Theory of Mössbauer effect in intermediate-valence compounds*

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Using a simple microscopic model, we study the response function corresponding to the Mössbauer effect in an intermediate-valence atom. We derive expressions for the spectra which can be used to analyze experimental results at all temperatures, as well as for different hosts in which the intermediate-valence ion may be embedded. For metallic hosts at high temperatures our theory justifies the use of the expressions previously proposed by Bauminger, Nowik, Ofer, Felner, and Mayer, based on Kubo's stochastic theory of line shape. At low temperatures, where the latter cannot be applied due to the non-Markovian character of the fluctuations, our results allow us to interpret experimental data and to obtain from them the parameters characterizing the intermediate-valence condition. For semiconducting hosts, where the phenomenological stochastic theory does not apply either, we can predict spectra which are consistent with experimental results.

I. INTRODUCTION

Intermediate-valence systems [or systems with interconfigurational fluctuations (ICF)] have attracted considerable attention during the last years.[1-3] The expression "intermediate valence" is used when observations of different properties are interpreted in terms of a mixed or hybridized ground state. The expression "interconfigurational fluctuations" is used when experimental results are interpreted in terms of temporal fluctuations in the occupation of the $4f$ shell.

Mössbauer experiments in compounds containing rare-earth atoms with nonintegral occupation support the ICF picture, since the equations proposed by Banminger *et al.*,[4] based on Kubo's stochastic theory of line shape, fit the experimentally determined isomer shifts and the linewidths, as well as their temperature dependence. This theory,[5,6] assumes a system that can resonate at two frequencies ω_A and ω_B stochastically alternating with Markovian modulation.

The spectrum is given by

$$I(\omega) = -\frac{1}{\pi}\frac{P_A P_B(\omega_A-\omega_B)^2\omega_c}{(\omega-\omega_A)^2(\omega-\omega_B)^2+\omega_c^2(\omega-\bar{\omega})^2}\,, \qquad (1)$$

where P_A and P_B are the occupation probabilities for the two states of interest, ω_c is the fluctuation frequency, and $\bar{\omega}=P_A\omega_A+P_B\omega_B$.

Bauminger *et al.* used Eq. (1) identifying the states A and B with the configurations $4f^n$ and $4f^{n+1}$, and ω_A and ω_B with the associated isomer shifts of the nuclear states.

For $\omega_c \gg |\omega_A-\omega_B|$, Eq. (1) leads to a single narrow resonance at $\omega\sim\bar{\omega}$, which is the motional narrowing regime. For $\omega_c \ll |\omega_A-\omega_B|$, Eq. (1) gives two lines in the neighborhood of ω_A and ω_B.

It has been shown[7] that the alternative points of view, intermediate-valence and ICF, are reconcilable and that the fluctuations can be interpreted as equilibrium fluctuations in the nondiagonal variable associated to the occupation of the $4f$ shell. These fluctuations are of a Markovian character only at high temperatures. This would mean that the applicability of Eq. (1) to Mössbauer spectra is restricted to this limit.

To analyze the experimental results at all temperatures, the authors of Refs. 4 and 8 have generalized Eq. (1) using *ad hoc* assumptions which are not always consistent with a single physical picture.

For these reasons it is necessary to develop a theory of the Mössbauer effect[9] in intermediate valence systems which can be consistently applied at all temperatures. In this paper it is shown that starting from a Hamiltonian which includes hybridization between localized orbitals and a continuum of states (representing this simplified model the $4f^n$ and $4f^{n-1}$ plus band states of the compound), the theory of linear response allows us to find Mössbauer spectra which are in agreement with experimental results.

For metallic hosts at high temperatures the calculated spectra coincide with those predicted by Eq. (1), a fact which is not surprising due to the Markovian character of the fluctuations in this case.[7] At low temperatures, the power spectrum of valence fluctuations shows the onset of memory effects which destroy the Markovian behavior. This situation must reflect itself in a complete theory of the Mössbauer spectra, as is shown below.

To make the calculations more transparent, we have developed them in the following sections using a simple model Hamiltonian. The arguments can be generalized to include a realistic

description of intermediate-valence compounds, and this is done in the Appendix. The results are compared with experiments in Sec. IV.

II. HAMILTONIAN

We study the linear response of a system consisting of a continuum of states $|k\rangle$ of energy ϵ_k, which have associated creation and annihilation operators $c_k^\dagger$ and c_k and are hybridized to a localized orbital of energy E and corresponding operators $d^\dagger$ and d.

