Intermediate Valence in $EuCo_{2-x}Ni_xP_2$: Interdependence of Structure and Energetics

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The solid solutions $EuCo_{2-x}Ni_xP_2$ were prepared for $x = 0.5, 0.8, 1.0, 1.2$, and 1.5 to explore the relationship between intermediate valent europium and P–P bonding. Two synthetic methods were used, tin flux synthesis from the elements and activated solid-state synthesis from $EuCo_2P_2$ and $EuNi_2P_2$. The samples were characterized by powder X-ray diffraction. Phase separation into cobalt-rich and nickel-rich phases was observed and reduced by improved synthesis. The transition from divalent to intermediate valent europium takes place sharply with increasing x between 0.5 and 0.8, as determined by changes in unit cell volume; concomitantly, a P–P single bond forms. It is proposed that a P–P single bond is required in order to decrease the unit cell volume sufficiently to accommodate the intermediate valent europium ion. Furthermore, phase separation occurs for compositions that would result in the Fermi level lower in energy than the $4f^7$ state (criterion for intermediate valence) but too high in energy to form a P–P bond (necessary to reduce the cell volume) because the P–P antibonding level is occupied.

Introduction

Conducting materials containing rare-earth ions that have more than one stable oxidation state (e.g., Ce, Sm, Eu, and Yb) can exhibit a phenomenon known as intermediate or fluctuating valence.[1] This phenomenon is unique because it is associated with fluctuations of electrons between the localized 4f state and the conduction band at frequencies of approximately 10^{13} Hz.[2] Because of the rapid time scale of these fluctuations, magnetic measurements and Mössbauer spectroscopy (when available) indicate nonintegral rare-earth valence.[1] Moreover, structural determinations by X-ray diffraction show that all the rare earth ions are equivalent and intermediate in size between the two integral valent extremes. We report here a study of the composition and structural features required for a transition from divalent to intermediate valent europium with increasing x in the solid solutions $EuCo_{2-x}Ni_xP_2$.

It is believed that intermediate valence occurs only when the 4f state and the Fermi level are nearly equienergetic.[3] Since the position of the Fermi level relative to the 4f state depends on composition, efforts to understand intermediate valence have included many studies in which changes in the rare-earth valence were probed as a function of composition. For example, there have been extensive investigations of chemical substitution in binary phases, such as $Tm_{1-x}Se$, $Sm_{1-x}Eu_xB_6$, and $Sm_{1-x}Gd_xS$.[1,4,5] More recently, ternary materials exhibiting intermediate valence have attracted attention.[6] One important advantage of systems with a transition metal as a ternary element is that it is possible to select dopant ions that vary the bandfilling but are similar in size so that direct perturbations to the structure are minimal. We chose to probe valence changes in the ternary solid solutions $EuCo_{2-x}Ni_xP_2$ because of the chemical similarity of Co and Ni.

Although the relationship between rare-earth valence and composition has been investigated previously, the interdependence of valence, structure, and bonding is largely unexplored.[6] We show here that even if the composition of a material is adjusted such that the 4f state matches the Fermi level in energy, intermediate valence may not occur. This is because the valence can change as a function of composition only in materials that can undergo a relatively large change in unit cell volume. Because divalent $EuCo_2P_2$ and intermediate valent $EuNi_2P_2$ are isostructural but have dramatically different unit cell volumes and P–P bond distances, solid solutions of these two phases are ideal for studies of the interplay between structure and intermediate valence.

$EuCo_2P_2$ and $EuNi_2P_2$ belong to a broad class of materials which crystallize in the $ThCr_2Si_2$ (AB_2X_2) structure type; several materials in this class exhibit intermediate valence, including $CeCu_2Si_2$, $EuNi_2P_2$, $EuPd_2P_2$, $EuNi_2Si_2$, $EuCu_2Si_2$, $EuPd_2Si_2$, and $YbCu_2Si_2$.[6] The structure of these materials can be viewed as $B_2X_2^{n-}$ layers with A^{n+} ions dispersed between these layers as depicted in Figure 1.[7] It is particularly noteworthy that among the various members of this class there are large variations in the X–X distance between the $B_2X_2^{n-}$ layers. Moreover, the overall unit cell volume depends both on the identity and valence of A.

