Direct Observation of Intraionic and Interconfigurational Excitations in an Intermediate-Valence Compound by Raman Spectroscopy

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Intraionic spin-orbit–split multiplet levels have been observed by electronic Raman scattering in the intermediate-valence compound $EuPd_2Si_2$. From the temperature dependence of the Raman peak positions and widths the interconfigurational excitation energy E_x and an upper limit of the interconfigurational mixing width T_f, respectively, have been obtained. This is the first spectroscopic support for the underlying assumptions of the ionic interconfigurational fluctuation model that has been proposed to describe intermediate valence.

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In rare-earth intermediate-valence (IV) systems the strongly correlated nature of the localized $4f$ states makes the theoretical treatment of their interaction with conduction electrons a rather difficult problem.[1] In the interconfigurational fluctuation (ICF) model an approach based on a purely ionic $4f$ configuration has been chosen.[2] In this model the interaction between two $4f$ configurations $(4f^n \leftrightarrow 4f^{n-1} + e^-)$ is parametrized by the interconfigurational excitation energy (E_x) and by the interconfigurational mixing width or fluctuation temperature (T_f) of the multiplet levels. The ionic model has been used to extract the temperature dependence of E_x and T_f from magnetic-susceptibility and Mössbauer data[3,4] and to provide a semiquantitative understanding thereof in the framework of phenomenological thermodynamics.[3,5] However, in our opinion there has been so far no direct spectroscopic proof for the validity of the basic assumptions of the ionic model. The latter concern the persistence of individual ionic $4f$ multiplet levels characterized by their total angular momentum J and the temperature-induced shift of the two rigid $4f^n$ and $4f^{n-1}$ multiplets with respect to each other, described by $E_x(T)$.

In this paper we report the spectroscopic observation of ionic spin-orbit–split J-multiplet levels in the IV compound $EuPd_2Si_2$ by means of electronic Raman scattering. The temperature dependence of E_x and of the upper limit of T_f is directly revealed in the Raman spectra. Our results support the salient features of the ionic ICF model[2] and are in reasonably good agreement with the E_x and T_f deduced from the Mössbauer and magnetic-susceptibility data.[4]

Raman-scattering measurements were carried out on freshly fractured polycrystals of $EuPd_2Si_2$ between 300 and 4.2 K. In Fig. 1 the Raman spectra of $EuPd_2Si_2$ obtained with 5309-Å laser excitation are shown for selected temperatures. On the top of the figure the J-multiplet levels observed by electronic Raman scattering in $SmSe$[6] are shown. The maxima observed in $EuPd_2Si_2$ are close in energy to the J-multiplet levels of $SmSe$. This is to be expected, since the J levels of Eu^{3+} should be the same as those of the $Sm^{2+}4f^6(^7F_J)$ configuration. The J-multiplet levels of IV $EuPd_2Si_2$ at 300 K are quite broad compared to the J levels of divalent $SmSe$. Upon cooling to 200 K, the J levels of $EuPd_2Si_2$ undergo an asymmetric broadening and this is most clearly seen for the $J=3$ and $J=4$ levels. This broadening develops into a well-pronounced splitting at 145 K, which is rather well seen in the case of $J=2,3$, and 4 levels. At 77 K the splitting of individual J levels has disappeared, yielding a single broadened peak for each one of the J levels. The spectrum at 4.2 K reveals well defined J-multiplet levels similar to the spectrum at 300 K. The reproducibility of the spectral features in Fig. 1 is slightly affected presumably by local strains giving rise to frequency shifts of the levels up to 3%. The overall background in Fig. 1 arises mainly from sample imperfections causing luminescence emission. So far we have not been able to observe any Raman-active phonons in $EuPd_2Si_2$, or in the reference compound $LaPd_2Si_2$, both of which crystallize in the tetragonal $ThCr_2Si_2$ structure.