The Hamiltonian is

$$H = Ed^\dagger d + \sum_k \epsilon_k c_k^\dagger c_k + V\sum_k (d^\dagger c_k + c_k^\dagger d)\,. \tag{2}$$

Nuclear excitations will be represented by an operator $a^\dagger$ (a) which, acting on the nuclear ground (excited) state raises (lowers) it to the corresponding excited (ground) state. We define $a^\dagger$, a satisfying anticommutation relations. The nuclear excitation energy will be ω_A when the localized orbital is empty and ω_B when it is occupied. Thus we add to the Hamiltonian (2) the term

$$H_{e\text{-}n} = \omega_A(1-n_d)a^\dagger a + \omega_B n_d a^\dagger a\,, \tag{3}$$

where $n_d = d^\dagger d$.

III. RESPONSE FUNCTION

The linear response of the system is given by[11]

$$\chi(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega' \tanh(\beta\tfrac{1}{2}\omega')\frac{\mathrm{Im}\langle\langle a; a^\dagger\rangle\rangle\omega' + i0}{\omega - \omega' + i0}\,, \tag{4}$$

where $\langle\langle a; a^\dagger\rangle\rangle$ is the Fourier transform of the retarded anticommutator Green's function. The absorptive part of the response function is

$$\chi''(\omega) = -\tanh(\beta\tfrac{1}{2}\omega)\mathrm{Im}\langle\langle a; a^\dagger\rangle\rangle\omega + i0\,. \tag{5}$$

It is convenient to separate the Green's function into

$$\langle\langle a; a^\dagger\rangle\rangle = \langle\langle (1-n_d)a; a^\dagger\rangle\rangle + \langle\langle n_d a; a^\dagger\rangle\rangle$$
$$= G_A + G_B\,.$$

Using the equations of motion we obtain from the total Hamiltonian a set of coupled equations, for G_A and G_B, which contain higher-order functions. To obtain a closed system of equations we neglect correlations between band states and nuclear excitations. As shown below this simplifying assumption is enough to give a satisfactory description of the phenomenon under study. The equations then reduce to

$$(\omega - \omega_A)G_A = I_A + \Sigma_A G_A - \Sigma_B G_B\,, \tag{6}$$

$$(\omega - \omega_B)G_B = I_B + \Sigma_B G_B - \Sigma_A G_A\,, \tag{7}$$

where

$$I_A = \frac{1}{2\pi}\left[1 - \langle n_d\rangle - V\sum_k\left(\frac{\langle d^\dagger c_k\rangle}{\omega - \epsilon_k + E - \omega_A} - \frac{\langle c_k^\dagger d\rangle}{\omega + \epsilon_k - E - \omega_B}\right)\right] \tag{8}$$

$$I_B = \frac{1}{2\pi}\left[\langle n_d\rangle + V\sum_k\left(\frac{\langle d^\dagger c_k\rangle}{\omega - \epsilon_k + E - \omega_A} - \frac{\langle c_k^\dagger d\rangle}{\omega + \epsilon_k - E - \omega_B}\right)\right], \tag{9}$$

$$\Sigma_A = V^2\sum_{kk'}\langle c_k^\dagger c_{k'}\rangle[(\omega - \epsilon_k + E - \omega_A)^{-1} + (\omega + \epsilon_k - E - \omega_B)^{-1}]\,, \tag{10}$$

$$\Sigma_B = V^2\sum_{kk'}\langle c_{k'} c_k^\dagger\rangle[(\omega - \epsilon_k + E - \omega_A)^{-1} + (\omega + \epsilon_k - E - \omega_B)^{-1}]\,, \tag{11}$$

A. Metallic hosts

We characterize a metallic host by defining the zero of energy at the Fermi level in a band of constant density of states ρ. Corrections arising from a finite bandwidth W are of order Γ/W, where Γ is the width of the resonant level $\Gamma = \pi V^2\rho$. For all cases of interest Γ/W will be very small.

By inspection of Eqs. (10) and (11) it is seen that the real parts of Σ_A and Σ_B are odd functions of $\omega - \omega_+$, where $\omega_+ = \frac{1}{2}(\omega_A + \omega_B)$. The imaginary parts are even functions of the same variable.

For the case of Mössbauer experiments the difference $|\omega_B - \omega_A|$ is smaller than any other energy parameter. When studying the response function for ω near ω_A and ω_B, we can approximate the real and imaginary parts of Σ_A and Σ_B by their first term in a Taylor series expansion

$$\Sigma_A' = S(\omega - \omega_+)\,;\quad \Sigma_A'' = -2\Gamma\langle n_d\rangle\,, \tag{12}$$
$$\Sigma_B' = -S(\omega - \omega_+)\,;\quad \Sigma_B'' = -2\Gamma(1 - \langle n_d\rangle)\,,$$

$S = 2[f(E) - \langle n_d\rangle]$, where $f(E)$ is the Fermi function.