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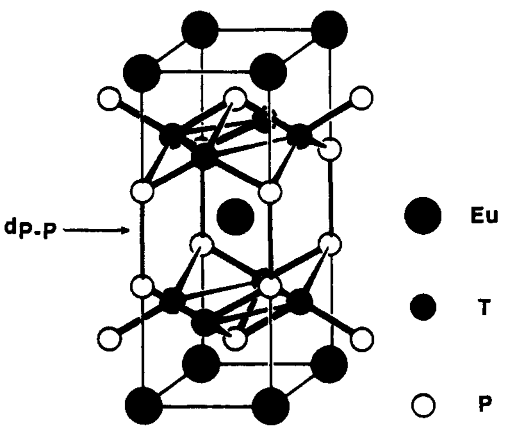

Figure 1. Unit cell of EuT_2P_2 (T = transition metal). The structure can be viewed as $T_2P_2^{n-}$ layers with Eu^{n+} ion dispersed between these layers. Among the various members of this class of materials, there are large variations in the unit cell volume and the P–P distances (d_{P-P}); while $EuCo_2P_2$ with divalent europium has a large volume (161.0 Å^3) and d_{P-P} is long (3.27 Å), the volume for $EuNi_2P_2$ with intermediate valent europium is small (146.4 Å^3) and d_{P-P} is short (2.36 Å).

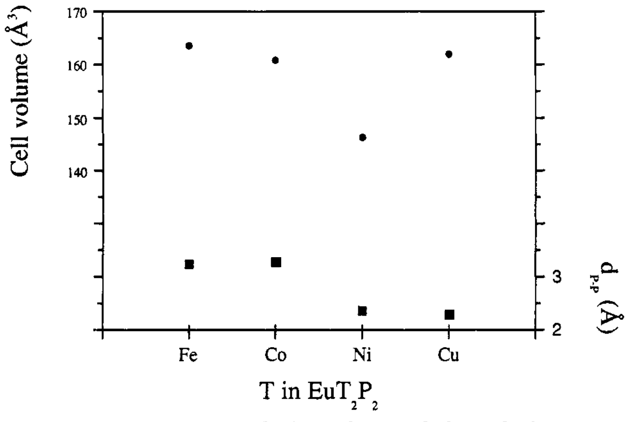

Figure 2. Cell volume (dark circles) and d_{P-P} (dark squares) versus 3d transition metal (T) for EuT_2P_2. The cell volume indicates that the europium is divalent in the Fe, Co, and Cu materials but intermediate valent in the material containing Ni. Furthermore, the decrease in d_{P-P} between Co and Ni indicates the formation of a P–P single bond in the Ni and Cu materials.

Across the series of europium first row transition metal phosphides, $EuFe_2P_2$, $EuCo_2P_2$, $EuNi_2P_2$, and $EuCu_{2-x}P_2$, the cell volume and the interlayer P–P distance vary significantly as can be seen in Figure 2.[8] It is worth noting that while $EuCu_{2-x}P_2$ is formally isostructural with the others, there is a pronounced flattening of the copper–phosphorus layers resulting in a large *a* and short *c* parameter. Since the P–P single bond length in P_4 is 2.21 Å, the decrease in d_{P-P} from Co to Ni to less than 2.5 Å indicates the formation of a P–P single bond in the Ni and Cu materials. As europium is the largest atom in the unit cell, the cell volume is an accurate indicator of the europium valence. In this series, the Fe, Co, and Cu materials with cell volumes greater than 159 Å^3 all contain divalent europium, while the Ni material with intermediate valent europium possesses a cell volume that is significantly smaller (146.4 Å^3). Direct measurements of the valence in these materials confirm the valence assigned by cell volumes.[9,10]

Hoffmann and Zheng have done a band structure calculation for materials with this structure type which shows that the position of the Fermi level decreases in energy from Fe to Cu.[7] We propose that the Fermi level is similar in energy to the $4f^7$ state (a criterion for intermediate valence) only for the $EuNi_2P_2$, but above the $4f^7$ state for $EuFe_2P_2$ and $EuCo_2P_2$, and below for $EuCu_{2-x}P_2$. Hoffmann and Zheng also show that making and breaking P–P bonds in these materials depends on the relative positions of the Fermi level and the P–P antibonding levels (σ^*). When the P–P σ^* level is empty because the Fermi level is lower in energy, a P–P single bond forms; this is the case for $EuNi_2P_2$ and $EuCu_{2-x}P_2$. For $EuFe_2P_2$ and $EuCo_2P_2$, the P–P σ^* level is filled, and the P–P distances are long.

