Cooperative Configuration Change in $EuPd_2Si_2$

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$4f^7 \rightleftarrows 4f^6 + e$ charge fluctuations (inferered from ^{151}Eu Mössbauer spectroscopy) in $EuPd_2Si_2$ show a strong nonlinear thermal dependence when compared to those observed in dilute Eu in $LaPd_2Si_2$. This nonlinear behavior is well described by extending the interconfigurational fluctuation model to include a cooperative intersite coupling of the interconfigurational fluctuation excitation energy to the $4f$ occupation number. Eu nuclear vibrational damping occurs in the region of greatest charge instability.

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The partitioning of the electrons in a solid into those lying in highly localized core states and those lying in delocalized band states is one of the most basic and useful approximations in solid-state physics. Charge fluctuations from a localized $4f$ level to the conduction band in interconfigurational (IC) rare-earth compounds constitute a breakdown of this very fundamental assumption and have understandably excited a great deal of interest in recent years.[1-3] The technique of Mössbauer spectroscopy has proven to be of great value in this field, being most extensively exploited in Eu compounds where the $4f^7$ Eu^{2+} and $4f^6$ Eu^{3+} configurations have quite different ^{151}Eu isomer shifts.

Previous Mössbauer-effect results on concentrated and dilute Eu systems (with the exception of $EuPd_2Si_2$) have all been successfully interpreted using a simple, single-atom-based interconfigurational fluctuation (ICF) model.[4-7] This success suggests that the concentrated IC europium compounds examined to date have all behaved as an assemblage of isolated centers with no evidence of any mutual coupling of charge fluctuations at different sites. Here we report isomer-shift measurements on isomorphous dilute (Eu in $LaPd_2Si_2$) and concentrated ($EuPd_2Si_2$) compounds. In the dilute system we again find single-atom IC behavior in contrast to the concentrated system which exhibits a cooperative valence transition. By extending the ICF model to include a cooperative shift in the excitation energy between the $4f^6$ and $4f^7$ configurations we obtain an excellent quantitative theoretical agreement with the experimental data. In addition, our results clearly show a strong coupling of the valence fluctuations in $EuPd_2Si_2$ to the material's elastic properties in the form of a damping of the Eu atom vibrational amplitude. This last observation constitutes the first application of Mössbauer spectroscopy to probe the anomalous lattice dynamic properties of an IC material.

Since the characteristic time of the present Mössbauer measurement is longer than the charge fluctuation time between the Eu^{2+} and Eu^{3+} configurations, the average isomer shift (I) provides a good measure of the average Eu valence. If the occupation probabilities of the Eu^{2+}-($4f^7$) and Eu^{3+}($4f^6$) configurations are respectively P_2 and P_3 then in the presence of the fast charge fluctuations

$$I = P_2 I_2 + P_3 I_3, \tag{1}$$

where I_2 and I_3 are the integral-valence isomer shifts. In the ICF model[4] these occupation probabilities depend on E, the energy separation between the Hund's-rule ground states of the two configurations, and follow Boltzmann statistics:

$$P_2 = 8\exp[-E/k\tau]/Z, \tag{2a}$$

$$P_3 = (1 + 3\exp[-480/k\tau] + 5\exp[-1330/k\tau] + \dots)/Z, \tag{2b}$$

where $P_2 + P_3 = 1$ defines Z. The substitution $\tau = (T^2 + T_f{}^2)^{1/2}$ is used to allow for a broadening (of magnitude T_f) of the various energy levels due to quantum mechanical hybridization. The energies of the excited spin-orbit states of the Eu^{3+} configuration have been assumed as previously.[8] It should be

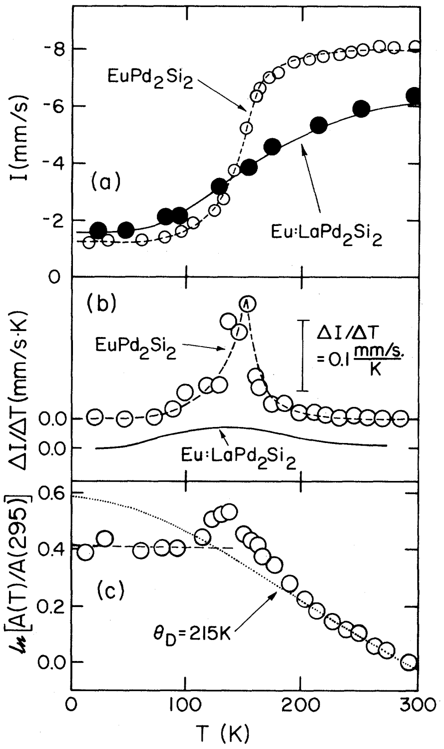

FIG. 1. (a) Experimental and theoretical isomer shift variations for EuPd$_2$Si$_2$ and Eu$_{0.01}$La$_{0.99}$Pd$_2$Si$_2$. (b) Experimental and theoretical values of $\Delta I/\Delta T$ for EuPd$_2$Si$_2$ and theoretical variation for Eu in LaPd$_2$Si$_2$. (c) Total area of the Mössbauer absorption signal in EuPd$_2$Si$_2$. The dotted line is the fitted high-temperature Debye-model variation (θ_D = 215 K). The dashed line is a guide to the eye indicating the extension of the low-temperature data into the valence transition region.

noted that this theory is basically a high-temperature theory for incoherent thermal charge fluctuations at temperatures greater than the level width T_f. It is in this spirit that we apply this model in this paper.

