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An Investigation of the Europium Valence in $EuCu_{1.75}P_2$ by Eu Mössbauer and Eu L_{III}-Edge X-Ray Absorption Spectroscopy

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The europium valence for $EuCu_{1.75}P_2$ is examined by Eu Mössbauer spectroscopy and Eu L_{III}-edge X-ray absorption spectroscopy. On the basis of previous measurements of related phases with the $ThCr_2Si_2$ structure-type, the europium valence in $EuCu_{1.75}P_2$ is expected to be intermediate valent or trivalent. In contrast, divalent europium is observed. This result is explained on the basis of a band argument in which the conduction band is filled, and thus, there is an extra electron in the Eu $4f^7$ state.

INTRODUCTION

EuT_2P_2 phases with the $ThCr_2Si_2$ structure (shown in Fig. 1) have been observed for T = Fe, Co, Ni, and Cu (1). The europium valence has been measured by Eu Mössbauer spectroscopy (MS) and Eu L_{III}-edge X-ray absorption spectroscopy (XAS) by Jeitschko and co-workers and found to be divalent in $EuFe_2P_2$ and $EuCo_2P_2$ and intermediate valent in $EuNi_2P_2$ (2, 3). While the europium valence has not been measured for the nonstoichiometric copper analog, $EuCu_{1.75}P_2$, it interests us because of contradictory evidence regarding the valence. On the basis of results for the Fe, Co, and Ni phases (2, 3) and of observations for other Cu-containing phases with this structure-type (4), the europium valence for the copper analog is expected to be intermediate valent or perhaps trivalent. However, the volume of the unit cell indicates divalent europium (1c). To assess these contradictory predictions, we have measured the europium valence in $EuCu_{1.75}P_2$ by Eu MS and L_{III}-edge XAS.

This investigation of the europium valence in $EuCu_{1.75}P_2$ was motivated further by our study of the relationship between structure, bonding, and europium valence (5). Analysis of the structure of these phases (1) suggests a correlation between the close phosphorus–phosphorus distance (d_{P-P}) along the c direction and the europium valence. As shown in Fig. 2, d_{P-P} varies from a nonbonding distance greater than 3 Å in $EuFe_2P_2$ and $EuCo_2P_2$ (both with divalent europium) to a single bond distance of less than 2.4 Å for $EuNi_2P_2$ (with intermediate valent europium); the latter distance is comparable to the P–P single bond distance of 2.21 Å in P_4 (6). In addition, the unit cell volumes for $EuFe_2P_2$ and $EuCo_2P_2$ are ~9% larger than that of $EuNi_2P_2$, consistent with the larger volume of divalent europium. Since our previous work on $EuCo_{2-x}Ni_xP_2$ also provides evidence for a correlation between d_{P-P}, the unit cell volume, and the europium valence, we could postulate that the formation of a P–P bond with the resultant compression of the structure drives the transition to intermediate valence. Determination of the europium valence in $EuCu_{1.75}P_2$ addresses this dependence of intermediate valence upon P–P bonding because while there is a single P–P bond and the europium is expected to be intermediate valent or trivalent, the large cell volume is consistent with divalent europium (see Fig. 2).

EXPERIMENTAL

$EuCu_{1.75}P_2$ was prepared by solid state reaction of the elements in stoichiometric ratios in an evacuated, sealed quartz tube as described previously (1). The elemental starting materials were europium (rods, 99.99%, Materials Preparation Center, Ames Laboratory, Ames, Iowa), copper (powder, 99.999%, Johnson Matthey Puratronic), and red phosphorous (lump, 99.99995%, Johnson Matthey

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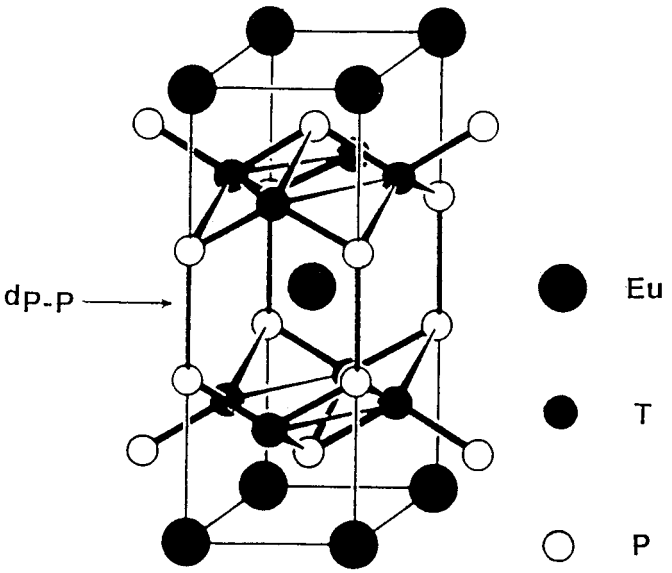

FIG. 1. Unit cell for EuT_2P_2 (T = Fe, Co, Ni, and Cu), space group $I4/mmm$.