An apparent correlation between intermediate valent europium and a short X–X distance in this structure type has been noted previously.[6] However, while intermediate valence and a P–P single bond are both found in $EuNi_2P_2$, $EuCu_{2-x}P_2$ contains divalent europium yet still has a single P–P bond. Therefore, while the P–P bond may be required for intermediate valence, it alone does not drive the transition to intermediate valence. The goal of our work has been to elucidate further the relationship between P–P bond formation and intermediate valence in these isostructural phosphides.

Our approach has been to synthesize and characterize the solid solution materials, $EuCo_{2-x}Ni_xP_2$, by two general routes. Dissolution of the required elements in tin was found to be well-suited for the synthesis of large single crystals of unsubstituted $EuCo_2P_2$ and $EuNi_2P_2$[9] but did not work as well for the solid solutions. Therefore, $EuCo_{2-x}Ni_xP_2$ materials were prepared for x = 0.5, 0.8, 1.0, 1.2, and 1.5 by an activated solid-state synthesis consisting of a solid-state reaction of $EuCo_2P_2$ and $EuNi_2P_2$ (each previously prepared by tin flux synthesis), enhanced by a smaller amount of tin. This synthesis proved advantageous in favoring single-phase products formed by quenching. Structural characterization by powder X-ray diffraction was employed to distinguish between materials that contain one and two phases, and to determine lattice parameters, d_{P-P}, and cell volumes.

Experimental Section

General Techniques. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. The elemental starting materials were europium (rods, 99.99%, Materials Preparation Center, Ames Laboratory, Ames, IA), cobalt (powder, 99.9985%, 22 mesh, Johnson Matthey Puratronic), nickel (powder, 99.999%, 100 mesh, Johnson Matthey Puratronic), red phosphorus (lump, 99.99995%, Gallard-Schlesinger), and tin (3-mm shot, purity 99.999%, AESAR Johnson Matthey). All elemental starting materials were stored and manipulated at room temperature under an argon atmosphere in a Vacuum Atmospheres Co. HE-63-P DRI-LAB glovebox with attached HE-493 DRI-TRAIN. The reactions were carried out in evacuated (less than 5×10^{-5} Torr) and sealed quartz tubes in an Astro A227 vertical tube furnace with an OMEGA Engineering CN2010 microprocessor-based temperature controller.

Tin Flux Synthesis. $EuCo_2P_2$ and $EuNi_2P_2$ were synthesized in a tin flux by the method described previously by Jeitschko *et*

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Table 1. Reactant Ratios for the Tin Flux Synthesis of $EuCo_{2-x}Ni_xP_2$

x	Eu	Co	Ni	P	Sn
0	1.2	2.0		2.0	20
0.5	1.2	1.5	0.5	2.0	20
1.0	1.3	1.0	1.0	2.3	16
1.5	1.3	0.5	1.5	2.3	16
2.0	1.3		2.0	2.3	16

al.[9] The solid solutions $EuCo_{2-x}Ni_xP_2$ were synthesized also by a similar method for total values of $x = 0.5$, 1.0, and 1.5. The ratios of Eu:Co:Ni:P:Sn that were used for these five samples are given in Table 1; these are not stoichiometric ratios, but rather reactant ratios adapted from those found by Jeitschko *et al.* to give optimum purity and the largest crystals.[9] For a typical reaction, the weight of europium was maintained in the range 0.25–0.40 g.

The elemental starting materials were heated in a quartz tube (12-mm o.d. × 150 mm) according to the following temperature profile: the temperature was raised to 425 °C in 4 h, held at 425 °C for 4 h, raised to 900 °C in 12 h, held at 900 °C for 8 days (192 h), and finally the samples were cooled to room temperature in 3 days (72 h). An additional sample was prepared for $x = 1.0$ for which the temperature was raised to 1050 °C (instead of 900 °C), cooled to 800 °C in 50 h, and quenched to room temperature from 800 °C. The tin-rich matrix was dissolved in concentrated hydrochloric acid. The hydrochloric acid was replaced repeatedly until further addition of acid no longer produced effervescence. Each product was washed three times with distilled water, washed three times with acetone, and allowed to dry in air. The products, $EuCo_2P_2$ and $EuNi_2P_2$, each consisted of single-crystal square plates and crystallites both of which were metallic and highly reflective. The three samples of $EuCo_{2-x}Ni_xP_2$ consisted of square plates which were metallic and highly reflective, and black, polycrystalline material.