The quantities I_A and I_B can be written in the form

$$I_A = (1/2\pi)(1 - n_d - Q)\,,$$
$$I_B = (1/2\pi)(n_d + Q)\,, \tag{13}$$

where

$$Q = V\sum_k\left(\frac{\langle d^\dagger c_k\rangle}{\omega - \epsilon_k + E - \omega_A} - \frac{\langle c_k^\dagger d\rangle}{\omega + \epsilon_k - E - \omega_B}\right). \tag{14}$$

For the same reasons as indicated above we can now approximate the real and imaginary parts of Q by the first nonvanishing terms in a serious

expansion. The real part coincide with S defined above $Q' = S$; the imaginary part is an odd function of $\omega - \omega_+$ and for $\omega \sim \omega_A$, ω_B it can be neglected.

In the high-temperature limit $\langle n_d \rangle \sim f(E)$ and therefore $S \sim 0$. In this case Eqs. (6) and (7) turn out to be identical with the equations derived by Kubo. The relaxation times are explicity given, in this limit by

$$\tau_A^{-1} = 2\Gamma \langle n_d \rangle ,$$
$$\tau_B^{-1} = 2\Gamma (1 - \langle n_d \rangle) . \tag{15}$$

The behavior of the response function is given by Eq. (1). The quantity 2Γ plays the role of the "fluctuation frequency" ω_c, a result which is consistent with the analysis of the spectrum of valence fluctuations done in Ref. 7.

In general we have

$$\chi''(\omega) = -I(\omega) = \frac{2\Gamma}{\pi} \frac{(1 - \langle n_d \rangle)\langle n_d \rangle (\omega_B - \omega_A)^2 + S(\omega_B - \omega_A)(\omega + - \bar{\omega})}{[(\omega - \omega_A)(\omega - \omega_B) + S(\omega - \omega_+)(\omega_B - \omega_A)]^2 + 4\Gamma^2(\omega - \bar{\omega})^2} , \tag{16}$$

where now $\omega = (1 - \langle n_d \rangle)\omega_A + \langle n_d \rangle \omega_B$. Figure 1 gives the loci of the zeroes of the denominator of Eq. (14) in the complex plane, as Γ is varied.

At high temperatures where the fluctuations are Markovian, the roots tend to follow the trajectories corresponding to Kubo's theory. At low temperatures, when the fluctuations loose their Markovian character, the trajectories have a different behavior.

Figure 2 shows the isomer shifts as functions of Γ for different temperatures, where a comparison with the results of the phenomenological theory is given. Notice that at low temperatures ($T \ll \omega_c$) the resonance frequencies do not join at $\bar{\omega}$ as Γ is increased. Instead one of them follows a behavior similar to that predicted by the phenomenological theory, whereas the other shifts away from the mean value.

It follows from Eq. (16) that for $\Gamma \gg |\omega_B - \omega_A|$ our approximation yields a single Lorentzian line in the neighborhood of $\bar{\omega}$, of width

$$[\Delta n_d^2 - S(n_d - \tfrac{1}{2})]\omega_-^2 / 2\Gamma^2 ,$$

where $\Delta n_d^2 = \langle n_d^2 \rangle - \langle n_d \rangle^2$. This width is different from zero even at zero temperature, and much smaller than the natural width of the Mössbauer resonances, a fact that makes it unobservable.

The origin of a finite line width at $T = 0$ can be understood on the basis of the Hamiltonian, Eqs. (2) and (3). Due to the term H_{e-n}, the states that diagonalize the total Hamiltonian span two orthogonal sets, corresponding to the two eigenvalues of the operator $a^\dagger a$. The oscillator strengths contributing to the spectrum at $T = 0$ are given by the matrix elements of the operator $a^\dagger$ between

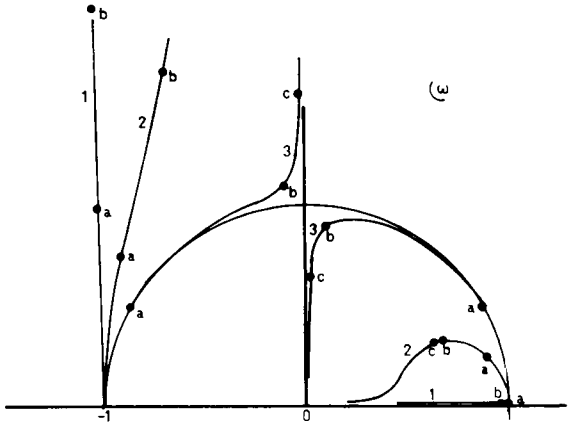

FIG. 1. Trajectories of the poles of $\langle\langle a; a^\dagger \rangle\rangle$ in the complex plane as Γ varies from zero to infinity. Curves 1, 2, and 3 correspond to 1, 20, and 1000 K, respectively. The points a, b, and c on each curve indicate the position of the poles for $\Gamma = 5$, 1, and 1.1 K, respectively ($E = 20$ K).