Puratronic). The reactants were heated at 800°C for 2 weeks and quenched to room temperature.

The product was characterized by powder X-ray diffraction on a Siemens D500 Diffractometer using Cu$K\alpha$ radiation. Silicon was used as an internal standard. The majority of the reflections in the diffraction pattern could be indexed to the tetragonal unit cell for $EuCu_{1.75}P_2$. Additional lower intensity reflections were attributed to an unidentified minor phase which always appeared, despite numerous variations of the synthetic conditions. Tetragonal lattice parameters for $EuCu_{1.75}P_2$ were obtained from a least squares refinement. The lattice parameters are a = 4.1122(2) Å and c = 9.5664(9) Å which are close to the reported values of a = 4.110(1) Å and c = 9.591(1) Å (1c).

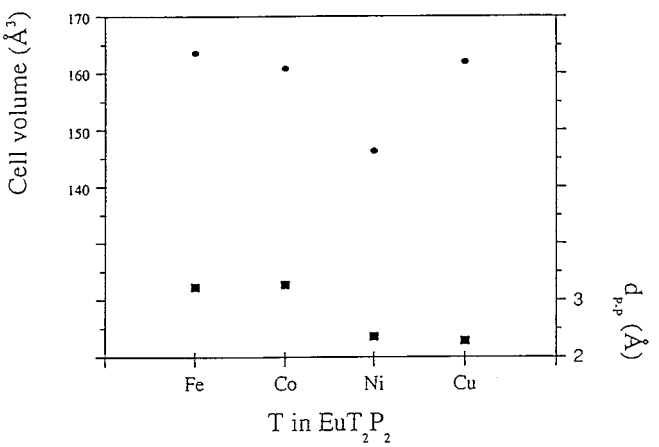

FIG. 2. Cell volume (dark circles) and d_{P-P} (dark squares) versus 3d transition metal (T) in EuT_2P_2.

The Eu Mössbauer spectrum was obtained at room temperature using the 21.53 keV level of ^{151}Eu in a standard transmission geometry with a 150 mCi $^{151}SmF_3$ source. Calibration of the spectrometer was verified with a EuF_3 reference. An isomer shift and linewidth were obtained by fitting the spectrum using a Lorentzian lineshape.

The Eu L_{III}-edge X-ray absorption spectrum was obtained at room temperature at beamline 7-3 of Stanford Synchrotron Radiation Laboratory (SSRL) using a Si(220) double crystal monochromator. A transmission geometry was employed, with the sample dispersed with BN. An iron reference spectrum was collected simultaneously for energy calibration. The raw absorption spectrum was corrected for a linear background, normalized at high energy to 1 and corrected for the slope in the postedge region.

RESULTS AND DISCUSSION

The Eu Mössbauer and L_{III}-edge X-ray absorption spectra are presented in Fig. 3. The Mössbauer spectrum shows a main absorption with an isomer shift of $-10.51(2)$ mm/s and a minor absorption with an isomer shift of $+1.4(2)$ mm/s. The main absorption is clearly due to the major phase of the sample, $EuCu_{1.75}P_2$, and falls well within the typical range for divalent europium, -14 to -8 mm/s. Therefore, $EuCu_{1.75}P_2$ is divalent. For comparison, the isostructural materials, $EuFe_2P_2$ and $EuCo_2P_2$, which are also divalent have isomer shifts of -10.6 and -10.3 mm/s, respectively (2).

The minor absorption is approximately 7% of the sample based on intensity and is attributed to a trivalent impurity phase. As mentioned above, the powder diffraction pattern contained an unidentified, minor impurity phase. This weak trivalent absorption is consistent with that observation.

The L_{III}-edge XA spectrum has a principal peak centered at 6967.6 eV, characteristic of divalent europium. Thus, XAS also demonstrates that europium is divalent in $EuCu_{1.75}P_2$. We also note a slight shoulder at higher energy, at approximately 6975 eV. This is at a reasonable energy for a minor trivalent impurity phase, consistent with the Mössbauer results.

