Population of Excited Electronic Levels by Beta Decay, and Its Influence on Mössbauer Source Spectra

L. L. Hirst,* J. Stöhr, G. K. Shenoy,† and G. M. Kalvius
Physik Department, Technische Universität München, 8046 Garching, German Federal Republic
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In a Mössbauer source experiment the β decay produces a large initial population of the excited electronic levels of the Mössbauer source atom. It is shown that this causes such excited levels to contribute more prominently in the source experiment than in the corresponding absorber experiment. These contributions can provide a particularly sensitive method for studying relaxation rates among the excited electronic levels. A detailed discussion and model calculations are given for dilute paramagnetic $4f$ impurities in a metal.

In Mössbauer (MB) source experiments there is initially a large population of high-lying electronic levels of the MB atom following the β decay. The relaxation of these populations toward their thermal-equilibrium values is referred to as rearrangement. In the past, rearrangement has been considered mainly in the special sense of the transfer of electrons to or from the source atom, i.e., *configurational* rearrangement.[1] Here we point out that the time for *intraconfigurational* rearrangement [e.g., the thermalization of initial populations of excited crystal-field (CEF) levels] can be appreciable even when the time needed for the configurational rearrangement is negligibly small. In such a case, the MB spectrum in a source experiment contains appreciable contributions from the intraconfigurational excited states which would be absent from the corresponding absorber spectrum. We shall indicate how these intraconfigurational rearrangement effects can be dealt with theoretically, and show that in favorable cases the MB source experiments provide a particularly powerful technique for investigating relaxation processes involving intraconfigurational excited levels.

Such intraconfigurational rearrangement effects can affect the MB source spectra of various substances, including insulators and intermetallic compounds.[2] For brevity, however, we restrict the present discussion to the MB spectra of dilute $4f$ impurities in metals.[3-5] To achieve sufficient intensity at high dilution, such impurities have always been studied as sources. Although absorber experiments appear impractical, it is still of interest to compare theoretical spectra for the source and absorber cases.

Experiments of the type considered here are performed using as a source a metal foil containing neutron-activated $4f$ impurities which are the radioactive parent of the MB atom. The β decay of such an impurity prepares the emission of the MB γ quantum, and also starts a rearrangement of the electronic shell of the impurity in response to the change in nuclear charge. The rearrangement proceeds as a multistep cascade from higher to lower levels, with different times characteristic of the various decay steps. Any decay step can be regarded as quasi-instantaneous as far as the MB effect is concerned when its characteristic time is short compared to $(\omega_{\text{hf}})^{-1} \approx 10^{-10}$ sec, where $\hbar\omega_{\text{hf}}$ is the total hyperfine splitting.[6]

Since the β decay increases the nuclear charge by one, the first rearrangement step to consider in the electronic shell is the configurational rearrangement $4f^{n-1} \rightarrow 4f^n$. The decay of the unstable configuration occurs by absorption of a conduction electron into the $4f$ shell via the Anderson mixing interaction. The rate is approximately $\Delta/\hbar \approx 2\times10^{13}$ sec^{-1}, where we have assumed a value of 0.01 eV for the virtual bound-state width Δ. The configurational rearrangement is therefore quasi-instantaneous.

The $4f^n$ ground configuration of the MB atom is split into various $[SL]$-J manifolds. The ground manifold is subject to an overall CEF splitting of ~0.01 eV, and the excited manifolds lie 0.1 eV or more above it. The configurational rearrangement will leave the electronic shell in a highly excited state within the ground configuration, so an intraconfigurational rearrangement is necessary to reach thermal equilibrium. This is provided by the k-f coupling in the sense of a generalized Schrieffer-Wolff effective interaction.[7,8] When written in its most general form, this interaction provides transitions among all pairs of states belonging to the ground configuration. In second-order perturbation theory the transition rate may be written[2,9]

$$w_{i\to f} \approx 2\pi\, |I\rho(\epsilon_F)|^2 \zeta(E_f - E_i, kT). \qquad (1)$$

Here $\rho(\epsilon_F)$ is the density of conduction-electron states, I is a coupling constant characterizing the generalized k-f interaction, and $\zeta(E, kT) \equiv E[\exp(E/kT) - 1]^{-1}$. We have omitted from Eq. (1) a sum over matrix elements which depends upon the specific transition but is of the order of unity. For the initial steps of the intraconfigurational rearrangement we are interested in decays from high-energy states, for which $E_i - E_f \gg kT$. Then $\zeta \approx E_i - E_f$, so that the decay rate is temperature independent and proportional to the energy difference. Taking $I\rho(\epsilon_F) = 10^{-2}$ from electron paramagnetic resonance (EPR) studies,[10] we find that such a high-energy decay is quasi-instantaneous ($w_{i\to f} \gg w_{\mathrm{hf}}$) when $E_i - E_f \gg 0.01$ eV. The rearrangement among $[SL]$-J manifolds can thus be regarded as quasi-instantaneous. The rearrangement among the lowest CEF levels, however, will in general be slow enough to influence the MB spectrum.