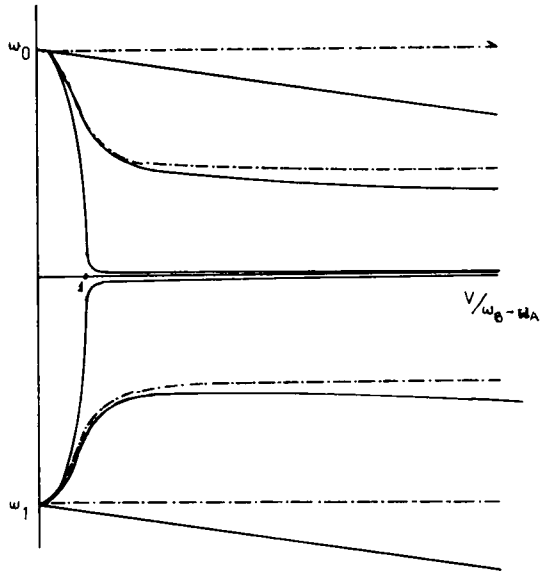

FIG. 2. Values of the resonance frequencies as a function of V. Full lines are the results of this paper, dashed lines correspond to the phenomenological Kubo theory.

the electronic ground state associated with $a^\dagger a = 0$ and any one of the states associated with $a^\dagger a = 1$. If this matrix element were nonvanishing for only one such state, the resulting spectrum would be a δ function. It can be verified that this is not the case, and that in the continuum limit there are infinitely many such states, not all at the same energy.

B. Semiconducting hosts

We characterize semiconducting hosts by setting the energy of the localized state at E and the bottom of the conducting band at $E+\Delta$ and assume a constant density of states ρ. For W in the range of interest the imaginary parts of both Σ_A and Σ_B are zero. Consequently Eqs. (6) and (7) are not equivalent to the Kubo equations in this case. This is connected with the fact that, as shown in Ref. 14, the autocorrelation function for valence fluctuations does not show Markovian behavior in any limit.

To our knowledge the only case where Mössbauer effect has been measured in an intermediate valence semiconductor is that of Sm compounds.[12,13] In these compounds, at room temperature, according to our calculations,[14] the mixing of localized and band states is small even at pressures near the transition pressure. The strength of the mixing is given by the parameter[14] $\rho V^2/\Delta \ll 1$.

The absorption frequencies turn out to be real, indicating that the width of the lines will correspond to the natural width, and are given by

$$\omega_B' = \omega_B - (\rho V^2/\Delta)(\omega_B - \tilde{\omega}), \tag{17}$$

$$\omega_A' = \omega_A + (\rho V^2/\Delta)(\tilde{\omega} - \omega_A), \tag{18}$$

and the residues at each of them are

$$R(\omega_B') = \frac{\langle n_d\rangle + (\rho V^2/\Delta)[2f(E) - F(T,\Delta)]}{1+\rho V^2/\Delta}, \tag{19}$$

$$R(\omega_A') = \frac{1 - \langle n_d\rangle - (\rho V^2/\Delta)[2f(E) - 1 - F(T,\Delta)]}{1+\rho V^2/\Delta}, \tag{20}$$

where

$$F = \Delta \int_{E+\Delta}^{\infty} \frac{f(\epsilon)}{(E-\epsilon)^2}\, d\epsilon \quad \text{and} \quad \tilde{\omega} = \omega_B F + \omega_A(1-F).$$

From (17) and (18) it can been seen that at zero temperature the response frequency ω_B' shifts towards ω_A, while ω_A' rests at the original value, whereas the intensities of the lines are one and zero, respectively. As the temperature is raised, the shift in ω_B' becomes smaller, and ω_A' shifts towards ω_B. The intensity corresponding to ω_A' increases, that corresponding to ω_B' decreases by the same amount.

IV. DISCUSSION AND APPLICATIONS

We have in the previous sections shown that the theory of motional narrowing can be used to interpret experimental results in metals only at high temperatures ($T \gg \omega_c$), a result to be expected in view of the conclusions of Ref. 7. At low temperatures, however, the fluctuations loose their Markovian character and consequently the phenomenological theory developed by Kubo does not apply. The absorption spectrum derived in Sec. III shows peculiar characteristics which reflect this fact.

