The above discussion of the Ni^{2+} compounds clearly indicates the inadequacy of a pure crystal-field description when there is significant hybridization. In those cases where a final-state crystal-field description is adequate, an initial-state description must fail. Even if one were to include the excited states of the $3d^n$ ion there is no simple correspondence between those of the $3d^{n-1}$ final state and those of the initial state. This is particularly clear in the case of a more than half-filled shell. (In compounds with metallic d-band conductivity many-electron effects may add another dimension of complexity.)[12]

We should ask whether it is currently possible to distinguish between localized and bandlike d electrons by XPS. With the resolution currently available (0.5 eV) it is difficult to distinguish between a bandwidth obtained in a one-electron band-structure calculation and the effects of final-state structure for localized d electrons. In cases where a localized description satisfactorily accounts for the observed structure, one may wish to assume that a localized description applies to the final state. It is not self-evident, however, that it must also apply to the unperturbed band.

Finally we should point out that these effects are not specific to XPS but should also manifest themselves in x-ray emission and photoabsorption experiments which have the same final state.

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Charge Fluctuations in Europium in Metallic $EuCu_2Si_2$

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Recoilless-absorption measurements of the 21.6-keV γ ray of Eu^{151} in $EuCu_2Si_2$ reveal an absorption line which has a strongly temperature-dependent isomer shift. The lines fall at neither the Eu^{3+} nor the Eu^{2+} valence positions, but in between. The results are interpreted in terms of fast fluctuations ($\tau < 3.5\times10^{-11}$ sec) of an electron between the localized $4f$ level and the conduction band. The difference in energy between the Eu^{2+} and the Eu^{3+} states in $EuCu_2Si_2$ is found to be about 0.07 eV.

We report here recoilless-absorption studies of the 21.6-keV γ ray of Eu^{151} in $EuCu_2Si_2$, which exhibit a strongly temperature-dependent isomer shift in a region corresponding neither to divalent nor to trivalent Eu ions. The results are interpreted in terms of fast fluctuations ($\tau < 3.5\times10^{-11}$ sec) of an electron between the localized $4f$ level and the conduction band, leading to a fluctuating charge (and spin) density at the Eu nuclei.

Europium ions are usually found to be either divalent or trivalent in metallic compounds as well as in insulators. The magnetic properties of the europium ions in the two valence states are quite different. The ionic ground state of $Eu^{2+}(4f^7)$ is $^8S_{7/2}$, the same as that of Gd^{3+}. Its free-ion magnetic moment is $7\mu_B$. The ionic ground state of $Eu^{3+}(4f^6)$ is $^7F_0$, which is diamagnetic. The ionic magnetic moment and the hyperfine fields are all zero for this state. Isomer shifts between Eu^{2+} and Eu^{3+} compounds, found in Mössbauer-effect studies with the 21.6-keV γ ray of Eu^{151}, are very large. All divalent Eu compounds have an isomer shift between -8.7 and -14.5 mm/sec relative to Eu_2O_3; all trivalent Eu compounds have an isomer shift between -1.0 and $+3.6$ mm/sec relative to Eu_2O_3. No metallic Eu compounds were found hitherto with an isomer shift in the intermediate region, between -1 and -8 mm/sec.[1,2]

Recoilless-absorption measurements were performed on the EuM_2Si_2 system where M is Fe, Cu, or Ag. The compounds were prepared by melting stoichiometric amounts of the elements in an argon atmosphere using an induction furnace. The compounds crystallize in the tetragonal $ThCr_2Si_2$ structure.[3,4] In $EuFe_2Si_2$ and $EuAg_2Si_2$, the Fe and Ag ions occupy the $4(d)$ sites and the Si ions occupy the $4(e)$ sites. In $EuCu_2Si_2$ the Cu and Si ions are distributed between the $4(d)$ and $4(e)$ sites, with the Cu ions preferring the $4(d)$ positions.[5]

The recoilless-absorption measurements on the EuM_2Si_2 compounds were performed at various temperatures between 4 and 670 K. The source used was $^{151}Sm_2O_3$. Some of the experimental spectra obtained are shown in Fig. 1.