The thermal variation of the isomer shift for the nominally 1% Eu in LaPd$_2$Si$_2$ sample is shown by the full circles in Fig. 1(a). The source used was Sm$_2$O$_3$. This is the second reported dilute europium compound showing intermediate valency behavior.[8] The data are well fitted over the whole temperature range using the ICF model as described above with $I_2 = -11.01$, $I_3 = -1.59$, $E = 492$ K, and T_f fixed at 50 K [see solid line in Fig. 1(a)]. Thus Eu in LaPd$_2$Si$_2$ shows a single-atom–type behavior qualitatively similar to that observed in all previous concentrated and dilute Eu systems.

We now turn to the results of Mössbauer absorption measurements for EuPd$_2$Si$_2$ (see Sampathkumaran *et al.*[9]). Our experimental spectra (which will be presented elsewhere)[10] are qualitatively similar to previously reported spectra on EuCu$_2$Si$_2$.[4] In particular in addition to the main absorption line we also observe other fully or partially resolved components. These extra components which have been observed in all europium IC compounds account in this compound for a maximum of about 20% of the total absorption area. As previous authors have done,[5,8] we exploit the microscopic nature of the Mössbauer probe to study the temperature dependence of the isomer shift of the main line only. The isomer shift of the main line was established by simultaneously fitting all component lines in the spectra.

The thermal variation of the isomer shifts of the dominant component in EuPd$_2$Si$_2$ is given by the open circles in Fig. 1(a). The thermal variation is much more dramatic than for the dilute sample. This difference is emphasized in Fig. 1(b) which compares the slopes of the isomer-shift variation for the concentrated sample (obtained experimentally by evaluating $\Delta I/\Delta T$ between successive points) and for the dilute sample (obtained by taking the derivative of the analytical fitted ICF model curve). This dramatic enhancement in the nonlinearity of the isomer-shift (valence) variation upon passing isomorphically from a dilute to a concentrated Eu system provides direct empirical evidence for cooperative interactions among the Eu charge fluctuations in the concentrated sample.

Understandably the isomer shift variation for EuPd$_2$Si cannot be fitted by the existing single-atom–based ICF model using a single excitation energy. Moreover a simple, linear thermal shift of the excitation energy due to thermal-expansion effects (as discussed by Nowik[4] for EuCu$_2$Si$_2$) is insufficiently nonlinear to fit our EuPd$_2$Si$_2$ results. To incorporate the intersite coupling between the Eu charge fluctuations into the ICF model we introduce an interaction shift of the excitation energy. This shift could be driven for example by a compression shift mechanism[11] or a Coulombic shift mechanism.[12] Since the results do not allow specification of a particular microscopic mechanism, we parametrize the microscopic variable n_f (the $4f$ level occupation number) by a related observable, namely the isomer shift value. A bootstrapping mechanism is then created by introducing a coupling of the excitation energy of the ith Eu atom (E_i) to the n_f value of the jth Eu atom (parametrized by I_j, its isomer shift):

$$E_i = E_i^0 + \sum_j \alpha_{ij}(I_j - I^0), \tag{3}$$

where E^0 and I^0 are the average excitation energy and isomer shift at $T=0$ for all atoms and where α_{ij} is the interaction coupling constant with j summed over the entire crystal. In a mean-field approximation where E_i and I_j are assumed to take on the same average values E and I at all lattice sites, this reduces to

$$E = E^0 + \alpha(I - I^0), \tag{4}$$

where α is the average interaction parameter resulting from the crystal sum over the α_{ij}.

Using the interaction-shifted excitation energy (4) along with the usual ICF model relations (1) and (2) we achieve an excellent fit to the Mössbauer results for $EuPd_2Si_2$ with $I_2 = -10.65$, $I_3 = -1.23$, $I_0 = -1.23$, $E^0 = 587$ K, and $\alpha = 57.7$, and with $T_f = 50$ K as before. The dashed lines in Figs. 1(a) and 1(b) are the results of this fit for $I(T)$ and $dI(T)/dT$, respectively. The slight difference in the limiting low-temperature isomer shift values for the dilute and concentrated system is of the correct sign and approximate magnitude to be due to a volume effect. In the fitting procedure the difference $I_2 - I_3$ was kept the same in the two cases.