From the experimentalist's point of view, one difficulty in interpreting Mössbauer spectra at low temperatures arises from the nonintegral occupation of the localized states. For this reason it has been necessary to propose new formulas to calculate the occupation numbers, based on physical intuition. For instance, in Ref. 8 the occupation numbers are calculated invoking a level width originated in hybridization, using an expression like

$$P_2(T) = \int_{-\infty}^{\infty} d\epsilon\, D(\epsilon) P_2^{(0)}(T,\epsilon), \tag{21}$$

where $D(\epsilon)$ is the density of states for the $4f$ level of interest and $P_2^{(0)}(T,\epsilon)$ is the occupation number for the level of zero width. Such formula corresponds to a distribution of infinitely narrow levels, with a density $D(\epsilon)$, a situation arising in an inhomogeneous sample in which the energy of the localized levels varies from site to site. In this case Eq. (21) would give the population of the levels averaged over the whole sample.

For an homogeneous sample in which there is an hybridization, which causes a level width at each site, Eq. (21) is not applicable, except only in the case where the states are nondegenerate or uncorrelated, where it happens to coincide with the correct expression.

If the sample were in fact inhomogeneous, Eq. (21) would be correct to calculate the relative populations, but there would be no physical agent to cause motional narrowing (hybridization) and the spectrum would show two peaks at the resonance frequencies corresponding to the two relevant valencies. Thus the physical picture is not quite consistent.

The theory developed here includes hybridization from the outset, which is the cause of the nonintegral occupation number and of the temporal fluctuations.

We may summarize the results by saying that the theory can (i) justify the use of the theory of motional narrowing in the high-temperature regime; (ii) show that even in the presence of

non-Markovian fluctuations (at low temperatures), a single line would be observed when $2\Gamma \gg |\omega_B - \omega_A|$; (iii) show how to obtain from the Mössbauer spectra the parameters that characterize the intermediate valence regime.

In the following we analyze the spectra corresponding to some Eu and Sm compounds.

A. Eu compounds

The Eu ion[4] appears in solids usually as Eu^{2+} or Eu^{3+}. The ground state of Eu^{2+} is $^8S_{7/2}$ and the first excited state lies far above in energy and need not be considered. The ground state of Eu^{3+} is $^7F_0$; the first excited state is $^7F_1$ and lies some 480 K above it. The second excited state corresponds to $J=2$ and is 1330 K above the ground state, so that both these states must be considered in order to explain experimental results in the temperature range that has been explored.

As shown in the Appendix one expects, on the basis of the theory developed here, a single line at $\omega = P_2\omega_2 + P_3\omega_3$, where ω_2 and ω_3 are isomer shifts corresponding to Eu^{2+} and Eu^{3+}, respectively, and P_2 and P_3 are the occupation probabilities.

For the two compounds mentioned above we obtain:

1. $EuCu_2Si_2$

This is a metallic system, whose Mössbauer spectrum has been determined by Nowik *et al.*[8]

We characterize the energy difference between the configurations Eu^{2+} and Eu^{3+} plus (one conduction electron at the Fermi energy) by the parameter $\Delta > 0$. The fit of the present theory to the experimental results is given in Fig. 3. The isomer shifts have been taken as $\omega_2 = 12.5$ mm/sec and $\omega_3 = 0.7$ mm/sec. Since our model Hamiltonian does not explicitly include all many-body interactions, it turns out that in order to fit the experimental data, (see Fig. 3) Δ must be taken to be a function of temperature. This variation can be best pictured by looking at the resulting relation between Δ and P_2 (see inset in Fig. 3) which turns out to be linear. This result would follow had we included in the Hamiltonian the dependence of Δ on the occupation number in a mean-field approximation, as was done for example, in the Falicov-Kimball model.

To make the fit we have taken $\Gamma = 100$ K, which gives Δ varying in the range 1000–600 K, for n between 0.09 and 0.5.

One can correlate these parameters with the Eu-Si distance. In $EuAg_2Si_2$, in which the smallest Eu-Si distance is 3.317 Å, the Eu ions are divalent. In $EuFe_2Si_2$ this distance is 3.073 Å, and the Eu ions are trivalent. In a first approximation one may think that the Eu-Si distance depends only on the number of $4f$ electrons at the Eu ion. With the parameters given above, we obtain $P_2 = 0.32$ and $P_3 = 0.68$ at room temperature. A weighed average of the Cu-Si distance gives 3.15 Å, which should be compared with the experimental value of 3.124 for the Eu-Si distance in $EuCu_2Si_2$.

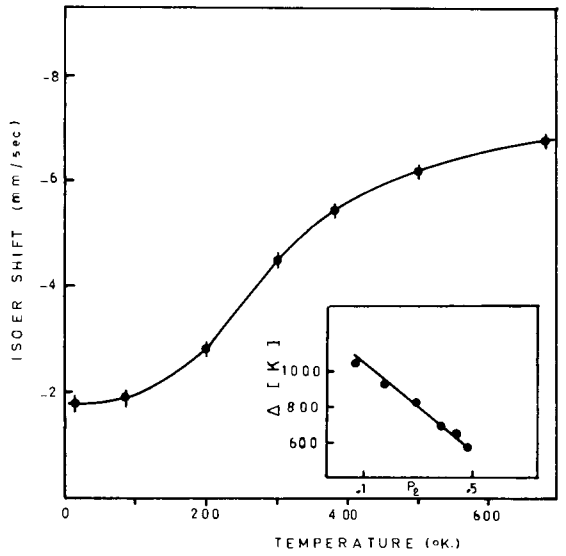

FIG. 3. Isomer shift as a function of temperature for $EuCu_2Si_2$. The inset shows the relation between Δ_0 and P_2. Γ was chosen equal to 500 K.

