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Valence instabilities and inhomogeneous mixed valence in some ternary europium compounds

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Abstract

Photoemission spectra and TB-LMTO-ASA band structure calculations of some mixed valency europium compounds have been studied. The band structures are compared with the band structures of the isostructural lanthanum and strontium compounds. Surprisingly a 4f density of states in the vicinity of the Fermi level is observed in inhomogeneous mixed valency EuPd$_3$B, Eu$_3$S$_4$, and EuPdP. Indeed a van Hove Singularity (vHS) derived from the d states of La and Pd or p states of boron or phosphorous are found in La$_3$S$_4$, LaPd$_3$B and SrPdP. The valence instability in the Eu compounds is thus not necessarily due to Eu 4f states. The results also provide some ground for the assumption that inhomogeneous mixed valency is an indicator for a vHS in the conduction band. The europium compounds order anti-ferromagnetically at low temperatures, whereas La$_3$S$_4$ becomes superconducting at 8 K. In La$_3$S$_4$, the vHS coincides with the Fermi level, whereas the singularity lies below the Fermi level in SrPdP and LaPd$_3$B. According to the van Hove scenario it must be possible to induce superconductivity via hole doping in SrPdP and LaPd$_3$B. © 1997 Elsevier Science S.A.

Keywords: van Hove scenario; Superconductivity; Valence fluctuations; Photoemission

1. Introduction

Europium is one of the unusual rare earth elements, because in solids it occurs in different valence states; it can be either divalent, trivalent or of mixed valency. A clear distinction can be made between homogeneous mixed valency compounds where all the europium ions occupy crystallographically equivalent sites (eg. EuNi$_2$P$_2$ [1]) and static mixed valency compounds (eg. Eu$_3$O$_4$ [2]) where the two europium ions occupy clearly different sites. In inhomogeneous mixed valency compounds the structure and the valency of the europium atoms depend strongly on the temperature, and above the so-called Verwey temperature T_V all europiums ions are equivalent (as seen, for example in Eu$_3$S$_4$ [3], Eu$_4$As$_3$ [4], EuBr$_x$ [5], EuPd$_3$B [6], EuPd$_3$Si$_{0.25}$ [7]). The Verwey transition is associated with charge ordering and a slight structural distortion. Because of their exceptional Mößbauer activity, two europium lines for the different valencies below T_V and one of fractional valence above T_V can be clearly identified in Eu compounds and it seems reasonable to assume that the 4f electrons border between localisation and delocalisation. Chemists describe localisation in real space by bound pairs and delocalisation by itinerant electrons. In momentum space localisation translates to mean flat parts in the band structure, such as van Hove Singularities and band minima or maxima, while delocalisation implies bands of high dispersion. These special features in the band structure are also found in superconductors with high T_c's, such as the cuprates, the A15 superconductors and LiTi$_2$O$_4$. van Hove singularities are common in low dimensional compounds, but are also possible in three dimensional systems. The occurrence of such a singularity depends on the symmetry of the crystal and the

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bonding situation. Surely this effect is not sufficient to invalidate the high-T_c mechanism [8], because in many superconducting systems with lower transition temperature singularities are found around E_F. A hint that there are similarities between superconductivity and inhomogeneous mixed valence is the fact that the lanthanum compound that is isostructural with Eu$_3$S$_4$ shows superconductivity around 8 K [9]. In this paper we compare the band structure of different inhomogeneous mixed valency europium compounds and the isostructural compound without 4f electrons to clarify this question. The photoemission results on EuPd$_3$B are new as are the band structure results on EuPd$_3$B, Eu$_3$S$_4$, LaPd$_3$B and La$_3$S$_4$. Other systems are taken for comparison from Felser et al. [10].

2. Sample preparation and measurements

Photoemission measurements were made with the PGM3 monochromator using synchrotron radiation at the Berliner Speicherring für Synchrotronstrahlung (BESSY). The samples are difficult to handle, because their surfaces are air- and water-sensitive, therefore pellets were scrapped in situ to keep the oxygen contamination below the limit of detection. Incident photon energies were chosen so as to make the Eu 4f emission the dominant process. The total resolution of 0.4 eV and the Fermi level was determined by measurement of the Fermi edge of Palladium.

3. Photoemission spectra

Core level spectroscopy (XPS) is not able to distinguish between divalent and trivalent europium and the different possibilities of mixed valency because of shake-up effects [11] and the lower resolution. Using synchrotron radiation it is possible to study the partial density of states at E$_F$ and the europium valence. One remaining problem is the problem of surface states. To compare the valence spectra of different mixed valency compounds we obtained the valence band spectra of divalent EuAuAs compared with the isostructural non-integral valency EuPdP, homogeneous mixed valency EuNi$_2$P$_2$ and inhomogeneous EuPd$_3$B. In Fig. 1 the energy distribution curves of EuAuAs, EuPd$_3$B, EuPdP and EuNi$_2$P$_2$ (bottom to top) are shown. The zero energy is taken at the Fermi level. A well established condition for homogeneous mixed valency compounds is the degeneracy of the 4f^6 and the 4f^7 initial states [12]. This yields a low lying europium 4f multiplet located at the Fermi level. As expected no 4f states from the f^6 final state in the vicinity of the Fermi level is observed in divalent EuAuAs (Fig. 1a). The 4f^6 final state can be decomposed in surface and bulk like by assuming a Lorentzian line shape because of the core character of the 4f electrons. For EuNi$_2$P$_2$ the conditions for homogeneous mixed valency is fulfilled as seen clearly in the sharp Fermi cut-off of the 4f states in Fig. 1d. Because of the resonant enhancement of the 4f electrons at this photon energy, we conclude that the density of states at the Fermi level has mainly europium 4f character. Furthermore, no decomposition of the 4f^6 multiplet into two Lorentzian lines is possible indicating that the 4f electrons no longer have core character. The higher resolution of the spectra obtained with synchrotron radiation compared with XPS spectra makes a distinction between homogeneous and inhomogeneous mixed valence possible. We observed a sharp Fermi cut-off in the case of EuNi$_2$P$_2$, whereas the Fermi edge of EuPd$_3$B (Fig. 1b) and EuPdP (Fig. 1c) have a logarithmic shape, similar to the Fermi edge of the cuprate superconductors. The line width of the 4f^6 final state in inhomogeneous mixed valency compounds is broader when compared with divalent compounds. From our photoemission results we assume that the 4f electrons have different degrees of delocalisation, the interaction of the 4f electrons with the conduction electrons in EuNi$_2$P$_2$ will be the strongest, whereas in EuAuAs the 4f electrons has mainly core character.