Activated Solid-State Synthesis. $EuCo_{2-x}Ni_xP_2$ materials were synthesized also by using $EuCo_2P_2$ and $EuNi_2P_2$ as reactants in combination with a small amount of Sn (29 mol %) as an activating agent. The starting materials were combined and ground together thoroughly to prepare 0.5–0.8 g of materials with $x = 0.5$, 0.8, 1.0, 1.2, and 1.5. The $EuCo_2P_2$ and $EuNi_2P_2$ were prepared as described above but in larger quantities; the weight of europium for a typical reaction was maintained in the range 1.5–2.5 g, and larger quartz tubes (25-mm o.d. × 300 mm) were used. Since $EuCo_2P_2$ and $EuNi_2P_2$ are completely stable and inert in air, handling of these phases did not require an inert atmosphere.

The $EuCo_2P_2$ and $EuNi_2P_2$ starting materials were heated in a quartz tube (12-mm o.d. × 150 mm) according to the following temperature profile: the temperature was raised to 910 °C in 15 h, held at 910 °C for 14 days (336 h), and then quenched quickly to room temperature. The tin was removed and the samples were washed as described above. The products typically consisted of a small number of tiny crystallites which were metallic and highly reflective and a shiny, grey-black powder.

Powder X-ray Diffraction. Powder X-ray diffraction patterns were collected on a Siemens D500 diffractometer with Cu $K(\alpha_1+\alpha_2)$ radiation. Silicon was used as an internal standard to correct the observed diffraction angles for systematic zero-point errors. After fitting each peak to yield the individual α_1 and α_2 components with the DIFFRAC/AT software program,[11] further data analysis was executed with the peak component due to diffraction of the Cu $K\alpha_1$ radiation.

The diffraction peaks were indexed satisfactorily to a tetragonal unit cell. Tetragonal lattice parameters were obtained from a least-squares refinement of 15–20 reflections by using the computer program LATPARM.[12] For a typical refinement, average absolute discrepancies in 2θ (observed − calculated) fell within the range of 0.01–0.04°. The interlayer phosphorus–phosphorus distances were calculated for the samples with $x >$ 0.5 from the c lattice parameters by assuming the $(0,0,z)$ position that has been reported previously for phosphorus in $EuNi_2P_2$ ($z = 0.3748(4)$); for the sample with $x = 0.5$, the position for phosphorus in $EuCo_2P_2$ was chosen instead ($z = 0.3558(2)$).[8a,b] We present these interlayer P–P distances to only two decimal places to account for the uncertainty introduced in assuming that the $(0,0,z)$ positions are completely unchanged upon substitution.

Table 2. Structural Results for $EuCo_{2-x}Ni_xP_2$: Tin Flux Synthesis

x	a (Å)	c (Å)	vol (Å^3)
0	3.7673(4)	11.344(2)	161.00(6)
0.5	3.800(2)	11.083(8)	160.0(3)
$1.0-\partial$	3.796(3)	11.10(1)	160.0(4)
$1.0+\partial$	3.9197(8)	9.536(3)	146.5(1)
1.5	3.9310(5)	9.468(2)	146.31(7)
2.0	3.9402(2)	9.431(1)	146.42(3)

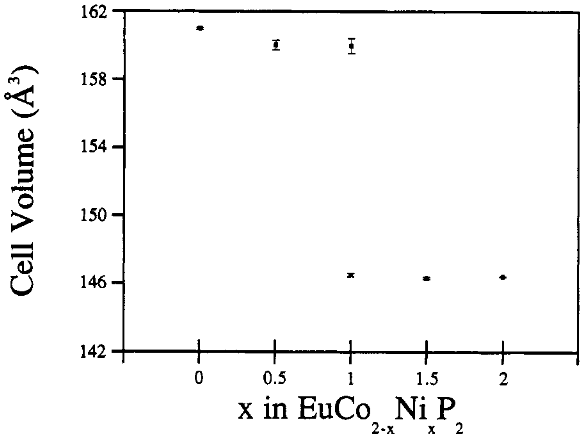

Figure 3. Cell volume versus x in the solid solutions, $EuCo_{2-x}Ni_xP_2$, for samples from tin flux synthesis. Single phases for $x = 0.5$ and 1.5 are indicated by one data point at each composition; two-phase behavior for $x = 1.0$ is illustrated by two data points. There is an overall decrease in cell volume with increasing x.