Solutions for MB spectra in the presence of electronic relaxation can be obtained by solving an appropriate equation of motion.[3,11] The intraconfigurational rearrangement results from the same electronic relaxation processes and hence is implicit in the equation of motion; all that is necessary is to make the proper choice of the initial population distribution appearing in the theory. For a MB *absorber*, the appropriate initial population is a thermal Boltzman weighting of the nucleonic eigenstates with the nucleus in its ground state. In the case of a $4f$ impurity as the MB *source*, the cascade of quasi-instantaneous decays through the higher electronic levels following the β decay will produce an essentially random initial population of the CEF levels within the $[SL]$-J ground manifold. The initial nuclear-spin orientation is also random. Hence, the proper initial population distribution is the one in which the occupation probability is equal for all nucleonic eigenstates containing the nucleus in its excited state and the electronic shell in its $[SL]$-J ground manifold.

The numerical evaluation of the above solution does pose practical problems, since, in general, it is necessary to include all CEF levels in the treatment. If the methods of Ref. 3 are applied straightforwardly, one obtains matrix equations with a dimensionality of several hundred in typical cases. This dimensionality can be reduced considerably by the application of symmetry considerations,[2] but the computational problem remains a major one. We shall therefore illustrate our discussion with model calculations for Yb^{3+} in a cubic CEF where only three levels exist. Such calculations are shown in Fig. 1. The solid curves show source spectra at various temperatures. For comparison the corresponding absorber spectra are shown as dashed curves. The CEF parameters were chosen to produce a Γ_7 doublet ground level, and Γ_8 and Γ_6 excited levels at 17.5 and 18.2 K, respectively. The relaxation arises from a generalized Schrieffer-Wolff[7,8] interaction with $I\rho(\epsilon_F) = 0.01$. The two main peaks of the low-temperature spectra result from the Γ_7 ground level.[5] The low-temperature source spectra show additional contributions from the

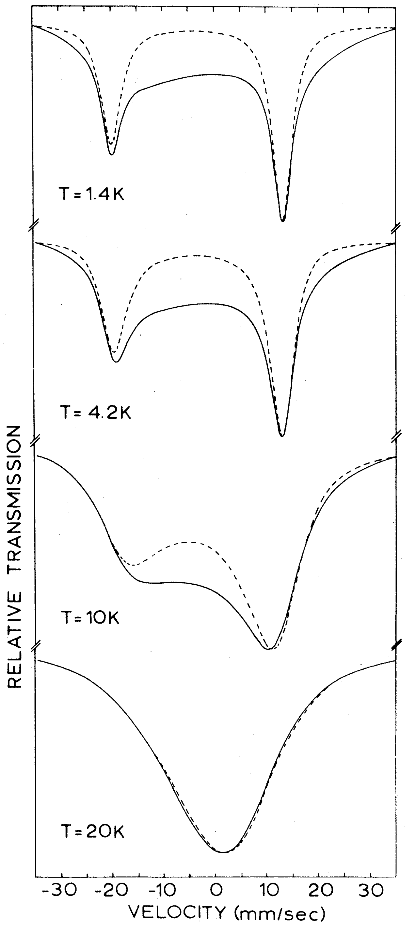

FIG. 1. Model calculations for the $2^+ \to 0^+$ Mössbauer spectrum of $^{170}\mathrm{Yb}^{3+}$ impurities in a metal, where the relaxation is produced by a generalized Schrieffer-Wolff coupling with $I\rho(\epsilon_F) = 0.01$. Source and absorber spectra are indicated by solid and dashed curves, respectively.

CEF excited levels, which are absent from the corresponding absorber spectra. As indicated by Eq. (1), the rate of relaxation from a higher to a lower CEF level approaches a finite limit for temperatures small compared to the CEF energy difference. Since the initial populations are also temperature independent in a source experiment, *the contributions from the excited CEF levels approach a finte limiting form at temperatures small compared to the CEF splittings.* This is in contrast to the absorber case, where contributions from excited CEF levels vanish in the low-temperature limit.

The CEF parameters of our Yb^{3+} model calculation have deliberately been chosen so as to produce Yb^{3+} CEF levels resembling the three lowest CEF levels believed[5,10] to occur in *Au*:Er. Actual calculations for Er^{3+} are not yet available because of its larger number of electronic levels; they can, however, be expected to yield spectra qualitatively similar to Fig. 1. In fact, our earlier measurements of the ^{166}Er resonance of dilute *Au*:^{166}Ho sources[5] yielded spectra with a central structure resembling that seen in Fig. 1. This structure was originally assumed to result from Ho clusters in the *Au*:Ho sources, since it could not be accounted for by a theory assuming a Boltzman initial population of the excited CEF levels.[5] However, much evidence (autoradiographs, good reproducibility of the results) points to an absence of clusters in this alloy, as opposed to other alloys such as *Ag*:Ho where clustering does occur.[12] We now believe the central structure observed in Ref. 5 to be the result of intraconfigurational rearrangement.

