetic neutron response of an impurity center, is expressed³³ in terms of the retarded Green's function

$$\chi_{if}^R(\tau) = -\langle T_\pi f_i^\dagger(\tau) f_f(\tau) f_f^\dagger(0) f_i(0) \rangle,$$

whose analytic continuation onto real frequencies has the following form:

$$\chi_{if}^{(0)R}(\Omega) = -|\Theta_{if}|^2 \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} \tanh\left(\frac{\epsilon}{2T}\right) [\text{Im } \mathcal{G}_i^R(\epsilon) \times \mathcal{G}_f^R(\epsilon + \Omega) + \text{Im } \mathcal{G}_f^R(\epsilon) \mathcal{G}_i^A(\epsilon - \Omega)] \quad (21)$$

(here Θ_{if} is a matrix element, which depends on the wave functions of the initial and final crystal-field states and determines the intensity of the neutron scattering peak). Representing the resonant part of the susceptibility $\chi_{if}^R(\Omega)$ at $\Omega \approx \Delta_{fi}$ in the form

$$\chi_{if}^R(\Omega) = \frac{\Xi_0}{\Omega - \Delta_{fi} + i\Gamma_{if}}, \quad (22)$$

where Ξ_0 is the residue at the respective pole), we can obtain the dependence of Γ_{if} on the corresponding natural dampings of the pseudofermion Green's functions. In the limit $\gamma_{i,f} \ll \Delta_{fi}$ or $\gamma_{f,i} \ll T$ the relation between the relaxation constant Γ_{if} extracted from the results of magnetic inelastic neutron scattering experiments and the natural damping of the pseudofermion Green's functions acquires a simple form:

$$\Gamma_{if} = \gamma_i(\omega = E_i) + \gamma_f(\omega = E_f). \quad (23)$$

Thus, in the cases which are most interesting for a reliable experimental analysis (where the width of the inelastic transition is smaller than its energy) the problem of determining the temperature dependence of the width Γ_{if} of a transition reduces to a calculation of the natural widths of the initial and final states.

Let us consider the influence of conduction electrons on the natural width of crystal-field states in the Cornut–Coqblin model. For this purpose we use the effective Hamiltonian (15) obtained in the preceding section as the interaction Hamiltonian. The natural widths are calculated by standard Feynman-diagram techniques at finite temperatures. This allows us to partially sum diagram series and to obtain a closed system of self-consistent equations. The departure from perturbation theory is critical in the case of fairly strong relaxation, since the natural width $\gamma_M(\omega = E_M)$ of each crystal-field state $|M\rangle$ depends on the relaxation widths of the entire system of crystal-field levels and must, therefore, be found self-consistently. To illustrate this point, we consider the interaction between the states $|M\rangle$ and $|M'\rangle$ with the energies E_M and $E_{M'} = E_M + \Delta_{M'M}$, respectively. The simplest diagram which leads to relaxation of the crystal-field states is shown in Fig. 1a. The dashed line correspond to the Green's function of the conduction electron

$$G(\mathbf{r}, \tau) = -\langle T_\tau \Psi_\xi(\mathbf{r}, \tau) \Psi_\xi^\dagger(0, 0) \rangle, \quad \xi = M, M' \quad (24)$$

(we neglect the difference between the Green's functions of the conduction electrons for different M). The diagrams corresponding to the vertex corrections can be classified in the following manner. The first are parquet diagrams, which are

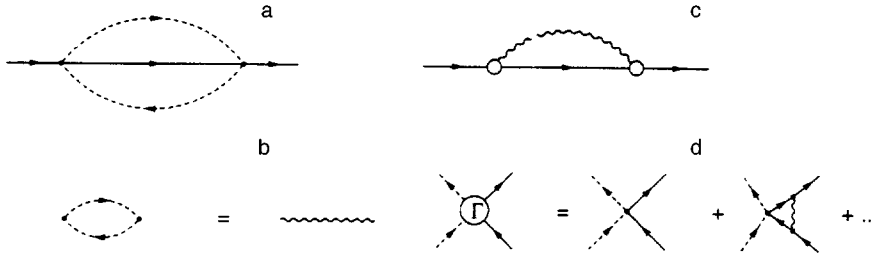


FIG. 1. Feynman diagrams: a—simple diagram describing the shift and damping of a crystal-field level (dashed line—conduction electron Green's function, solid line—crystal-field excitations); b—conduction electron polarization operator, which describes the electromagnetic interaction between crystal-field excitations; c—eigenenergy part of the crystal-field excitations with consideration of the vertex renormalization; d—skeletal diagrams for vertex corrections.

similar to the Abrikosov diagrams considered in the analysis of the Kondo effect in Ref. 33. Consideration of the contribution from the first nonvanishing term leads to the appearance of an interaction in the channel $\Gamma_{M=M'} \sim (I_{MM'}^2/W) \ln(W/\Delta_{MM'})$ and to the corrections $\delta\Gamma_{MM'}^{(3,p)} \sim (I_{MM'}^3/W^2) \ln^2(W/\Delta_{MM'})$ (W is the width of the conduction electron band). The second are nonparquet diagrams.³⁴ Consideration of the contribution from the first correction (Fig. 1d) leads to the additional contribution $\delta\Gamma_{MM'}^{(3,pp)} \sim (I_{MM'}^3/W^2) \ln(W/\Delta_{MM'})$. We shall henceforth assume $I_{MM'}/W \ll 1$ and $(I_{MM'}/W) \ln(W/\Delta_{MM'}) \ll 1$ and neglect the vertex corrections in the perturbative approach. Under these circumstances

$$\sigma_M(i\omega_n) = [\bar{I}^{MM'}]^2 T^2 \sum_{\epsilon_1 \epsilon_2} \frac{1}{\mathcal{N}^2} \sum_{\mathbf{p}_1, \mathbf{p}_2} G(\mathbf{p}_1, \epsilon_1) G(\mathbf{p}_2, \epsilon_2) \times \mathcal{S}_{M'(\neq M)}(\epsilon_1 + \epsilon_2 - \omega) \quad (25)$$