Results and Discussion

Tin Flux Synthesis. The $EuCo_2P_2$ and $EuNi_2P_2$ materials precipitated from the tin flux were very crystalline, as determined by the narrow line widths of the powder X-ray diffraction peaks. The patterns obtained confirmed that each was a pure phase, with lattice parameters in agreement with values reported previously. In contrast, the relatively broader diffraction peaks for the $EuCo_{2-x}Ni_xP_2$ samples indicate that the solid solutions are less homogeneous. For the samples with $x = 0.5$ and 1.5, all the X-ray diffraction peaks could be indexed to one phase with a tetragonal unit cell. However, the sample with $x = 1.0$ showed two tetragonal phases; as might be expected for a sample with more than one phase, the diffraction pattern showed poorer resolution than for a single phase and the lattice parameters for each phase had considerably larger errors. The lattice parameters and cell volumes for these three solid solutions and the two end members ($EuCo_2P_2$ and $EuNi_2P_2$) are given in Table 2.

Overall, the results in Table 2 show that with increasing x in $EuCo_{2-x}Ni_xP_2$, a increases and c decreases as expected based on the lattice parameters of unsubstituted $EuCo_2P_2$ and $EuNi_2P_2$. However, the lattice parameters do not vary linearly with composition. As shown in Figure 3, the cell volumes for the samples with $x = 0.5$ and 1.5 are not very

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[11] *DIFFRAC/AT* software by SOCABIM, 1986. SOCABIM SARL, 9 bis, villa du Bel-Air 75012, France.

[12] LATPARM Version II program for the Vax by B. Chambers. Modified version of LATCONLSQ.

different from those of $EuCo_2P_2$ and $EuNi_2P_2$, respectively. The sample with a total $x = 1.0$ consists of two phases, one with a volume similar to $EuCo_2P_2$ and the other similar to $EuNi_2P_2$; this suggests that one of the phases is cobalt rich ($x = 1.0 - \delta$) and the other is nickel-rich ($x = 1.0 + \delta$). We conclude that a complete solid solution does not form, but there is a miscibility gap in the region near $x = 1.0$. Moreover, there is an abrupt change in volume between the cobalt-rich and nickel-rich samples.

We postulate that this miscibility gap is associated with a change in the valence of the europium ion. On the basis of the volume, it is evident that the cobalt-rich samples with the larger cell volumes contain divalent europium and the nickel-rich samples with the smaller cell volumes contain intermediate valent europium. We suggest that there is a range of compositions for which the $4f^7$ state and the Fermi level are close enough in energy for intermediate valence, but the structure cannot conform to the smaller intermediate valent europium ion. Therefore, solid solutions in this composition range are unstable with respect to phase separation. As discussed further below, the formation of a P–P single bond is pivotal in stabilizing intermediate valence because it brings about a decrease in the cell volume.

Having found that a single phase with the composition $x = 1.0$ does not form in a tin flux with slow cooling from 900 °C, we concluded that altering the synthetic temperature profile might produce a single phase. Often, in solid solutions in the range of composition where phase separation dominates, a single phase can be synthesized at higher temperatures. In an attempt to prepare such a single phase, with $x = 1.0$, a sample was quenched from 800 °C, rather than cooled slowly to room temperature. The results showed reduced phase separation. The lattice parameters for the majority phase match those of the nickel-rich materials; only two weak peaks could be attributed to the cobalt-rich material. However, since the crystallinity (as judged by the broad diffraction peaks) was diminished substantially, this method was not pursued further. Instead, a much smaller amount of tin was used to obtain single phase samples in the range $x = 0.5$–1.5 as described below.

Activated Solid-State Synthesis. $EuCo_{2-x}Ni_xP_2$ materials for $x = 0.5$, 0.8, 1.0, 1.2, and 1.5 were prepared by quenching from 910 °C in an attempt to prepare single-phase samples by equilibration at a temperature above the miscibility gap. A higher temperature was not chosen because we had observed the decomposition of cobalt-rich materials and formation of CoP near 980 °C. Only a small amount of tin was used to activate the reaction; too much tin could cause complete redissolution of the elements. As compared with the sample that was prepared by dissolution in a tin flux and subsequently quenched from 800 °C, these reactions with a smaller amount of tin yielded materials that were more crystalline as determined by the line width and intensities of the peaks in the powder X-ray diffraction patterns.