2. $EuRh_2$

For this metallic system the Mössbauer spectrum has also been reported in Ref. 8. We have taken the same set of configurations as in the previous case. Here again Δ turns out to be linear function of P_2. The isomer shift and the variation of Δ are given in Fig. 4.

For this compound, at room temperature, we obtain $P_2 = 0.2$, a value in agreement with the conclusions of the x-ray photoemission spectra.[8]

B. Sm compounds

SmB_6 was one of the earlier compounds to be noticed as a mixed-valence system.[15,18] It was the first intermediate-valence system in which Mössbauer spectroscopic studies were undertaken.[13] Recently Coey, Ghathak, and Avignon have performed Mössbauer effect experiments in SmS.[12]

The relevant states of the Sm ion in intermediate-valence systems are Sm^{2+} and Sm^{3+}. The ground state of divalent samarium is the $^7F_0$ and the first excited state which lies 420 K above it, corresponds to the configuration $^7F_1$. Trivalent

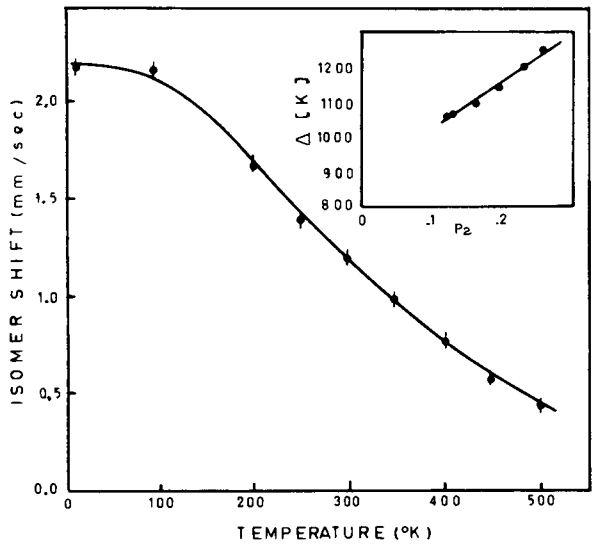

FIG. 4. Isomer shift for $EuRh_2$. Inset shows the relation between Δ_0 and P_2 ($\Gamma = 800$ K).

samarium has a magnetic ground state ($^6H_{5/2}$). Since the first excited state is well above the ground state in energy, it needs not be considered.

1. SmS

This compound is, at room temperature and zero pressure, a semiconductor with an energy gap $\Delta \sim 0.2$ eV (2000 K). In this phase the Sm ion is essentially divalent. On applying pressure, SmS undergoes a first order transition[16] into a metallic phase. Correspondingly there is a change of the predominant valence of the Sm ion from Sm^{2+} to Sm^{3+}.

The theoretical spectrum obtained for this system in the semiconducting phase[17] shows two lines at frequencies given by

$$\omega = \omega_2 - 4\rho(V_0^2/\Delta)(2J+1)(\omega_2 - \omega_3)$$

$$\omega = \omega_2 - 4\rho(V_1^2/\Delta')(2J+1)(\omega_2 - \omega_3),$$

where ω_2 and ω_3 are the isomer shifts corresponding to Sm^{2+} and Sm^{3+}. V_0 and V_1 are the hybridization matrix elements that mix the configurations $^7F_0$ and $^7F_1$ with the state $^6H_{5/2^+}$ (one conduction electron). Δ and Δ' are the corresponding energy gaps ($\Delta' = \Delta - 420$ K). $J = \frac{5}{2}$ is the angular momentum corresponding to the ground state of Sm^{3+}.

These two lines, originate in the fact that there is a different mixing for the two intervening configurations of the Sm^{2+} ion with the ground-state configuration of Sm^{3+}. For realistic values of the parameters the splitting between them is much smaller than the natural width, so that in practice they will be observed as a single line.