(\mathcal{N} is the total number of conduction electrons). Performing the analytic continuation of the expression (25) into the upper half-plane of the complex variable ω according to the usual rules,^{35–37} we obtain the following expressions for the eigenenergy parts at real frequencies (the analogous equations for the sf exchange Hamiltonian were obtained by Maleev in a treatment of the relaxation of the crystal field in cubic metals¹⁹):

$$\begin{aligned} \gamma_M(\omega) &= -\text{Im} \sigma_M^R(\omega) \\ &= \frac{1}{\pi} [\bar{I}^{MM'}]^2 \int_{-\infty}^{\infty} dx \frac{1}{\mathcal{N}} \sum_{\mathbf{p}} [N(x) + n(x + \omega)] \text{Im} \mathcal{S}_{M'(\neq M)}^R(x + \omega) \text{Im} \Pi_{MM'}^R(\mathbf{p}, x). \end{aligned} \quad (26)$$

Here $N(x) = (e^{x/T} - 1)^{-1}$, $n(x) = (e^{x/T} + 1)^{-1}$, $\Pi(\mathbf{p}, x)$ is the polarization operator of the conduction electrons (Fig. 1b), whose imaginary part describes the two-particle density of states:

$$\text{Im} \frac{1}{\mathcal{N}} \sum_{\mathbf{p}} \Pi^R(\mathbf{p}, x) = -\frac{\pi}{2} N_0^2 x, \quad (27)$$

where N_0 is the single-particle density of states of the conduction electrons at the Fermi level, in terms of which the dimensionless coupling constants $g_{MM'}$ are expressed:

$$g_{MM'}^2 = \frac{1}{2} [I^{MM'} N_0]^2. \quad (28)$$

In the integrals (26) we perform the replacement $\omega + \mu = \tilde{\omega}$ corresponding to the displacement of the energy reference point. Allowing μ to tend to $-\infty$, we neglect the Fermi function on the right-hand side. This replacement has a simple physical meaning: the singularities of the functions \mathcal{S} are determined by a far larger energy scale, and, therefore, the terms corresponding to consideration of the poles of the pseudofermion functions should be omitted.³⁸

According to (23), the natural damping γ of the crystal-field states at the frequencies corresponding to the energies of the crystal-field levels must be calculated to determine the width of a neutron transition. Thus, in the case of the interaction of $|M\rangle$ and $|M'\rangle$, the quantities $\gamma_M(\omega = E_M)$ and $\gamma_{M'}(\omega = E_{M'})$ must be calculated. Determining the damping at the poles of the corresponding Green's functions, we obtain the system of coupled equations

$$\begin{cases} \gamma_M(\omega \rightarrow E_M) = \pi g_{MM'}^2 \int_{-\infty}^{\infty} dx x N(x) P \\ \quad \times (x - \Delta_{M'M}, \gamma_{M'}), \\ \gamma_{M'}(\omega \rightarrow E_{M'} + \Delta_{M'M}) = \pi g_{MM'}^2 \int_{-\infty}^{\infty} dx x N(x) \\ \quad \times P(x + \Delta_{M'M}, \gamma_M), \end{cases} \quad (29)$$

where $P(x, \gamma)$ is the spectral function normalized to unity:

$$P(x, \gamma) = \frac{1}{\pi} \frac{\gamma}{x^2 + \gamma^2}. \quad (30)$$

The expressions obtained are easily generalized to the case of an arbitrary set of constants in the Hamiltonian (15) ($\{I^{MM'}\}$; $M, M' = 1, \dots, 2J_{\text{imp}} + 1$) and an arbitrary system of crystal-field states with the energies E_M . Proceeding precisely as in the derivation of (25)–(29), we obtain the expressions for the frequency-dependent damping rates

$$\begin{aligned} \gamma_M^R(\omega) &= -\text{Im} \sigma_M^R(\omega) \\ &= \frac{1}{\pi} \sum_{M'=1}^{2J_{\text{imp}}+1} I_{MM'}^2 \int_{-\infty}^{\infty} dx \frac{1}{\mathcal{N}} \sum_{\mathbf{p}} [N(x) + n(x + \omega)] \text{Im} \mathcal{S}_{M'}^R(x + \omega) \text{Im} \Pi_{MM'}^R(\mathbf{p}, x), \\ M &= 1, \dots, 2J_{\text{imp}} + 1. \end{aligned} \quad (31)$$

Neglecting the Fermi function on the right-hand side of (31), we obtain the system of self-consistent equations

$$\gamma_M(\omega) = - \sum_{M'=1}^{2J_{\text{imp}}+1} g_{MM'}^2 \int_{-\infty}^{\infty} dx x N(x) \text{Im} \mathcal{E}_{M'}^R(x + \omega),$$

$$M = 1, \dots, 2J_{\text{imp}} + 1. \quad (32)$$

Here the dimensionless coupling constants are expressed in terms of the parameters of the Hamiltonian (15):

$$g_{MM'}^2 = g_{M'M}^2 = \frac{1}{2} [I^{MM'} N_0^{MM'}]^2, \quad (33)$$

where $N_0^{MM'}$ is the partial density of states of the conduction electrons corresponding to the $M \rightarrow M'$ transition.

The system of equations for finding the natural relaxation constants at the frequencies which determine the widths of the neutron transitions [see (23)] can be represented in the explicit form²⁾

$$\gamma_M(\omega \rightarrow E_M) = \int_{-\infty}^{\infty} dx x N(x) \times \sum_{M'=1}^{2J_{\text{imp}}+1} g_{MM'}^2 P(x - \Delta_{M'M}, \gamma_{M'}),$$

$$M = 1, \dots, 2J_{\text{imp}} + 1, \quad (34)$$

where

$$\Delta_{M'M} = E_{M'} - E_M.$$

4. CLASSIFICATION OF THE TEMPERATURE DEPENDENCE OF RELAXATION WIDTHS

The temperature dependence of the natural relaxation widths (and the widths of the neutron transitions determined by them) depends on the relationship between the different constants in the Hamiltonian (15) and on the energies of the crystal-field states. In this section we shall classify the types of temperature dependence for cases in which solutions of the self-consistent system of equations (34) can be obtained explicitly.