Table 3. Structural Results for $EuCo_{2-x}Ni_xP_2$: Activated Solid-State Synthesis

x	a (Å)	c (Å)	vol (Å^3)	d_{P-P} (Å)
0	3.7673(4)	11.344(2)	161.00(6)	3.27(1)
0.5	3.8023(4)	11.103(3)	160.52(8)	3.20(1)
0.8	3.9062(8)	9.710(5)	148.2(1)	2.43(1)
1.0	3.9141(8)	9.646(3)	147.8(1)	2.42(1)
1.2	3.9182(4)	9.586(3)	147.17(8)	2.40(1)
1.5	3.9303(5)	9.509(2)	146.89(7)	2.38(1)
2.0	3.9402(2)	9.431(1)	146.42(3)	2.36(1)

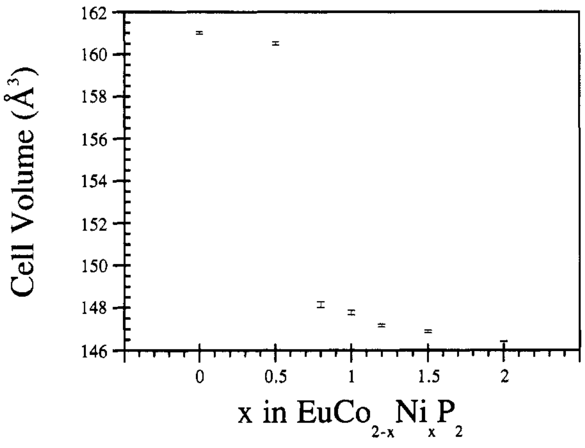

Figure 4. Cell volume versus x in the solid solutions, $EuCo_{2-x}Ni_xP_2$, for samples from activated solid-state synthesis. The cell volume decreases abruptly as x increases above 0.5 and continues to decrease slightly from $x = 0.8$ to 2.0 ($EuNi_2P_2$).

The nominal compositions of these samples were considered identical with the starting compositions, under the assumption of no binary phase impurities. The samples with $x = 1.0$, 1.2, and 1.5 were pure phases, and all the peaks could be indexed to a tetragonal unit cell. However, the samples with $x = 0.5$ and 0.8 contained one or two additional low-intensity reflections that we attribute to 5% of a secondary $EuCo_{2-x}Ni_xP_2$ phase. Therefore, there is a small amount of phase separation, but since the sample with $x = 1.0$ is a pure phase, the range of immiscibility is only slightly greater than 0.3. In other words, the $x = 0.5$ and 0.8 samples each contain two phases, one with $x = 0.5 - \alpha$ and the other with $x = 0.8 + \alpha$ (with $\alpha < 0.2$) but in different relative amounts. The lattice parameters for these five samples are given in Table 3. It is notable that the lattice parameters for $EuCo_{1.5}Ni_{0.5}P_2$ and $EuCo_{0.5}Ni_{1.5}P_2$ agree well with those obtained for samples prepared by precipitation from a tin flux as described above.

On the basis of the similarities of the lattice parameters and cell volumes (see Figure 4) for samples with $x = 0.8$, 1.0, 1.2, and 1.5 with those of $EuNi_2P_2$, we conclude that these four materials contain intermediate valent europium. The sample with $x = 0.5$ has cell dimensions similar to $EuCo_2P_2$, which is indicative of divalent europium. Therefore, the transition from divalent to intermediate valent europium occurs abruptly between $x = 0.5$ and 0.8. Since intermediate valence depends on rather unique structural and electronic features, one might expect only a narrow range of solid solutions with stable intermediate valent europium as has been observed in other systems that have been investigated. For example, intermediate valence is found in $EuPd_{2-x}Au_xSi_2$ only for a relatively narrow range of compositions, from $0 < x < 0.36$.[13] We find that $EuCo_{2-x}Ni_xP_2$ is unusual in that intermediate valence exists over a relatively wide range of compositions, from $0.8 < x < 2.0$.