In the $EuFe_2Si_2$ measurements, a single absorption line with an isomer shift of -0.7 ± 0.1 mm/sec is obtained at all temperatures. Such a shift is typical for trivalent europium compounds. The $EuAg_2Si_2$ spectra are magnetically split below 20 K. Above 20 K, single unsplit absorption lines are obtained. The isomer shift of the $EuAg_2Si_2$ spectra is -11.4 ± 0.1 mm/sec at all temperatures, typical for divalent europium compounds. In the $EuCu_2Si_2$ spectra, two absorption lines are seen. The isomer shift of the weaker line (which has a relative intensity of about 20% and is split at 4.2 K) is -12.4 ± 0.2 mm/sec at all temperatures, typical for divalent Eu in a metallic environment. The isomer shift of the intense line is temperature dependent. It changes from -1.8 mm/sec at 4 K to -7 mm/sec at 670 K (Figs. 1 and 2). These changes in the isomer shift are

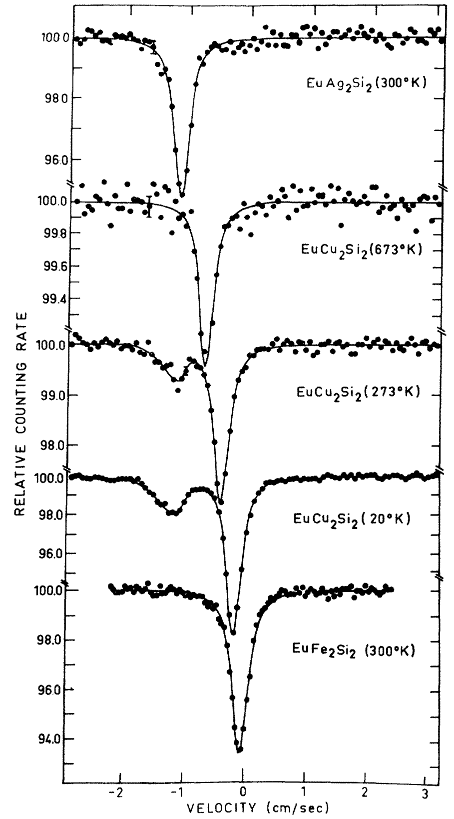

FIG. 1. Recoilless-absorption spectra of the 21.6-keV γ ray of Eu^{151} in $EuFe_2Si_2$, $EuCu_2Si_2$, and $EuAg_2Si_2$.

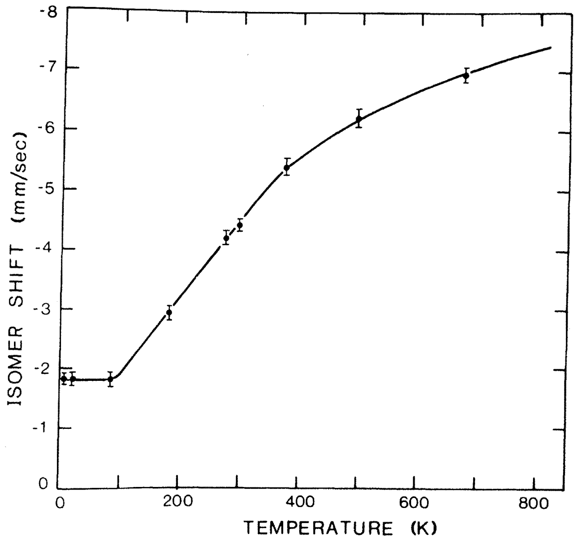

FIG. 2. Isomer shift of the intense line in the recoilless-absorption spectrum in $EuCu_2Si_2$ as a function of temperature. A smooth curve is drawn through the experimental points.

about 100 times larger than those produced by the temperature-dependent second-order Doppler shift. We believe that the intense line corresponds to Eu ions which have 8 Cu ions as their first nearest neighbors [in the 4(d) positions], whereas the weak line corresponds to Eu ions which have one or more Si ions as their first nearest neighbors. The relative intensity of the weak line decreases with temperature, indicating that the recoil-free fraction corresponding to this line is strongly dependent.