The simplest condition under which the system of equations (34) is decoupled is that the relaxation widths be small ($\gamma_M \rightarrow 0$). In this case, instead of the system of equations (32), we obtain the following expressions for the non-self-consistent widths of the levels $\gamma_M^{(0)}$:

$$\gamma_M^{(0)} = \pi \sum_{M'=1}^L \int_{-\infty}^{\infty} g_{MM'}^2 x N(x) \delta(x - \Delta_{MM'}). \quad (35)$$

The calculation of (35) permits separation of the contributions to the temperature dependence of the natural width $\gamma_M(T)$ into three types:

$$\gamma_M(T) = \gamma_M^{(\text{eq})}(T) + \gamma_M^\uparrow(T) + \gamma_M^\downarrow(T). \quad (36)$$

The first type is associated with the relaxation caused by the interaction of the crystal-field state $|M\rangle$ with the levels $\{|M'\rangle\}$, whose energies $E_{M'}$ equal E_M :

$$\gamma_M^{(\text{eq})}(T) = \pi T \sum_{M'}^{E_{M'}=E_M} g_{MM'}^2. \quad (37)$$

The contributions to the natural relaxation width of the level $|M\rangle$ from higher-lying ($E_{M'} > E_M$) and lower-lying ($E_{M'} < E_M$) levels are given by the expressions

$$\gamma_M^\uparrow(T) = \pi \sum_{M'}^{E_{M'} > E_M} g_{MM'}^2 \Delta_{M'M} N(\Delta_{M'M}) \quad (38)$$

and

$$\gamma_M^\downarrow(T) = \pi \sum_{M'}^{E_{M'} < E_M} g_{MM'}^2 \Delta_{MM'} [N(\Delta_{MM'}) + 1], \quad (39)$$

respectively. In the limit of high temperatures, $T \gg \max(E_M)$, in accordance with the results in Refs. 17–21, the temperatures dependences of all three contributions to the relaxation are indistinguishable. All three contributions obey a Korringa law, and the expression for the natural relaxation width takes the form

$$\gamma_M(T) = \pi T \sum_{M'=1}^{2J_{\text{imp}}+1} g_{MM'}^2. \quad (40)$$

At low temperatures the contributions of the higher-lying ($E_{M'} > E_M$) and lower-lying ($E_{M'} < E_M$) crystal-field levels differ significantly. In the limit $T \rightarrow 0$, $N(\Delta)$ is exponentially small, $N(\Delta) \rightarrow \exp(-\Delta/T)$, and (38)–(39) take the form

$$\gamma_M^\uparrow(T) = \pi \sum_{M'}^{E_{M'} > E_M} g_{MM'}^2 \Delta_{M'M} \exp\left(-\frac{\Delta_{M'M}}{T}\right), \quad (41)$$

$$\gamma_M^\downarrow(T) = \pi \sum_{M'}^{E_{M'} < E_M} g_{MM'}^2 \Delta_{MM'}. \quad (42)$$

Thus, as $T \rightarrow 0$, the contributions to the natural relaxation width from the higher-lying levels tend exponentially to zero, and the contributions from the lower-lying levels do not depend on the temperature.

Since the shape of the line for the neutron transition $|i\rangle \rightarrow |f\rangle$ is measured directly in an experiment, it would be interesting to analyze the temperature dependence of the width of the transition $\Gamma_{i \rightarrow f}(T) = \gamma_i(T) + \gamma_f(T)$ (see Fig. 2) for different relationships between the constants of the Hamiltonian (1). The diagonal interactions I^{ii} (I^{ff}) lead to a contribution $\sim \pi g_{ii}^2 T$ ($\sim \pi g_{ff}^2 T$), which is proportional to the temperature. In the case of the relaxation of only the initial (final) state as a result of interactions with the upper (\uparrow) levels, we have $[\Gamma_{i \rightarrow f}^\uparrow(T)]^{i(f)} \sim N(\Delta_{\uparrow i(f)})$, which leads to exponentially small damping, $\sim \exp(-\Delta_{\uparrow i(f)}/T)$, at low temperatures. When only the initial (final) state relaxes as a result of interactions with lower (\downarrow) levels, we have $[\Gamma_{i \rightarrow f}^\downarrow(T)]^{i(f)} \sim \Delta_{i(f)\downarrow} [N(\Delta_{i(f)\downarrow}) + 1]$, which can be described by a constant $\sim \Delta_{i(f)\downarrow}$ at low temperatures. The fourth special case is the one in which relaxation is mediated by the interaction between the initial and final states I^{if} . In this case $\Gamma_{i \rightarrow f}^{if}(T) \sim \Delta_{fi} [2N(\Delta_{fi}) + 1] = \Delta_{fi} \cosh(\Delta_{fi}/2T)$.

If the special cases just described are realized in the system being studied, they are easily distinguished from one another even by qualitative visual inspection. The situation in which relaxation of the initial and final levels occurs only because of the influence of the higher-lying levels is easily distinguished (the dotted line in Fig. 3). In this case

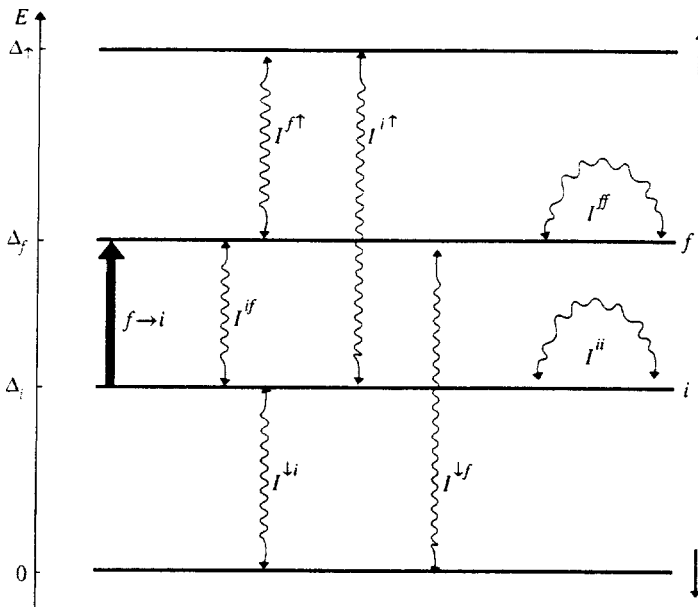


FIG. 2. General case of the classification of sources for the relaxation of the levels of the initial (*i*) and final (*f*) states of a transition (thick vertical arrow) due to interactions with lower-lying levels (I^{li} and I^{lf}) and higher-lying levels (I^{li} and I^{lf}) and due to mutual coupling of the initial and final states (I^{if} , wavy lines).