In Fig. 2 we show a schematic energy-level diagram explaining the electronic Raman scattering from the J-multiplet levels in an IV Eu compound. The $(Eu^{2+})4f^7$ and $(Eu^{3+})4f^6 + e^-$ configurations are
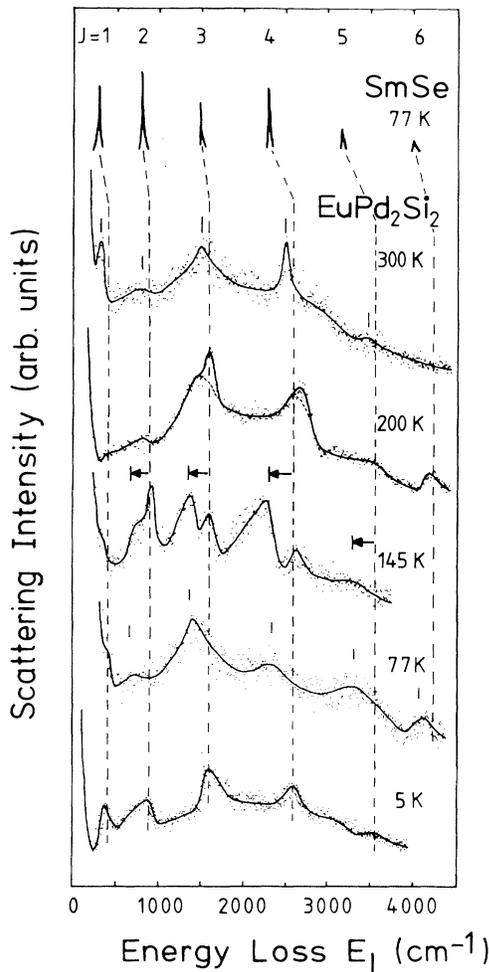
FIG. 1. Raman spectra of $EuPd_2Si_2$ at different temperatures under 5309-Å laser excitation. Vertical dashed guide lines mark the intraconfigurational excitations $(E_{L,intra})$ of the $Eu^{3+}4f^6(^7F_J)$ configuration; solid lines through spectra are guide lines to the eye. Top of the figure: electronic Raman scattering due to the $Sm^{2+}4f^6(^7F_J)$ configuration of SmSe (Ref. 6).
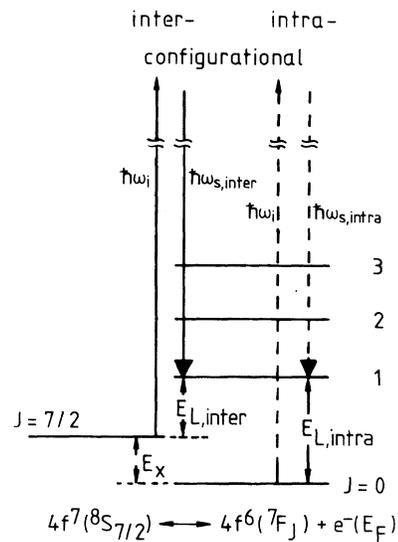

FIG. 2. Schematic representation of the electronic Raman scattering process in an intermediate-valence Eu compound showing an interconfigurational excitation energy $E_x\neq0$. Indicated are the *intra*configurational energy losses $(E_{L,intra})$ and the *inter*configurational energy losses $(E_{L,inter} = E_{L,intra} - E_x)$ of the incident photon $\hbar\omega_i$ with respect to the $J=0$ and $J=\frac{7}{2}$ initial state, respectively.

nearly degenerate and separated by E_x. When $E_x\neq0$ two sets of inelastic energy losses $E_{L,intra}$ and $E_{L,inter} = E_{L,intra} - E_x$ are possible for the J-multiplet levels of the $4f^6$ configuration. These are the *intra*configurational excitations $(E_{L,intra})$ of the $J = 1,...,6$ levels with respect to the $(4f^6)$ $J = 0$ initial state and the *inter*configurational excitations $(E_{L,inter})$ with respect to the $(4f^7)$ $J = \frac{7}{2}$ initial state. The interconfigurational excitation energy E_x itself should also show up with respect to the $J = 0$ initial state. The inelastic scattering intensity of the interconfigurational excitations $(4f^7 \leftrightarrow 4f^6 + e^-)$ is obtained in second-order perturbation theory and should be stronger than for the magnetic-dipole allowed intraconfigurational excitations $(J = 0 \rightarrow J\neq0)$. The latter contribute to

the scattering cross section in third-order perturbation theory involving spin-orbit coupling.