This work demonstrates that $EuCu_{1.75}P_2$ has both divalent europium and a single P–P bond. The larger divalent europium ion is accommodated by an increase in the a lattice parameter from 3.94 Å in $EuNi_2P_2$ to 4.11 Å. Thus, the formation of a P–P bond alone is not sufficient to drive the transition to intermediate valence. Moreover, the europium valence is not intermediate valent or trivalent as expected from trends based on the isostructural phases.

A possible explanation for divalent europium can be obtained upon examination of the band structure reported by Hoffmann and Zheng for the $ThCr_2Si_2$ structure-type (7). Based on their band filling argument, as one goes across the periodic table for the 3d transition metals, the P–P

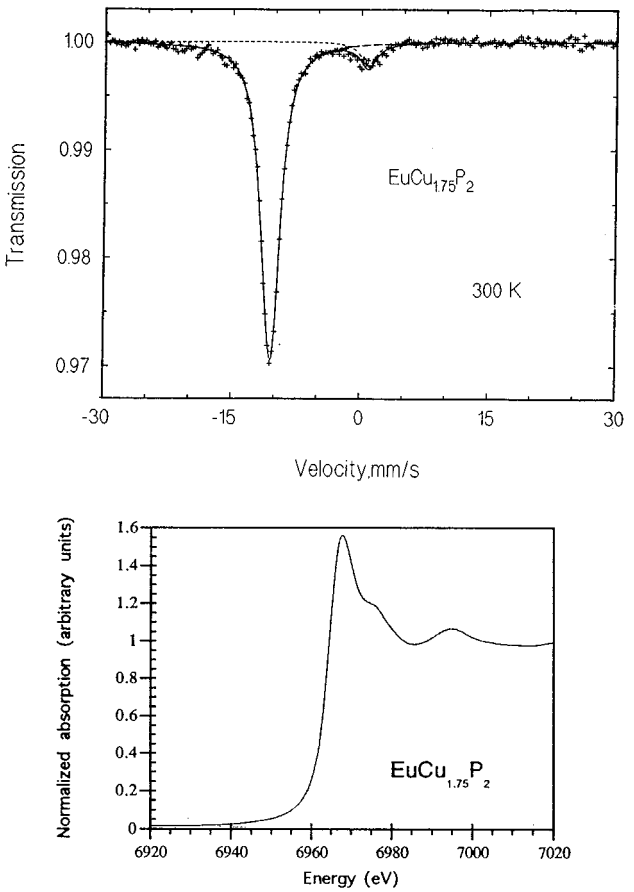

FIG. 3. (a) Eu Mössbauer spectrum and (b) Eu L_{III}-edge X-ray absorption spectrum of $EuCu_{1.75}P_2$.

antibonding band is emptied between Co and Ni and remains empty for Cu as well. Their calculations justify the single P–P bond in both $EuNi_2P_2$ and $EuCu_{1.75}P_2$.

The europium valence in EuT_2P_2 also depends upon the band structure and band filling. The most common model for intermediate valent europium places the Eu $4f^7$ state above the Fermi level. As explained above, in EuT_2P_2 the Fermi level decreases as one goes from T = Co to Cu. Thus, $EuCo_2P_2$ with the Fermi level above the $4f^7$ state is divalent, while $EuNi_2P_2$ with its Fermi level slightly lower in energy than the $4f^7$ state is intermediate valent.

On the basis of those arguments, $EuCu_{1.75}P_2$ should be intermediate valent or trivalent. However, as shown by Hoffmann and Zheng, the conduction band is quite narrow and almost filled for the copper analog due to increasing nuclear charge and tighter d electron binding (7). We propose that one explanation for the divalent europium in $EuCu_{1.75}P_2$ is that the conduction band is actually completely filled. This leaves an extra electron for the Eu $4f^7$ state and causes the europium to become divalent. A filled band could also explain the copper-deficient stoichiometry observed because electrons from additional copper atoms would have to go into bands of higher energy, and this is not favorable.

CONCLUSIONS

In conclusion, we have shown by Eu MS and XAS that the europium in $EuCu_{1.75}P_2$ is divalent, in contrast to predictions based on trends with the single P–P bond observed for isostructural $EuFe_2P_2$, $EuCo_2P_2$, and $EuNi_2P_2$. Applying a band structural model, we propose that the copper analog contains divalent europium and is nonstoichiometric because the conduction band is filled.

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