Previous reports indicate that the average valence for the europium in $EuNi_2P_2$ is approximately 2.5.[14] We

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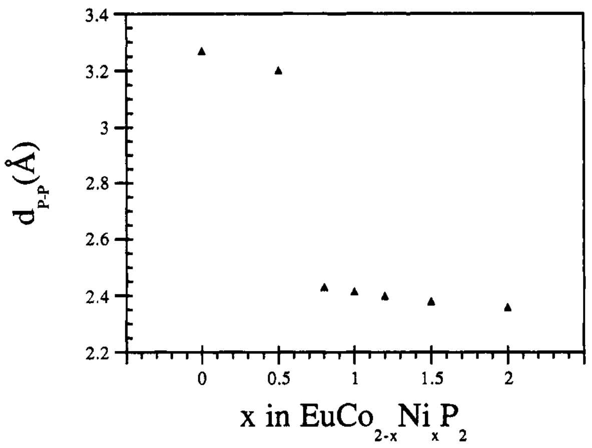

Figure 5. P–P distance (d_{P-P}) versus x in the solid solutions, $EuCo_{2-x}Ni_xP_2$, for samples from activated solid-state synthesis. There is an abrupt decrease in d_{P-P} as x increases above 0.5, as was observed for the cell volume (see Figure 4).

observe that the cell volumes of the materials that contain intermediate valent europium decrease slightly with increasing x. Since the cell volume reflects the average europium valence, we conclude that the average valence increases as x increases from 0.8 in $EuCo_{1.2}Ni_{0.8}P_2$ to 2.0 in $EuNi_2P_2$; we will present Eu Mössbauer spectra and Eu L_{III}-edge X-ray absorption spectra elsewhere that support this conclusion. This observation is consistent with the band structure calculations that show that the Fermi level decreases in energy relative to the $4f^7$ state upon substitution of nickel. Thus, the electrons spend less time in the $4f^7$ state, and the average valence increases. However, it is notable that although the average valence is not fixed at one intermediate value, it appears that the valence does not vary continuously; instead, there is an abrupt change in volume (and hence, valence) between $x = 0.5$ and 0.8. This indicates that materials with average valences close to 2, but not exactly 2, cannot be formed.

Because these samples were predominantly single phases and of good quality, the lattice parameters are precise enough for evaluating trends in changes in the P–P distances. These were derived from the *c* lattice parameter and are given in Table 3 and plotted in Figure 5. Both $EuCo_2P_2$ and $EuCo_{1.5}Ni_{0.5}P_2$ have long P–P distances (3.27–3.20 Å), whereas all the samples with intermediate valent europium have much shorter P–P distances (2.43–2.36 Å). Since these latter distances are comparable to the P–P bond length of 2.21 Å in P_4, we conclude that a P–P single bond exists in the materials with $x = 0.8$, 1.0, 1.2, and 1.5, as in $EuNi_2P_2$.

The changes in d_{P-P} with composition correlate with the changes in cell volume (compare Figures 4 and 5) and consequently with the changes in europium valence. A P–P single bond forms abruptly with increasing x between 0.5 and 0.8, and concomitantly, intermediate valence is observed. We postulate that this correlation between structure and valence, along with the observation of phase separation suggests that the $4f^7$ state is higher in energy than the P–P antibonding level (σ^*), as sketched in Figure 6a. As the Fermi level decreases in energy with increasing nickel content until it is below the $4f^7$ state but above the P–P σ^* level, there is a region of immiscibility. Although the condition for intermediate valence is met (proximity of the Fermi level and the $4f^7$ state), the volume is too large to accommodate the small intermediate valent europium ion due to the long nonbonding P–P distances. Therefore, materials in this range of compositions are unstable.