$\Gamma_{i \rightarrow f}^\uparrow(T \rightarrow 0) \rightarrow 0$. The mutual relaxation processes (the solid line in Fig. 3) are also visually distinguishable from the variants in which the broadening is a consequence of the interactions of the initial or final state with lower-lying levels (the dashed line in Fig. 3). The sharpness of the temperature dependence can serve as a criterion in these cases. In the former variant (see Fig. 3) we have $\Gamma_{i \rightarrow f}^{if}(T = 2\Delta_{MM'}) / \Gamma_{i \rightarrow f}^{if}(T = 0) \approx 4$, and in the latter variant we have $\Gamma_{i \rightarrow f}^\downarrow(T = 2\Delta_{MM'}) / \Gamma_{i \rightarrow f}^\downarrow(T = 0) \approx 2.5$.

5. CONSEQUENCES OF THE SELF-CONSISTENT PROCEDURE

Beside the obvious quantitative influence of the self-consistent procedure manifested as renormalization of the numerical values of the natural relaxation constants, there is a qualitative difference, which is expressed by the nonzero value of the relaxation width of the ground state $|G\rangle$ at zero temperature.

In the non-self-consistent procedure [see (41)] the width $\gamma_G^{(0)}(T \rightarrow 0) = \pi g_{GE}^2 \Delta_{EG} \exp(-\Delta_{EG}/T) \rightarrow 0$ (E is the higher-lying level with the smallest value of Δ_{EG}). The solution of the system of self-consistent equations (29) (for $M = G$, $M' = E$) gives a nonzero width: $\gamma_G^{(sc)}(T = 0) \neq 0$. Under the conditions $T \ll \gamma_{EG}$ and $T \ll \Delta_{EG}$ an explicit expression can be obtained for the width $\gamma_G^{(sc)}(T = 0)$ of the level. Since at low temperatures the non-self-consistent natural width of the crystal-field excited level is $\gamma_E^{(0)}(T \rightarrow 0) = \pi g_{GE}^2 \Delta_{EG}$, the weak corrections caused by the influence of the lower level can be neglected. Then the self-consistent width of the lower level is proportional to the square of the coupling constant:

$$\gamma_G^{(sc)} \approx \pi g_{GE}^2 \gamma_E^{(0)} \ln\left(\frac{W}{\Delta_{GE}}\right) \tag{43}$$

(in the calculation we cut off the integral (29) at the width of the conduction electron band W). Substituting the expression for $\gamma_E^{(0)}$ into (43), we obtain³⁾

$$\gamma_G^{(sc)} \approx \pi^2 g_{GE}^4 \Delta_{EG} \ln\left(\frac{W}{\Delta_{GE}}\right). \tag{44}$$

Since the corrections associated with the influence of the width of the lower level on the upper level contain an additional small factor $\sim g_{GE}^2$, (43) is the explicit solution of the system of self-consistent equations to within terms $\sim g_{GE}^4$ inclusively.

This result, which is unexpected from the standpoint of perturbation theory, can have a physical interpretation in the self-consistent theory. It should, first of all, be taken into account that $|G\rangle$ is the ground state of the system only when the interactions are disregarded. When the interaction with the delocalized conduction electrons is included, the nomenclature of the localized states is no longer the true quantum-mechanical basis, and $|G\rangle$ is not the true ground state.

A specific mechanism, which causes damping of the crystal-field state $|G\rangle$ at zero temperature, can be pointed out. The physical cause of the damping of $|G\rangle$ is the nonzero broadening of the excited state $|E\rangle$ (which also occurs in perturbation theory). Figure 4 presents the spectral functions of $|E\rangle$ [$P(x - 1, \gamma_E^{(0)} = 0.4)$] and $|G\rangle$ [$P(x, \gamma_G^{(0)} = 0) = \delta(x)$] in the perturbative approximation. The width of $|G\rangle$ in the

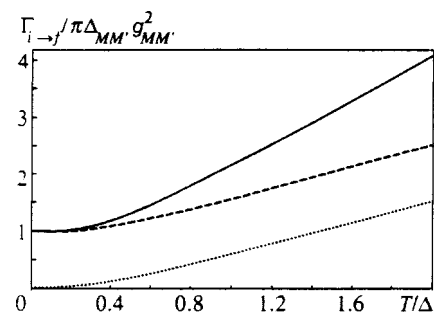


FIG. 3. Reduced temperature dependences of the total inelastic scattering width Γ_{if} due to relaxation processes with a higher-lying level (dotted line) and a lower-lying level (dashed line) and mutual processes (I^{if} , solid line).

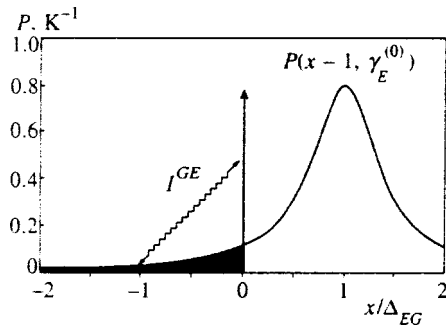


FIG. 4. Illustration of the origin of the finite width of the crystal-field ground state $|G\rangle$ (vertical arrow at $x/\Delta_{EG}=0$) due to relaxation processes (wavy lines with arrows) which couple the $|G\rangle$ level to the low-energy tail (darkened region) of the spectral function $P(x-1, \gamma_E^{(0)} \neq 0)$ of the upper $|E\rangle$ state.

self-consistent approach is nonzero ($\gamma_G^{(sc)} \neq 0$) because of the allowed transitions I^{GE} induced by the width of the upper level $|E\rangle$ to the low-energy tail (the darkened area in Fig. 4) of the Lorentzian contour of the upper level.