The valency of the Eu ions in the $\mathrm{Eu}M_2\mathrm{Si}_2$ compounds depends strongly on the interatomic distances. In $\mathrm{EuAg_2Si_2}$, in which the Eu-M distance is relatively large (2.006 Å),[4] the Eu ions are divalent. In $\mathrm{EuFe_2Si_2}$, where the Eu-M distance is relatively small (1.814 Å),[5] the Eu ions are trivalent. In $\mathrm{EuCu_2Si_2}$, the Eu-M distance (1.886 Å)[5] is intermediate between the corresponding distances in $\mathrm{EuFe_2Si_2}$ and $\mathrm{EuAg_2Si_2}$. We interpret the line moving with temperature in the recoilless absorption spectra in $\mathrm{EuCu_2Si_2}$ as due to Eu ions with undefined valency. These Eu ions can be described in terms of an electron fluctuating rapidly between the localized $4f$ level and the conduction band, leading to fluctuations between the divalent and trivalent Eu states.

The change in position of the absorption line as a function of temperature is produced by the change in the relative population of the divalent and trivalent states. At low temperatures, practically only the trivalent state is populated, whereas at 670 K, the populations of the two states are about equal. If we denote by p_2 and p_3 the relative populations of the 2+ and 3+ states, respectively (normalized so that $p_2+p_3=1$), then the isomer shift δ for very short fluctuation times will be given by

$$\delta = p_2\delta_2 + p_3\delta_3, \tag{1}$$

where δ_2 is the isomer shift of Eu^{2+} (~ -12 mm/sec in our case) and δ_3 is the isomer shift of Eu^{3+} (~ -1.8 mm/sec in our case). From the positions of the absorption line (shown in Fig. 2), the values of p_2 and p_3 as a function temperature were determined. (The data have not been corrected for second-order Doppler effects which are expected to be very small.)

Our experimental results show that the width of the moving line does not change as a function of temperature. This proves that the characteristic fluctuation time τ is very short $[\tau(\delta_2-\delta_3) \ll 1]$. For short fluctuation times the width of the line, Γ, is given by

$$\Gamma = \Gamma_0 + \pi(\delta_2-\delta_3)^2\tau[1-(p_2-p_3)^2], \tag{2}$$

where Γ_0 is the linewidth in the absence of fluctuation phenomena. (Γ, Γ_0, and δ are expressed in units of sec^{-1}.) Formula (2) can be derived from the general equations describing dynamic phenomena in Mössbauer spectra.[6] Using Eq. (2), and considering the fact that within the experimental accuracy Γ does not change with temperature, an upper limit of 3.5×10^{-11} sec is determined for the fluctuation time τ.

The difference in energy $\Delta(T)$ between the Eu^{2+} state and the Eu^{3+} state in $\mathrm{EuCu_2Si_2}$ can be estimated from the values of $p_2(T)$ and $p_3(T)$, calculated from the positions of the absorption line. The multiplicity of the Eu^{2+} ground state ($J=\frac{7}{2}$) is 8, the ground state of Eu^{3+} is a singlet ($J=0$), and the multiplicity of the first excited state of Eu^{3+} ($J=1$), which lies at ~480 K, is 3. The value of p_2/p_3 is therefore given by

$$\frac{p_2}{p_3} = \frac{8\exp(-\Delta/kT)}{1+3\exp(-480/kT)}. \tag{3}$$

The calculations of Δ depend on the value assumed for δ_2. For all known divalent intermetallic compounds of Eu, the values of δ_2 are between -9 and -14 mm/sec. The values obtained for Δ are plotted in Fig. 3 as a function of T, assuming two different values of δ_2 (-11.5 and -14 mm/sec). It is seen that for $\delta_2=-11.5$ mm/sec, the value of Δ is 0.063 ± 0.003 eV (or 735 ± 35 K) at all temperatures. For $\delta_2=-14$ mm/sec, Δ changes from 0.065 eV at 180 K to 0.086 eV at 670 K. (A dependence of Δ on temperature may be associated with the change of interatomic distances with temperature.) The conclusion is