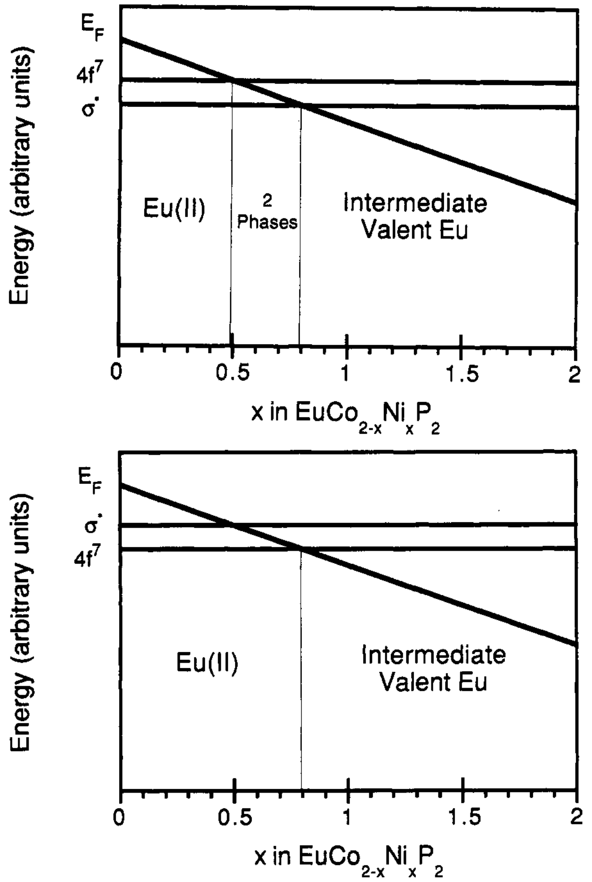

Figure 6. Schematics of two possible band structures for $EuCo_{2-x}Ni_xP_2$: (a) The proposed ordering of the $4f^7$ state above P–P σ^* energy level is shown. The Fermi level decreases in energy with increasing x from above the $4f^7$ state for $EuCo_2P_2$ to below the P–P σ^* energy level for $EuNi_2P_2$. For compositions with x between approximately 0.5 and 0.8, the Fermi level is lower in energy than the $4f^7$ state, but too high in energy to forma P–P bond. This results in the observed miscibility gap. (b) The inverted ordering with the P–P σ^* energy level above the $4f^7$ state is shown. When the Fermi level decreases in energy with increasing x to below the $4f^7$ state, intermediate valent europium would become stable abruptly, without immiscibility.

It is worth pointing out that although we conclude that intermediate valence in this structure type requires the formation of a P–P bond to reduce the unit-cell volume sufficiently, the reverse is not true. We propose that it would be possible to form a P–P single bond and retain divalent europium by stretching the unit cell volume along the *a* direction. There is precedence for a sufficiently large *a* lattice parameter in the divalent $EuCu_{1.75}P_2$.[8c] Therefore, if the Fermi level were below the P–P σ^* level but above the $4f^7$ state (the opposite situation from above, as shown in Figure 6b), the europium would remain divalent, and we postulate that there would then be no region of immiscibility. As x increased, first there would be an abrupt decrease in the *c* lattice parameter (due to P–P bond formation) along with an increase in the *a* lattice parameter to keep the volume constant. At a larger value of x, the conditions for intermediate valence would be met and both the *a* lattice parameter and volume would decrease abruptly. Since this scenario is not observed, we believe that the $4f^7$ state is indeed higher in energy than the P–P σ^* (shown in Figure 6a).

Conclusions

Our investigation of the solid solutions, $EuCo_{2-x}Ni_xP_2$, reveals the need for careful attention to synthetic conditions and structural data in order to understand better the composition dependence of the europium valence. We conclude that under the conditions described here, it is not possible to prepare solid solutions with continuously varying composition. Specifically, for samples quenched from 910 °C, there is a region of immiscibility for total values of x between $0.5 - \alpha$ and $0.8 + \alpha$ (where $\alpha < 0.2$).

The transition from divalent to intermediate valent europium and the formation of a P–P bond both take place with increasing x between 0.5 and 0.8. It is notable that at this transition, there is a large decrease in P–P bond distance (from 3.20 to 2.43 Å) and a large increase in europium valence, as estimated from the change in cell volume (from 160.5 to 148.2 Å^3). The P–P bond distance changes abruptly rather than continuously due to the formation of a P–P bond induced by the emptying of the P–P σ^* orbital. Likewise, the transition to intermediate valence also occurs abruptly apparently because exact energetic and structural requirements are met. Since there is a large volume change at the transition rather than a continuous change in volume, we conclude that all values for the europium valence are not possible. However, the fact that intermediate valent europium is observed over a wide range of compositions ($0.8 < x < 2.0$) demonstrates that once stable, intermediate valence is not energetically unique. Rather, we observe for these materials that the average europium valence can increase as the fluctuations to the $4f^7$ state grow less favorable energetically.

We conclude that phase separation occurs near the transition from divalent to intermediate valent europium because the $4f^7$ state is higher in energy than the P–P σ^* level. Compositions that would result in the Fermi level lower in energy than the $4f^7$ state (criterion for intermediate valence), but too high in energy to form a P–P bond (necessary to reduce the cell volume) by emptying the P–P antibonding level are unstable; in other words, in this range of compositions, intermediate valence is energetically allowed, but structurally forbidden. When the Fermi level decreases in energy with increasing x to below both the $4f^7$ state and the P–P σ^*, abruptly, intermediate valent europium becomes stable, since it is energetically allowed and structurally allowed by the formation of the P–P bond. Intermediate valence in this system should thus be considered the outcome of a subtle interplay between structure, bonding, and the relative energies of the localized 4f and delocalized conduction band states.

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