The result obtained, which attests to the nonzero contribution to the natural relaxation width of the ground-state level, calls for caution in approaching methods for estimating the characteristic temperature T^* in Kondo systems from the full width at half maximum (FWHM) of the quasielastic neutron scattering peak at zero temperature. According to the generally accepted approach,^{39,40} the characteristic temperature is determined from the relation $T^* = \Gamma_{qe}^{exp}(T=0)/2$, where $\Gamma_{qe}^{exp}(T=0)$ is the experimentally observed quasielastic scattering width at zero temperature. In this procedure it is assumed that the width of the peak $\Gamma_{qe}^{exp}(T=0)$ is determined only by the anomalous width $\Gamma_K(T=0)$, which is associated with Kondo scattering processes on the lowest crystal-field state. However, the presence of the nonzero contribution $\gamma_G^{(sc)}(T=0)$ from the normal relaxation processes calls for additional refinement in the case of strong relaxation broadening in systems with soft crystal fields. In this situation, since the experimental width $\Gamma_{qe}^{exp}(T=0)$ is determined not only by the anomalous width $\Gamma_K(T=0)$, but also by the relaxation contribution $\gamma_G^{(sc)}(T=0)$, we have

$$\Gamma_{qe}^{exp}(T=0) = \Gamma_K(T=0) + 2\gamma_G^{(sc)}(T=0), \quad (45)$$

and the standard relation should be rewritten in the form

$$T^* = \frac{\Gamma_{qe}^{exp}(T=0) - 2\gamma_G^{(sc)}(T=0)}{2}. \quad (46)$$

Thus, when there is strong relaxation in systems with soft crystal fields, the determination of the characteristic temperature is complicated by the nonzero relaxation contribution at $T=0$. Nevertheless, the use of (46) and (44) provides an estimate in this case too. To analyze the contribution from the normal relaxation processes of a specific compound, we must determine the parameters (the crystal-field splitting $\Delta_{MM'}$ and the dimensionless relaxation constants $g_{MM'}$) which describe the relaxation in the particular material. The set of techniques discussed in the next section can be useful in solving this problem.

6. PARAMAGNETIC LABELING

Studying the electronic structure by measuring the relaxation of a paramagnetic label requires the observance of several conditions, which must be satisfied by the compound being studied $A_l\{B\}$ and the paramagnetic ion P. In this section we describe the most desirable general conditions, under which performing and interpreting paramagnetic labeling experiments are simplest, and we present some examples of compounds which satisfy these necessary conditions.

One necessary condition which must be satisfied by the compound $A_l\{B\}$ being studied is the existence of a reference compound $P_l\{B\}$ containing the paramagnetic label P. The reference compound must be a structural analog of the compound being studied. In the first stage the properties of the reference compound $P_l\{B\}$ must be investigated. The purpose of studying the reference compound is to obtain information on the crystal-field energies and wave functions of the paramagnetic label. This information can be obtained by analyzing experimental data from measurements of magnetic neutron scattering (or Raman scattering) and the thermodynamic properties (the magnetic susceptibility and specific heat). For neutron scattering experiments, which require a fairly large quantity of the material, it should be noted that a single-crystal sample is not required. This greatly facilitates implementation of the method, since magnetic susceptibility data suitable for reconstructing the crystal-field wave functions can be obtained from measurements on tiny single-crystal samples.

In the second stage, for which a polycrystalline sample suffices, inelastic neutron scattering experiments are performed on the compound $(A_{1-x}P_x)_l\{B\}$. The theoretical analysis requires information on the crystal-field states of the paramagnetic label P in $(A_{1-x}P_x)_l\{B\}$. The experimental neutron scattering data provide information on the energies of the crystal-field levels of the paramagnetic label in the compound being studied. Since it is impossible to study the crystal-field states of an ion of P in $(A_{1-x}P_x)_l\{B\}$ by thermodynamic methods, additional information on the crystal-field wave functions is needed. This information can be obtained by studying the trends in the variation of the crystal-field parameters of a family of compounds $R_l\{B\}$ (where $R=A, P, \dots$). There are presently several families of compounds for which such investigations have already been performed: RA_3 ,⁹⁻¹¹ RNi_5 ,¹²⁻¹⁴ and RNi .¹⁴⁻¹⁶ (R is a rare-earth ion). In these families the main contribution to the formation of the crystal field is made by the ions in the local environment and the conduction electrons. Therefore, the structures of the crystal-field wave functions of the paramagnetic label P in the reference compound and in the compound being studied are practically identical. Thus, the systems which are suitable for the proposed procedure are compounds in which the nearest neighbors of each ion of A that is replaced by the paramagnetic label are ions from an unsubstituted formula unit of $\{B\}$. The best systems for application of the method are materials in which the crystal-field parameters are determined predominantly by the nearest neighbors.

The next necessary condition is a small concentration of the ions of the paramagnetic label, $x \ll 1$, in $(A_{1-x}P_x)_l\{B\}$.

This condition permits consideration of the crystal fields and their relaxation as purely single-ion phenomena. A small value of x is also necessary to be sure that doping with the paramagnetic label did not lead to significant alteration of the electronic structure of the compound being studied.

An important desirable restriction imposed on the paramagnetic label is nondegeneracy of the crystal-field ground state of the ion. Fulfillment of this condition significantly simplifies the interpretation of the experimental data, since the natural width of the crystal-field ground state is specified by a simple exchange Hamiltonian of the form (15). A degenerate ground state $|G\rangle$ can lead to a Kondo effect, which results in the appearance of a specific temperature dependence of the quasielastic neutron scattering width: $\Gamma_{qe}(T) = 2\gamma_G(T) = a + b\sqrt{T}$.⁴⁰ The presence of a specific temperature dependence of the natural width of the crystal-field ground state greatly complicates the interpretation, since the width $\Gamma_{GM}(T) = \gamma_G(T) + \gamma_M(T)$ of any inelastic transition from the ground state contains this poorly studied component. This circumstance greatly complicates the analysis, since the theoretical treatment is simplest, if the temperature dependence of the natural widths $\gamma_M(T)$ of the levels is determined during the experiment. This dependence can be extracted from the solution of the system of equations

$$\Gamma_{MM'}(T) \approx \gamma_M(T) + \gamma_{M'}(T), \quad (47)$$

whose features must be analyzed separately for each specific case.