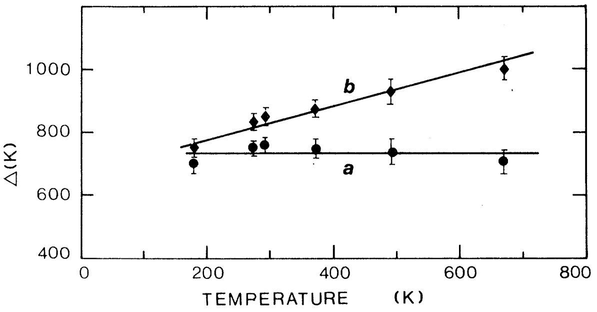

FIG. 3. Difference in energy between the Eu^{2+} state and the Eu^{3+} state in $\mathrm{EuCu_2Si_2}$ as a function of temperature. (a) Assuming a value of -11.5 mm/sec for δ_2; (b) assuming a value of -14 mm/sec for δ_2.

therefore that the difference in energy between the Eu^{2+} and the Eu^{3+} states in EuCu$_2$Si$_2$ is about 0.07 eV in the temperature range between 180 and 670 K. The isomer shifts of all known trivalent metallic compounds of Eu relative to Eu$_2$O$_3$ lie in the region between $+1$ and $+4$ mm/sec. We tend to believe that even at low temperatures the Eu ion in EuCu$_2$Si$_2$ is not in a pure 3+ state. Because of the small difference in energy between the Eu^{2+} and Eu^{3+} states, the 2+ state is probably slightly mixed into the ground state by various perturbations.

The fluctuation effect observed in the present work is different from the hopping effect observed before in Eu$_3$S$_4$.[7] In Eu$_3$S$_4$ the exchange of an electron is between two Eu ions, whereas in EuCu$_2$Si$_2$ the exchange takes place between a localized $4f$ level and the conduction band. In Eu$_3$S$_4$ the relative population of the divalent and trivalent Eu ions (p_2/p_3) is determined by the stoichiometric formula of the compound. The position of the center of mass of the absorption spectrum of Eu$_3$S$_4$ is therefore temperature independent and only the hopping rate is a function of temperature. In EuCu$_2$Si$_2$, p_2, p_3, and τ are functions of temperature.

Phenomena associated with a nonunique charge state of Eu ions may be expected in other compounds of Eu, e.g., in some compounds having the Laves phase structure (EuM_2 compounds with the MgCu$_2$ structure). In EuM_2 compounds with relatively large unit cells (e.g., in EuAl$_2$ with $a = 8.11$ Å), the Eu ion is divalent.[2] In EuM_2 compounds with relatively small unit cells (e.g., in EuRh$_2$ with $a \sim 7.53$ Å or in Eu in SmFe$_2$ with $a = 7.40$ Å), the Eu ion is trivalent. For intermediate unit cells, phenomena associated with nonunique charge states of Eu may be expected. Preliminary recoilless absorption measurements show indeed that the charge state of the Eu ions in SmPt$_2$ ($a = 7.66$ Å) is not unique. We tend to believe that the peculiar magnetic properties of EuIr$_2$[8] ($a = 7.56$ Å) are also connected with the existence of two charge states for the Eu ions in this compound.

Charge fluctuation effects may also be expected in other elements which can exist in more than one charge state, e.g., Sm,[9] Yb, Ce, and the actinide elements.

Finally, we would like to comment that the above described phenomena could, in principle, be explained also by a model which does not assume fluctuations between two states. A possible model would be that of a single state which does not have a pure $4f^7 5s^2 5p^6$ or $4f^6 5s^2 5p^6$ configuration. (It may have, e.g., a nonintegral $4f$ configuration or a $4f^6 5s^2 5p^6 5d^x 6s^y$ configuration.[9]) However, this explanation seems to us very unlikely, as, according to it, the wave function of the Eu ground state has to be strongly temperature dependent in order to explain the temperature dependent isomer shifts. On the other hand, the spin-fluctuation model describes successfully the experimental results in terms of two states with a temperature-independent energy separation [Fig. 3(a)].

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