We now turn to the interconfigurational excitation energy E_x and its temperature dependence which is given by the *common, rigid shift* of all interconfigurational excitations $(E_{L,inter})$ with respect to the intraconfigurational J-multiplet excitations $(E_{L,intra})$. The latter have been indicated in Fig. 1 by the dashed vertical lines, whose positions are fixed by the sequence of highest energy losses as found for 200 K and 145 K. The intraconfigurational transition energies are in first order temperature independent. Any shifts of these energies due to temperature-dependent mixing or local-environment effects should increase with increasing J value. Such a behavior is found by incorporation of the free rare-earth ion into the solid, like for SmSe or SmS,[6] but is not observed in $EuPd_2Si_2$. At 300 K the more intense interconfigurational excitations $E_{L,inter}$ (indicated by tick marks) are slightly shifted to lower energy with respect to the dashed lines, implying $E_x \simeq 50$ cm^{-1} (70 K). At 200 K a further increase of E_x $(E_x \simeq 150$ K) is indicated by the asymmetric broadening of the peaks at their low-energy side. The clearest evidence for a pronounced increase in E_x $(E_x \simeq 350$ K) is found in the spectrum at 145 K, in which the $E_{L,intra}$ and $E_{L,inter}$ peaks are clearly split. At 77 K this splitting has disappeared, although the energy positions of the dominant

interconfigurational excitations $E_{L,\text{inter}}$ (see tick marks) imply that E_x is still about the same as at 145 K. The spectrum at 5 K shows again rather narrow peaks near the positions of the dashed lines, implying that E_x is about of the order of the room-temperature value. The temperature dependence of E_x directly revealed in our Raman spectra is plotted in Fig. 3(a).

We will now consider the temperature dependence of T_f, characterizing the quantum-mechanical mixing of the two $4f$ configurations (see bottom of Fig. 2). This information is mainly contained in the *spectral width* of the Raman peaks. Although the experimentally observed widths of the different J levels differ significantly at 300 K, their additional variations upon cooling below 300 K are very similar. Since we observe the joint mixing width of initial and final state in the scattering process, we ascribe the temperature-dependent common contribution to the width of all energy-loss peaks primarily to T_f of the initial state (ground state). The upper limit of T_f of the ground state is set by the narrowest energy-loss peak observable, i.e., $J = 1$ at 300 and 5 K, and $J = 3$ at all other temperatures. These values inferred from the spectral features are presented in Fig. 3(b) as a function of temperature.

This independent determination of E_x and of the upper limit of T_f is consistent for the following reasons. At 300 K, T_f is of the order of E_x and therefore no splitting between the $E_{L,\text{inter}}$ and $E_{L,\text{intra}}$ excita-

tions is detectable. At 200 K, T_f is slightly smaller than E_x, thus allowing for the observation of the asymmetric broadening of the peaks. Because of the much smaller T_f at 145 K compared to E_x the splitting between $E_{L,\text{intra}}$ and $E_{L,\text{inter}}$ excitations is most clearly seen. The disappearance of this splitting at 77 K is due to the dramatic increase of T_f to a value equal in magnitude to E_x, namely 350 K. At 5 K the upper limit of T_f is larger than E_x and consequently no splitting can be detected.

It is most encouraging that our data in Fig. 3 show good qualitative agreement with those obtained by Schmiester et al.,[4] on totally different experimental grounds. By use of the ionic ICF model, these authors have deduced the temperature dependence of E_x and T_f for $EuPd_2Si_2$ from the Mössbauer isomer shift and the magnetic susceptibility. While the plateau of E_x near 100 K is found in both analyses, our maximum $E_x \simeq 350$ K is somewhat smaller than $E_x \simeq 500$ K deduced in Ref. 4. We note here that a consistent interpretation of our data is achieved only with $E_x > 0$ at 300 K, contrary of Ref. 4. However, since $k_B T \gg E_x$ this is not in conflict with the valence $v = 2.2$ at 300 K.[7] In agreement with Ref. 4 the maximum of T_f is found near 80 K.