It is also noteworthy that one of the significant advantages of the method can be the possibility of regulating the selection rules by choosing different paramagnetic labels. It can easily be seen that different symmetries for the crystal-field states of the paramagnetic label will lead to different types of temperature dependence of the relaxation process. Therefore, significant information can be obtained by analyzing situations with different ions serving as the paramagnetic label in relaxation spectroscopy.

7. RELAXATION OF THE PARAMAGNETIC LABEL Pr^{3+} IN $\text{Pr}_{0.03}\text{Ce}_{0.97}\text{Al}_3$ AND $\text{Pr}_{0.03}\text{La}_{0.97}\text{Al}_3$

An example of a favorable combination of properties for the paramagnetic label and the compound being studied is the Pr^{3+} ion in the hexagonal compounds RAl_3 (R is a lanthanide). The crystal-field ground state (level 1 in Fig. 5) in pure PrAl_3 is the singlet $|\Gamma_1\rangle = |0\rangle$, and the only allowed transition at $T \rightarrow 0$ is the $|\Gamma_1\rangle \rightarrow |\Gamma_6\rangle$ transition to the $|\Gamma_6\rangle = |\pm 1\rangle$ state (level 2 in Fig. 5). The crystal fields of the praseodymium ion in PrAl_3 were studied in detail in Ref. 9 (see Fig. 5, in which the crystal-field levels are numbered from 1 to 6 in order of increasing energy). The singlet character of the ground state rules out both the Korringa relaxation channel $\sim |I^{11}|^2$ and the relaxation channel associated with Kondo processes.

The relaxation of the paramagnetic label Pr^{3+} was studied in $\text{Pr}_{0.03}\text{Ce}_{0.97}\text{Al}_3$ and $\text{Pr}_{0.03}\text{La}_{0.97}\text{Al}_3$. The crystal-field splitting energy of the praseodymium ion Δ_{21} in both $\text{Pr}_{0.03}\text{Ce}_{0.97}\text{Al}_3$ and $\text{Pr}_{0.03}\text{La}_{0.97}\text{Al}_3$ differs only slightly from the crystal-field energy $\Delta_{21}^R \approx 4.5$ meV in the reference com-

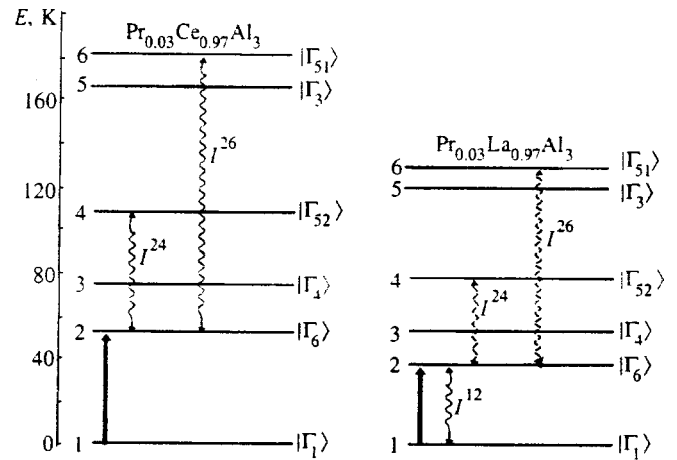


FIG. 5. Level scheme of the paramagnetic label Pr^{3+} in CeAl_3 (on the left) and LaAl_3 (on the right). Wave functions of the levels:⁹ $|\Gamma_1\rangle = |0\rangle$; $|\Gamma_6\rangle = |\pm 1\rangle$; $|\Gamma_4\rangle = 2^{-1/2}|3\rangle - 2^{-1/2}| -3\rangle$; $|\Gamma_{52}\rangle = a|\pm 4\rangle - \sqrt{1-a^2}|\mp 2\rangle$; $|\Gamma_3\rangle = 2^{-1/2}|3\rangle + 2^{-1/2}| -3\rangle$; $|\Gamma_{51}\rangle = \sqrt{1-a^2}|\pm 4\rangle + a|\mp 2\rangle$. The neutron transition studied in Ref. 9 is denoted by a vertical arrow. The postulated relaxation channels affecting the initial and final states are denoted by wavy lines with arrows.

ound PrAl_3 . More specifically, in $\text{Pr}_{0.03}\text{Ce}_{0.97}\text{Al}_3$ $\Delta_{21} \approx 4.2$ meV, and in $\text{Pr}_{0.03}\text{La}_{0.97}\text{Al}_3$ $\Delta_{21} \approx 3.5$ meV. Therefore, in the simplest approximation the wave functions of the crystal-field states of the paramagnetic label in the compounds studied can be assumed to be only slightly altered from those in the reference. To describe the relaxation of the paramagnetic label in CeAl_3 , we selected a system of levels which coincides with the crystal-field system in pure PrAl_3 , and to analyze the relaxation in LaAl_3 , we chose a system in which all the splitting energies are reduced by a factor of $3.2/4.5 \approx 0.711$ (see Fig. 5). The thoroughly studied laws governing the variation of the crystal field of the paramagnetic label in $\text{Pr}(\text{La})\text{Al}_3$ (Refs. 9 and 10) can be used for a more exact calculation.

In the experiments in Ref. 11 measurements of the temperature dependence of only the transition width $\Gamma_{12}(T)$ were performed (the FWHM of the Lorentzian, which corresponds to 2Γ in our notation, was measured in Ref. 11), while the natural relaxation widths $\gamma_1(T)$ and $\gamma_2(T)$ were not distinguished. Nevertheless, even in this case definite conclusions regarding the difference between the relaxation behavior of the paramagnetic label in CeAl_3 and LaAl_3 can be drawn.

Since level 1 of the paramagnetic label in CeAl_3 corresponds to the ground state, the relaxation of level 1 in interactions with lower-lying levels is impossible. Moreover, a visual comparison of the experimental data (Fig. 6) with the calculated dependences shown in Figs. 2 and 3 allows us to state that the mutual relaxation processes I^{12} are also absent. This conclusion can be drawn on the basis of a comparison of the widths at low and high temperatures: there is no temperature-dependent contribution at $T < 20$ K. Therefore, the only possible sources of natural relaxation broadening of levels 1 and 2 are the interactions of levels 1 and 2 with higher-lying levels 3, 4, 5, and 6.

