Comment on the Giant Quadrupole Interaction in Eu$_x$Rh$_3$B$_2$

The Eu^{2+} ion in stoichiometric and non-stoichiometric Eu$_x$Rh$_3$B$_3$, $0.81 \leqslant x \leqslant 1.03$, exhibits an exceptionally large nuclear quadrupole interaction —the largest reported for any europium compound ($e^2qQ = 44$–48 mm/s).[1,2] By analogy with the matrix-isolated Eu^{2+} dimer ($e^2qQ = 21$ mm/s),[3] this quadrupole interaction was attributed to an exceptionally large lattice contribution to the electric field gradient, associated with the anomalously small europium separation along the c axis of the ternary borides. We wish to point out that this interpretation is inconsistent with the lack of any significant quadrupole splitting in the Eu^{3+} compounds of somewhat different stoichiometry, and furthermore suggest that the Eu^{2+} state with a large electric field gradient competes with the intermediate-valence state when europium in ternary intermetallic compounds is on the verge of valence instability.

Our first point is best made by comparing samples II and III of Shaheen et al.,[1] which have $x = 0.89$ and 0.61, respectively. Europium in the former is largely divalent whereas in the latter it is essentially all in the trivalent state. The quadrupole splitting e^2qQ for sample II is greater than 40 mm/s while that of sample III is less than 5 mm/s. Although most of the Eu^{3+} have one vacant nearest-neighbor site, point-charge calculations indicate that the Eu^{3+} field gradient should produce a quadrupole splitting of at least 20 mm/s. The argument concerning the ratio of Eu^{2+} to Eu^{3+} quadrupole interactions is substantially the same whether the ions form zigzag or linear chains along the c axis. Even if the Eu ions in Eu$_x$Rh$_3$B$_2$ were spaced equidistantly along c, the difference between the $x = 0.89$ and $x = 0.61$ samples remains inexplicable in terms of a lattice contribution to the field gradient: The anomalously large field gradient is therefore a characteristic feature of the Eu^{2+} in Eu$_x$Rh$_3$B$_2$.

Some insight into the origin of this unusual Eu^{2+} state may be obtained by considering the isostructural series of compounds EuM_2Si$_2$ (ThCr$_2$Si$_2$ structure), where M is a transition metal. Normally one would expect the Fermi level E_F to rise relative to the 4f levels on changing of M by moving to the right along a row or down a column of the periodic table. As E_F crosses the 4f^6 level, a sequence

$$\text{Eu}^{3+} \rightarrow \text{intermediate valence} \rightarrow \text{Eu}^{2+}$$

is expected. That EuRh$_2$Si$_2$ stands out as an exception to this expected trend is clearly shown in Fig. 1. The compound is anomalously divalent, *with a large quadrupole splitting*, although it is followed in both the horizontal and vertical sequences by an intermediate-valence europium silicide with the same structure. It
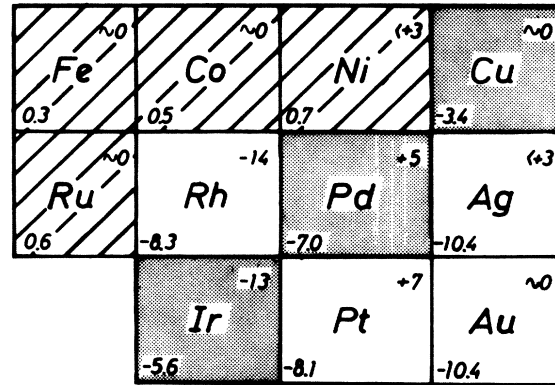

FIG. 1. Quadrupole splitting (millimeters per second) (top right) and isomer shift (millimeters per second) (bottom left), relative to EuF$_3$, of ^{151}Eu in EuM_2Si$_2$ (M = transition metal). Trivalent, intermediate-valent, and divalent Eu are represented by lined, shaded, and blank squares, respectively.

appears that when the 4f^7 level is close to E_F, the divalent state with a large electric field gradient may be stabilized with respect to the intermediate-valence state.

How can this come about? A possibility is strong hybridization of Eu 4f and Rh 4d energy levels which produces a significant admixture of 4f character into the rhodium conduction band, thereby creating a field gradient at the Eu^{2+} nuclei due to conduction electrons. This possibility has been discussed in other Eu compounds,[4,5] and it seems to be the only way to explain the unusually large electric field gradient in the intermetallic compounds of Eu with Rh. The mechanism does not apply for Eu^{3+} because its 4f level is several electronvolts below E_F.

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