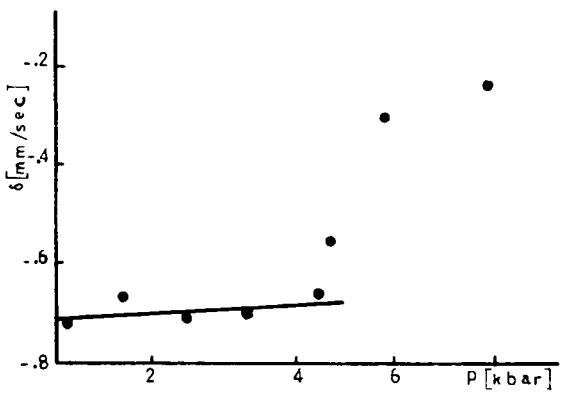

FIG. 5. Fit of the data of Ref. 10 using our model for semiconducting hosts. It was assumed that the energy gap was 2000 K at zero pressure and that it diminishes at a rate of 100 K/kbar.

Applied external pressure[14] changes Δ. Asssuming a linear relation between Δ and pressure the isomer shift can be fit to experimental data in the semiconducting phase as shown in Fig. 5.

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APPENDIX

The calculation of the isomer shifts using relistic ionic configurations which include from the outset the important intra-atomic interactions can be done by defining projection operators[10, 19, 20, 21] which can be characterized by the ket $|n, J, S, L, M, \nu\rangle$, where n indicates the number of $4f$ electrons, J, S, L are the total angular momentum, o orbital angular momentum, and spin, M is the z projection of J. The quantum number ν refers to the nuclear state; we need only consider the ground state ($\nu = g$) and a nongenerate excited state ($\nu = e$). We shall group in what follows the quantum numbers J, S, L into the single variable λ.

To illustrate the method of calculation we consider a Hamiltonian which includes states corresponding to n and $n+1$ $4f$ electrons. For the first case we consider a nondegenerate electronic ground state ($\lambda = 0$) and a $2J_1 + 1$ degenerate multiplet ($\lambda = 1$). For the second configuration we consider only a $2J_2 + 1$ degenerate multiplet ($\lambda = 2$).

The ionic Hamiltonian will be

$$H_i = \sum_\nu E_0^\nu |n,0,\nu\rangle\langle n,0,\nu| + \sum_\nu \sum_{M_1} E_{1M_1}^\nu |n,1M_1,\nu\rangle\langle n,1,M_1,\nu| + \sum_\nu \sum_{M_2} E_{2M_2}^\nu |n+1,2,M_2,\nu\rangle\langle n+1,2,M_2,\nu|. \quad \text{(A1)}$$

In the following we shall make use of the operator

$$A^\dagger = |n,0,e\rangle\langle n,0,g| + \sum_{M_1} |n,1,M_1,e\rangle\langle n,1,M_1,g| + \sum_{M_2} |n+1,2,M_2,e\rangle\langle n+1,2,M_2,g|.$$

which is the equivalent of the operator $a^\dagger$ used in the previous sections.

It is a good approximation, based on experimental observations, to take $E_0^e - E_0^g \cong E_{1M_1}^e - E_{1M_1}^g = \omega_n$ independent of M_1. This means that we take a single nuclear absorption frequency when the ion is in the configuration $4f^n$, irrespective of the wave function.

Analogously we take $E_{2M_2}^e - E_{2M_2}^g = \omega_{n+1}$, independent of M_2.

The relevant part of the conduction electron dynamics can be described through

$$H_b = \sum_{k\sigma} \epsilon_{k\sigma} C_{k\sigma}^\dagger C_{k\sigma}, \quad \text{(A2)}$$

where $C_{k\sigma}^\dagger$ ($C_{k\sigma}$) creates (annihilates) an electron of energy $\epsilon_{k\sigma}$.

The hybridization Hamiltonian mixes the ionic states corresponding to $n+1$ f electrons with those containing n f electrons,

$$H_{\text{hyb}} = \sum_\nu \sum_{M_1 k\sigma} V_{0M_1}^{k\sigma} C_{k\sigma}^\dagger |n,0,\nu\rangle\langle n+1,2,M_2,\nu| + \sum_\nu \sum_{M_1 M_2 k\sigma} V_{M_2 M_1}^{k\sigma} C_{k\sigma}^\dagger |n,1,M_1,\nu\rangle \times \langle n+1,2,M_2,\nu| + \text{H.c.} \quad \text{(A3)}$$

The response of the system to the electromagnetic field of the γ rays will be given by the Green's function $\langle\langle A; A^\dagger\rangle\rangle$, which as before can be separated as

$$\langle\langle A;A^\dagger\rangle\rangle = G_0 + G_1 + G_2,$$

where

$$G_0 = \langle\langle |n,0,g\rangle\langle n,0,g|A;A^\dagger\rangle\rangle,$$

$$G_1 = \sum_{M_1} \langle\langle |n,1,M_1,g\rangle\langle n,1,M_1,g|A;A^\dagger\rangle\rangle, \quad \text{(A4)}$$

$$G_2 = \sum_{M_2} \langle\langle |n+1,2,M_2,g\rangle\langle n+1,2,M_2,g|A;A^\dagger\rangle\rangle.$$