Although the only quantum numbers in whose nomen-

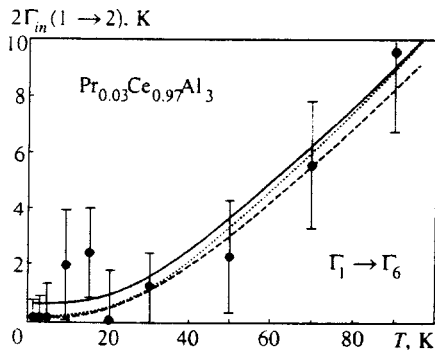


FIG. 6. Temperature dependence of the FWHM ($2\Gamma_{in}$) of the inelastic $|\Gamma_1\rangle \rightarrow |\Gamma_6\rangle$ transition in CeAl_3 for the paramagnetic label Pr using the level scheme in Fig. 5. Dotted line—best fitting in the non-self-consistent approximation for $g = g^{(0)} = 0.115$. Solid line—best fitting in the self-consistent approximation for $g = g^{(sc)} = 0.111$. Dashed line—non-self-consistent width for $g = g^{(sc)} = 0.111$.

clature correct arguments can be advanced are the indices of the irreducible representations $M = \Gamma_1, \Gamma_3, \Gamma_4, \Gamma_6, \Gamma_{51}$, and Γ_{52} , we shall demonstrate that the nomenclature of the projections m of the spherical representation [see (5)] is also useful for a qualitative analysis of relaxation.

Using the known wave functions of the crystal-field states (see the caption to Fig. 5), we can rule out the transitions with $\delta m = \pm 1$ because of the lack of the $|\Gamma_1\rangle \leftrightarrow |\Gamma_6\rangle$ mutual relaxation channel. The transitions with $\delta m = \pm 2$ should lead to interactions of $|\Gamma_1\rangle$ with $|\Gamma_{51}\rangle$ and $|\Gamma_{52}\rangle$ and of $|\Gamma_6\rangle$ with $|\Gamma_4\rangle$ and $|\Gamma_3\rangle$. However, if the occurrence of transitions with $\delta m = \pm 2$ is assumed, the relaxation of $|\Gamma_6\rangle$ according to a Korringa law ($\propto T$) should be observed. Then (if it is assumed within a qualitative analysis that the interaction constants are identical for all the transitions with $\delta m = \pm 2$) the occurrence of relaxation according to a Korringa law does not correspond to the weak dependence of Γ_{12} on the temperature in the range $0 < T < 20$ K (see the experimental points in Fig. 6). Therefore, the occurrence of transitions with $\delta m = \pm 2$ should also be ruled out.

The next possible change in the spherical projection, $\delta m = \pm 3$, leads to interactions of $|\Gamma_1\rangle$ with $|\Gamma_4\rangle$ and $|\Gamma_3\rangle$ and of $|\Gamma_6\rangle$ with $|\Gamma_{52}\rangle$ and $|\Gamma_{51}\rangle$. These interactions do not lead to a contribution that is proportional to T to the widths of the levels of the initial state (γ_1) and the final state (γ_2) and do not contradict the weak temperature dependence of Γ_{12} at $T < 20$ K. The energy splittings Δ_{42} and Δ_{62} corresponding to the interactions of the $|\Gamma_6\rangle$ level are smaller than the corresponding splittings Δ_{41} and Δ_{51} for the $|\Gamma_1\rangle$ level. Therefore, the contribution $\propto \exp(-\Delta/T)$ to the transition width Γ_{12} at $T < 100$ K (under the assumption of approximately equal values of g for all $\delta m = \pm 3$) from the natural width $\gamma_2(T)$ of the $|\Gamma_6\rangle$ level can be considered the main contribution.

In the quantitative calculations presented below we took into account only the interaction constants I^{24} and I^{26} . In such an approximation the natural width of the crystal-field ground state is $\gamma_1(T) = 0$, and, therefore, $\Gamma_{12} = \gamma_2(T)$. For simplicity, the values of I^{24} and I^{26} were set equal to one another (see Fig. 5). The conduction electron band was ap-

proximated by a constant density of states with a width of 2 eV. The best fit for the experimental data in the non-self-consistent approximation is achieved with the value of the dimensionless coupling constants $g^{(0)} = g_{|\Gamma_6\rangle|\Gamma_{52}\rangle}^{(0)} \equiv g_{|\Gamma_6\rangle|\Gamma_{51}\rangle}^{(0)} = 0.115$. The self-consistent procedure gives the best results when $g^{(sc)} = g_{|\Gamma_6\rangle|\Gamma_{52}\rangle}^{(sc)} \equiv g_{|\Gamma_6\rangle|\Gamma_{51}\rangle}^{(sc)} = 0.111$. It is noteworthy that the self-consistent value of the natural width $\gamma_{\Gamma_6}(T = 0)$ obtained in the numerical calculation coincides to within a few percent with the results of the analytical formula (44). Figure 6 presents a comparison of the theoretical temperature dependences of the width of the $1 \rightarrow 2$ inelastic neutron transition with experimental data. The theoretical data are presented in different approximations, viz., the self-consistent and non-self-consistent approximations. To illustrate the influence of the self-consistent approximation, the figure shows the temperature dependences of the self-consistent and non-self-consistent widths (the solid and dashed lines, respectively) calculated for the same dimensionless constant $g^{(sc)} = 0.111$. It is seen from Fig. 6 that the self-consistent width is greater than the non-self-consistent width for the same value of the interaction constant. The effect of the self-consistent approximation, $\Gamma_{12}^{(sc)}/\Gamma_{12}^{(0)} \gg 1$, is most easily observed when the non-self-consistent width is small. Unfortunately, the instrumental errors of the neutron scattering method make it difficult to reliably isolate the effects of the self-consistent approximation. Therefore, the performance of Raman scattering experiments, whose experimental errors are considerably smaller, can provide important additional information.