We have also performed Raman scattering measurements on mechanically polished samples of $EuPd_2Si_2$. It is known that the polishing may produce residual stresses up to about 10 kbar within the scattering volume.[7] This would actually allow us to check whether the present data are consistent with the temperature-pressure phase diagram.[8] The Raman spectrum of the polished sample at 300 K did not exhibit the detailed multiplet structure shown in Fig. 1, except for one prominent peak near 330 cm^{-1} (480 K). Because of its strong intensity it is attributed to the interconfigurational excitation E_x between the $J = 0$ initial state and the $J = \frac{7}{2}$ final state, which is close in energy to the $J = 1$ level. Interestingly enough, this spectroscopically observed value of E_x is in good agreement with that deduced in Ref. 4 at 300 K for a pressure of 10 kbar.

In previous Raman studies on $Sm_{1-x}Y_xS$[6] no evidence of the J-multiplet levels was found for concentrations beyond configuration crossover $(x > 0.15)$. However, the situation in $Sm_{1-x}Y_xS$ is more complicated because of the $Sm^{3+}4f^5(^6H_J)$ configuration as compared to the single $4f^7(^8S_{7/2})$ level of Eu^{2+}. The $4f^5$ configuration shows a splitting of about 900 cm^{-1} between the $J = \frac{5}{2}$ and $J = \frac{7}{2}$ levels, and additionally both may also be further split by the crystalline electric field. Moreover, in a solid-solution system inhomogeneous broadening of the J levels may also play a role. On the other hand, in our Raman study of $EuPd_2Si_2$ the use of different laser excitation energies $\hbar\omega_l$ resulted in an overall resonantly enhanced scatter-
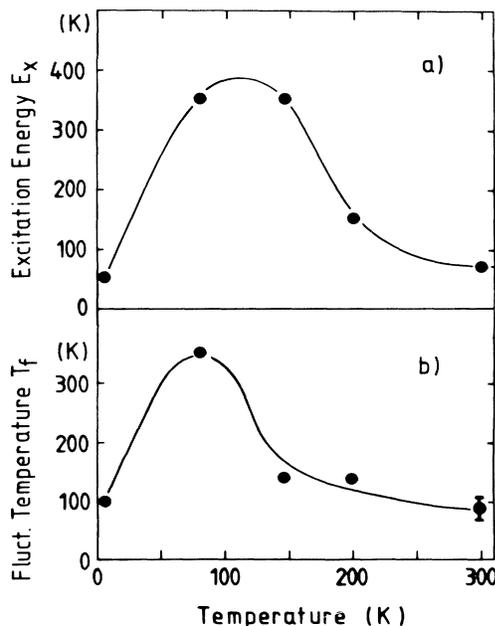

FIG. 3. Temperature dependence of (a) the interconfigurational excitation energy (E_x) and (b) the *upper limit* of the fluctuation temperature T_f of $EuPd_2Si_2$ as directly revealed in the Raman spectra of Fig. 1.

ing cross section for $\hbar\omega_i \simeq 2.4$ eV, most likely due to strong f-d electric-dipole transitions.

In conclusion we would like to emphasize that electronic Raman scattering in $EuPd_2Si_2$ has given the first direct spectroscopic evidence for the persistence of intraionic J-multiplet levels in an intermediate-valence state. Until now this could be inferred only indirectly from maxima in the nonlinear relationship of $T_f(E_x)$.[3] Furthermore, our Raman spectra have enabled us to evaluate directly the temperature dependence of E_x and of the upper limit of T_f. So far E_x and T_f have been obtained as adjustable parameters from susceptibility and Mössbauer data analysis by use of the ionic ICF model.[3-5,9,10] The dramatic valence change of $EuPd_2Si_2$ near 150 K[4,8-10] has been shown to arise from the near degeneracy of the (Eu^{2+}) $J = \frac{7}{2}$ and the (Eu^{3+}) $J = 1$ levels and their interconfigurational mixing. We believe that the results reported in this paper provide direct experimental verification of the underlying assumptions of the ionic ICF model.

In recent neutron-scattering experiments on $EuPd_2Si_2$[11] the quasielastic linewidth has been determined, which agrees above 50 K with our temperature dependence of the upper limit of T_f.

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