If the parameters are changed so as to decrease $w_{e\rightarrow g}$, the rate of decay from an excited CEF level to the ground level, then the excited-level contributions become more prominent and finally take the form of well-resolved peaks. If $w_{e\rightarrow g}$ is increased, the excited level contributions become less prominent and disappear in the limit $w_{e\rightarrow g} \gg \omega_{\mathrm{hf}}$. In this case, the excited CEF levels may still influence the spectrum insofar as they provide an additional channel for relaxation.[2,9,10]

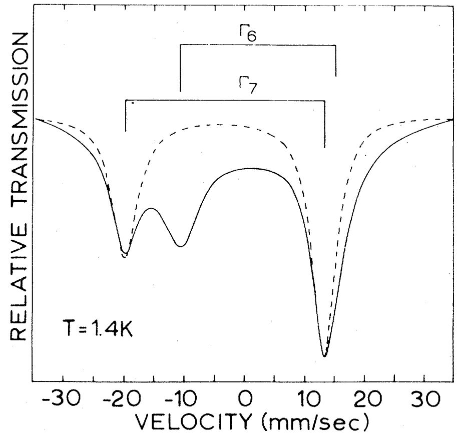

FIG. 2. Model calculations as in Fig. 1, except that the relaxation is produced by an "exchange" coupling $-2J_{\mathrm{ex}}'\vec{J}\cdot\vec{s}$. We take $2J_{\mathrm{ex}}'\rho(\epsilon_F)=0.0031$, which produces the same relaxation rate within the CEF ground doublet as the coupling used in Fig. 1. The source spectrum (solid curve) is a superposition of two narrow-line contributions from the Γ_7 CEF ground level and two from the Γ_6 excited level; in the absorber spectrum (dashed curve) the excited-level contributions are negligible.

In Fig. 2 we present a further model calculation for Yb^{3+} with the same CEF parameters as before, but with a *k*-*f* coupling of the "exchange" form $-2J_{\mathrm{ex}}'\vec{J}\cdot\vec{s}$, which has traditionally been assumed in discussing the EPR of 4*f* impurities in metals.[9,10] Whereas the generalized Schrieffer-Wolff coupling[7,8] produces comparable transition rates between any pair of CEF levels (aside from the energy dependences), the selection rules on the vector operator $\vec{J}$ do not allow a direct transition from the Γ_6 excited CEF level to the Γ_7 ground level. The large initial population of the Γ_6 excited level in a MB source experiment can only decay slowly via the Γ_8 level and thus contributes a well-resolved hf structure to the spectrum. The differences between Figs. 1 and 2 demonstrate that MB source experiments provide an unusually sensitive test for the form of the *k*-*f* coupling.

Finally, we remark that intraconfigurational rearrangement effects similar to those discussed here need also to be taken into account in the analysis of perturbed angular correlation experiments.

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*Present address: Institut für Theoretische Physik, Universität Frankfurt am Main, Frankfurt am Main, German Federal Republic.

†Permanent address: Laboratoire de Chimie Nucléaire, 67037 Strasbourg, Cedex, France.

[1] H. H. Wickman and G. K. Wertheim, in *Chemical Applications of Mössbauer Spectroscopy,* edited by V. I. Goldanskii and R. H. Herber (Academic, New York, 1968).

[2] L. L. Hirst, to be published.

[3] L. L. Hirst, J. Phys. Chem. Solids 31, 655 (1969).

[4] F. Gonzalez-Jimenez, P. Imbert, and F. Hartmann-Boutron, Phys. Rev. B 9, 95 (1974).

[5] G. K. Shenoy, J. Stöhr, and G. M. Kalvius, Solid State Commun. 13, 909 (1973).

[6] Our estimate applies to the usually encountered case $(\omega_{hf})^{-1} < \tau$, where τ is the lifetime of the nuclear excited state. If one had $\tau < (\omega_{hf})^{-1}$ then the comparison would be to τ instead of $(\omega_{hf})^{-1}$.

[7] B. Coqblin and J. R. Schrieffer, Phys. Rev. 185, 847 (1969).

[8] L. L. Hirst, Z. Phys. 244, 230 (1971).

[9] L. L. Hirst, Phys. Rev. 181, 597 (1969).

[10] D. Davidov, C. Rettori, A. Dixon, K. Baberschke, E. P. Chock, and R. Orbach, Phys. Rev. B 8, 3563 (1973).

[11] The treatment of Ref. 3 included only the CEF ground level, but the extension to many CEF levels is immediate.

[12] J. Stöhr and G. K. Shenoy, Solid State Commun. 14, 583 (1974).