A qualitative analysis of the experimental temperature dependence of the relaxation in LaAl_3 like the analysis performed above for CeAl_3 shows that the main relaxation channel corresponds to a change in the spherical projection $\delta m = \pm 1$. We note that this channel does not lead to Korringa relaxation for the initial state 1 or the final state 2. In this approximation relaxation of the initial state is possible only in the mutual I^{12} processes, and relaxation of the final state is possible both in the mutual I^{12} processes and in the I^{24} and I^{26} interactions with higher-lying levels (see the right-hand part of Fig. 5).

Since the non-self-consistent width is greater at all temperatures, it is difficult to observe the effects of the self-consistent approximation. Therefore, we calculated the transition width only in the non-self-consistent approximation (Fig. 7). It is noteworthy that the results of the fitting with consideration of only I^{12} are in better agreement with the experimental data than are the results of the calculations with consideration of equal values for all the interaction constants $I^{12} = I^{24}/\sqrt{1-a^2} = I^{26}/a$. These results are reminiscent of the qualitative character of the estimates based on the nomenclature of the spherical projections of the angular momentum m . A more rigorous approach would take into account, for example, that the contributions of the $m = 0 \leftrightarrow m = \pm 1$ and $m = \pm 1 \leftrightarrow m = \pm 2$ transitions, which are both associated with a change in the spherical projection $\delta m = \pm 1$, can be significantly different in a lattice of fairly low symmetry.

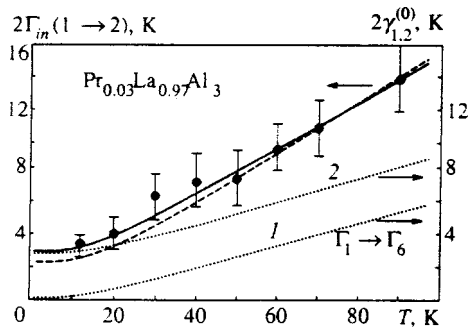


FIG. 7. Temperature dependence of the FWHM ($2\Gamma_{in}$) of the inelastic $|\Gamma_1\rangle \rightarrow |\Gamma_6\rangle$ transition in LaAl_3 for the paramagnetic label Pr in the non-self-consistent approximation using the level scheme in Fig. 5. Dashed line—model with $g_{12} = g_{24}/\sqrt{1-a^2} = g_{26}/a = 0.094$; solid line—model with $g_{24} = g_{26} = 0$, $g_{12} = 0.108$. The dotted line 1 (2) corresponds to the natural relaxation width $\gamma_{\Gamma}(T)$ ($\gamma_{\Gamma}(T)$) of the levels.

8. CONCLUSIONS

The proposed self-consistent microscopic theory of the spectroscopy of the crystal-field levels of an impurity ion in a normal metal has several consequences, which can have a significant influence on our understanding of the relaxation processes in highly correlated systems.

Most importantly, the proposed approach, which is based on the Coqblin–Schrieffer–Cooper approach, rather than the formal *sf* exchange model, permits a first-principles microscopic calculation of the temperature dependence of the relaxation width of crystal-field states. A comparison of such calculations with experimental data, as well as the use of the conventional methods of infrared, Raman, and photoemission spectroscopy, makes it possible to test the faithfulness of the band calculations. Like the traditional methods, the proposed method permits the performance of a quick qualitative visual analysis of the experimental results obtained. An additional significant feature of the proposed spectroscopic method is the possibility of regulating the selection rules by choosing an appropriate paramagnetic label, which is impossible within the traditional methods.

The new soft spectroscopic method considered in this paper permits the investigation of the role of strong electron correlations in shaping the relaxation processes of crystal-field states. Since strong correlations can significantly alter the simple form of the effective Hamiltonian (15), relaxation features, whose characteristic temperatures are not related to the crystal-field splitting energies, can be observed in a highly correlated system. The observation of such features provides weighty evidence in support of the important role of strong correlations in the compound being studied. Moreover, the calculations performed in the self-consistent approach indicate that in the case of strong relaxation broadening the upper crystal-field levels have a significant influence on the experimentally measured characteristics, which, as was previously assumed, are determined only by the properties of the ground state of a highly correlated system. An example of the properties of the ground magnetic state of ions in highly correlated systems, which can be subject to a significant influence from crystal-field excited states, is the residual width of the magnetic quasielastic neutron scattering

peak at zero temperature $\Gamma_G(T=0)$. In the case of soft crystal-field splittings, employment of the widely accepted phenomenological formula $T^* = \Gamma_G(T=0)/2$ to determine the characteristic temperature T^* of the Kondo system is in need of additional analysis.

In conclusion, we wish to note that the proposed approach should be useful in the case of the analysis of systems in which the crystal-field states transform into more complicated objects as a result of strong electron correlations. Such systems include concentrated Kondo systems, in which the rare-earth ions form a coherent lattice. In this case the localized crystal-field ground-state levels transform into a coherent continuum,⁴¹ which has been termed a spin fluid. When there are sufficiently soft crystal-field splittings, a spin fluid undergoes strong interactions with localized excited states,⁴² which should produce features in the relaxation of the magnetic states. Since crystal-field states are nothing more than well defined levels, this relaxation cannot be studied in a neutron scattering experiment within the proposed method. However, the relaxation in the magnetic subsystem should have a significant influence on the spectroscopic characteristics of the system that can be detected using resonance methods, such as muon spin rotation (μSR) and nuclear magnetic resonance. These processes can be studied experimentally and calculated theoretically after the proposed formalism is appropriately generalized.

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¹Below we shall consider a case which corresponds to the conditions of the proposed experimental method. In this situation the concentration of the paramagnetic label is chosen small enough that the interactions between the impurities can be neglected in each specific case.²⁹ For this reason, the influence of the impurity on the state of the conduction electrons can be neglected.³⁰

²All the expressions presented above were obtained without consideration of the vertex corrections (Fig. 1d),³⁷ which, however, are insignificant in the case of sufficiently small dimensionless interaction constants $g_{MM'}^2 \ll 1$.

³Consideration of the vertex corrections in the perturbative approach, unlike (44), leads to correction of the coefficient in front of the exponentially small natural width (41).

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