The equations of motion for these Green's functions can be derived from the total Hamiltonian using conventional methods. One obtains

$$\begin{aligned}(\omega-\omega_n)G_0 &= I_0 + \Sigma_0 G_0 - \Sigma_{02} G_2,\\ (\omega-\omega_n)G_1 &= I_1 + \Sigma_1 G_1 - \Sigma_{12} G_2, \quad \text{(A5)}\\ (\omega-\omega_{n+1})G_2 &= I_2 + (\Sigma_{02}+\Sigma_{01})G_2 - \Sigma_0 G_0 - \Sigma_1 G_1,\end{aligned}$$

where the I's and Σ's are defined by expressions similar to those given in the text.

The poles of the Green's function associated with the isomer shifts are given by the roots of the equation

$$\Omega_0\Omega_1\Omega_2 - \Sigma_0\Sigma_{02}\Omega_1 - \Sigma_1\Sigma_{12}\Omega_0 = 0,$$

with

$$\Omega_0 = \omega - \omega_n - \Sigma_0, \quad \Omega_1 = \omega - \omega_n - \Sigma_1,$$

$$\Omega_2 = \omega - \omega_{n+1} - \Sigma_{02} - \Sigma_{12}.$$

For a metallic matrix, we have obtained a computer solution to this equation. An analysis of the results shows that the real parts of self-energies can be neglected under the condition that $\Gamma_0 = \pi\rho|V_0|^2$ and $\Gamma_1 = \pi\rho|V_1|^2$ be much greater than $|\omega_n - \omega_{n+1}|$. This condition is met for realistic values of the parameters.

It also turns that for the root with the smallest imaginary part, a simple analytic expression can be obtained by further neglecting $(\omega-\omega_n)(\omega-\omega_{n+1})\Sigma_0$ as compared to $(\omega-\omega_{n+1})\Sigma_0\Sigma_1$. The relevant solution is given by

$$\omega = \frac{\omega_n(\Sigma_1''\Sigma_{02}'' + \Sigma_0''\Sigma_{12}'') + \omega_{n+1}(\Sigma_0''\Sigma_1')}{\Sigma_1''\Sigma_{02}'' + \Sigma_0''\Sigma_{12}'' + \Sigma_0''\Sigma_1''}. \quad \text{(A6)}$$

It can be shown[17] that the expressions for the self energies can be evaluated in an approximate

fashion to give

$$\Sigma_0'' = 2\Gamma_0 \frac{P_2}{P_0 + [1/(2J_2+1)]P_2},$$

$$\Sigma_1'' = 2\Gamma_1 \frac{P_2}{[1/2J_1+1)]P_1 + [1/2J_2+1)]P_2},$$

$$\Sigma_{02}'' = (P_0/P_2)\Sigma_0'',$$

$$\Sigma_{12}'' = (P_1/P_2)\Sigma_1''.$$

The quantities P_0 and P_1 give the population of the states corresponding to $\lambda = 0$ and $\lambda = 1$, respectively.

The consistency of the calculation requires that the populations be evaluated within the decoupling scheme that we used throughout and are thus given as a solution of

$$\frac{P_2}{2J_2+1} = \left(P_0 + \frac{P_2}{2J+1}\right)\left\{\frac{1}{2} - \frac{1}{\pi}\,\mathrm{Im}\,\psi\left[\frac{1}{2} + \frac{\Gamma_0}{2\pi T}\left(P_0 + \frac{P_2}{2J_2+1}\right) + i\frac{\Delta_0}{2\pi T}\right]\right\} \frac{P_2}{2J_2+1} = \frac{P_1}{2J_1+1} + \frac{P_2}{2J_2+1}$$

$$\times \left\{\frac{1}{2} - \frac{1}{\pi}\,\mathrm{Im}\,\psi\left[\frac{1}{2} + \frac{\Gamma_1}{2\pi T}\left(\frac{P_1}{2J_1+1} + \frac{P_2}{2J_2+1}\right) + i\frac{\Delta_1}{2\pi T}\right]\right\}, \tag{A7}$$

$$P_0 + P_1 + P_2 = 1.$$

Inserting Eqs. (A7) into (A6) it follows that the isomer shift is given by

$$\omega = \omega_n(P_0 + P_1) + \omega_{n+1}P_2. \tag{A8}$$

These formulas generalize the results obtained for the simplified Hamiltonian of Sec. II, for a more realistic description of the $4f$ shell. Their structure is quite similar to those obtained from Kubo's theory. There is an important difference, however, in the fact that in expression (A8) the populations are calculated including hybridization and thus provide a consistent and coherent way to describe the effect of intermediate valence on the Mössbauer spectra at $T = 0$.

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