On the basis of analysis of the isomer shift data we estimate the ground-state valence of Eu in $EuPd_2Si_2$ to be 2.9 ± 0.1. The higher estimate of the fitted ICF model (mandated specifically by the fitted value of I_3) is an artifact both of constraining the $4f$ width parameter, T_f, to be constant and of extending the model to temperatures below T_f. In fact it has been pointed out[4] that an increase in T_f is to be expected in the course of the transformation $Eu^{2+} \rightarrow Eu^{3+}$. In recent work it has also been proposed that the fitted values of I_2 and I_3 (within the ICF model) not be associated with the isomer shift values in the pure valence states.[13]

Associated with the rapid change in average valence (isomer shift) observed near 150 K in $EuPd_2Si_2$ there is also a well-defined anomalous peak in the total Mössbauer absorption area, that is in the combined areas of the main and subsidiary lines [Fig. 1(c)]. The background variation of $\ln A$ is well fitted by a Debye model variation (with $\theta_D = 215$ K) for temperatures between 220 and 600 K. The low-temperature absorption-area data are too limited to be fitted to a Debye model. Relative to the Debye-model variation the peak value of the anomalous increase in $\ln A$ corresponds to a *decrease* in the mean squared displacement (MSD) per Eu atom of about $(0.039\ \text{Å})^2$. This anomalous increase in $\ln A$ has a thermal variation analogous to that of dI/dT for the same sample.

Breathing charge fluctuations of an IC atom have in some cases been shown to buffet its nearest neighbors (non-IC atoms), thereby *increasing* their MSD.[14,15] We believe that the observed *decrease* in the MSD of the Eu atoms is related to a breathing charge fluctuation damping of the IC atoms' amplitude of oscillation (possibly due to anharmonic strains). A definitive interpretation on this point must wait for a new generation of samples where the fraction of Eu atoms not involved in the valence transition is reduced. The unique utility of Mössbauer-effect measurements in probing the local elastic properties of such IC systems is, however, clear from our results and represents a potentially valuable new tool in this field.

The experimental results presented here emphasize that intersite charge-fluctuation interactions can play an important role in Eu systems. Indeed, within the model developed here these interactions drive a first-order valence transition upon a modest decrease in the ratio of the model parameters E^0/α. With the use of alloys which either expand the lattice or increase the conduction-band filling it should be possible to decrease the excitation energy E^0 and perhaps thereby to drive this valence transition to a first-order one.

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Sidebands in the Luminescence Spectra of Amorphous Hydrogenated Carbon

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Periodic oscillations in the luminescence spectra of amorphous hydrogenated carbon are reported. The period of these oscillations is 0.185 ± 0.010 eV, which is equal to the C-H wagging-mode energy. These oscillations are a function of the photoexcitation energy $E_{\rm ex}$; they appear when $E_{\rm ex} \leq 2.16$ eV and are absent when $E_{\rm ex} \geq 2.60$ eV, suggesting that localized electron-hole pairs are created by the former and extended states by the latter.

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Very recently, Cohen and Sturge reported periodic oscillations in the photoluminescence spectra of the crystalline alloy $\mathrm{CdS}_x\mathrm{Se}_{1-x}$.[1] These sidebands were observed at the following energies:

$$E = E_{\rm ex} - m\hbar\omega, \qquad (1)$$

where $E_{\rm ex}$ is the photoexciting photon energy, m is an integer, and $\hbar\omega$ is the $\mathrm{CdS}_x\mathrm{Se}_{1-x}$ longitudinal optic (LO) phonon energy. These sidebands were seen in a narrow range of values of $E_{\rm ex}$ when only localized excitons are photoexcited.

We report similar sidebands in luminescence spectra of amorphous hydrogenated carbon (α-C:H) that are observed in a limited range of $E_{\rm ex}$ and where $\hbar\omega$ is the C-H wagging-mode energy.

Anderson[2] and more recently Meyerson and Smith[3] grew α-C:H thin films from the plasma deposition of acetylene ($\mathrm{C_2H_2}$). Our films were grown on ground quartz and Si substrates mounted on the anode of a capacitively coupled plasma reactor using acetylene as the feedstock and operating under the following conditions: substrate temperature, ~300 °C; pressure, 0.35 Torr; flow rate, 0.4 std cm^3/min; and rf power, ≈25 W. The optical absorption α of our films was measured as a function of energy $h\nu$. For $h\nu > 2.3$ eV, $(\alpha h\nu)^{1/2}$ vs $h\nu$ gave a straight line with an energy intercept of 2.0 eV; for $h\nu < 2.3$ eV, an additional absorption—an exponential tail—was present.

The samples grown on quartz substrates were carefully cleaned in methanol, mounted inside a Dewar, immersed in liquid nitrogen or liquid helium, and photoexcited with less than 0.1 W of unfocused laser light from either an Ar-ion laser (2.60–2.71 eV) or an Ar-ion–pumped rhodamine 590 dye laser (1.94–2.16 eV). The luminescence was collected from the rear, analyzed by a $\frac{1}{4}$-m grating monochromator, and detected by a cooled Ge photodiode. The laser beam passed through a cutoff filter and the luminescence passed through an orthogonal cut-on filter, so that no signal was detected when the sample was removed. The luminescence spectra were then calibrated to a tungsten lamp standard.

The luminescence spectrum at 77 °K photoexcited by $E_{\rm ex} = 2.60$ eV is shown in Fig. 1. The spectrum is unchanged if photons with energies up to 2.71 eV are used. However, when $E_{\rm ex}$ is reduced to 2.16 eV or below, periodic oscillations in the luminescence spectra are observed.