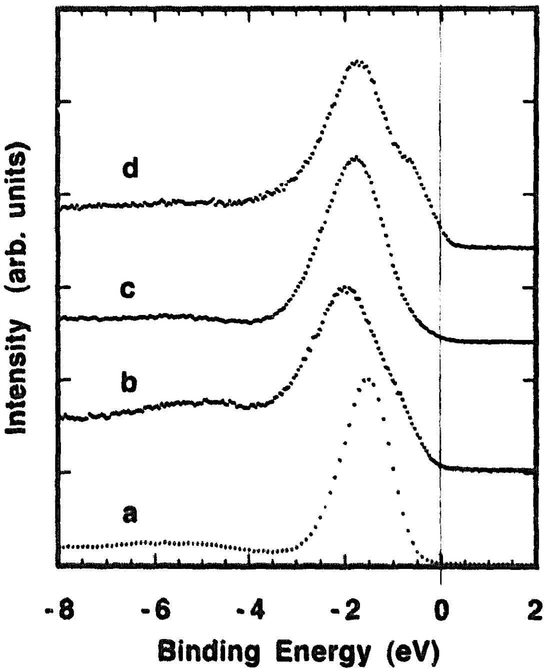

Fig. 1. The EDC's of: (a) divalent EuAuAs; (b) inhomogeneous mixed valency EuPdP; (c) inhomogeneous mixed valency EuPd$_3$B; and (d) homogeneous mixed valency EuNi$_2$P$_2$. All spectra were recorded with a photon energy of $h\nu = 140$ eV. The zero energy is taken at the Fermi level.

4. Computation details and band structures

To obtain deeper insights into the band structures, and into the differences between homogeneous and inhomogeneous mixed valency compounds, band structure calculations have been performed using first principles, self-consistent LMTO-ASA methods within the local density approximation (LDA) [13]. A detailed description of the LMTO-ASA method, including its application to the electronic structure of compounds, has been given elsewhere [14,15]. We shall, therefore only give some details of the calculations here. The calculations were semi-relativistic, i.e. all relativistic effects were taken into account except for the spin-orbit coupling. The angular momentum expansion of the basis functions included $l = 3$ for europium, palladium and gold, and $l = 2$ for sulfur, boron and phosphorous and arsenic. The k integrated functions were evaluated by the tetrahedron method [16] on a grid of ≈ 735 k points in the irreducible part of the BZ. On the one hand the 4f electrons are core-like lying well inside the filled $5s^2 5p^6$ shells. In most rare earth materials, except Ce, they are considered to be localized due to their large intra-atomic Coulomb correlation. On the other hand binding energies of only a few eV and valence fluctuation are characteristic for valence electrons. The aim of our calculations is to investigate the effects of 4f hybridization. Therefore in all calculations reported herein the 4f electrons are treated as hybridized valence electrons in a spin polarized calculation. All calculations are performed with the theoretical lattice parameters [17] in their undistorted structure type. The distortion, in all compounds, is small, and therefore we expect no important change in the general features of the band structure. Similarly we find that the small structural distortions (from cubic) in A15 superconductors leave the band structure relatively unchanged. The Brillouin zone (BZ) is as described in reference [18], where the symmetry points and lines are labelled in accordance with the standard notation. As an overview of the electronic properties, Fig. 2 shows the density of states of EuAuAs, EuPdP and $EuPd_3B$. As discussed in an earlier publication [10] the difference between the divalent europium compound and the inhomogeneous mixed valency compounds is the DOS peak at E_F, which hints at a van Hove singularity. In EuAuAs the europium is divalent and no 4f density of states at E_F is observed in agreement with our photoemission results. The DOS of EuAuAs is representative for all divalent europium compounds with the ZrBeSi structure type. In case of the divalent compounds the conduction band has mainly Eu d character. In contrast to that a peak coincides with the Fermi level in $EuPd_3B$ and EuPdP. An analysis of the partial DOS shows that this peak has mainly europium 4f character. While the first conclusion is that a singularity of the f electrons in the band structure is responsible for the electronic and structural instability of these compounds, superconductivity in La_3S_4 and the phase transitions in the inhomogeneous mixed valency compounds and La_3S_4 are a sign that the conduction electrons play an important role. Therefore we calculated the density of states (Fig. 3) and the band structure of the isostructural lanthanum and strontium compounds. In agreement with the fact that La_3S_4 is a superconductor, the Fermi level coincides with a density of states peak. The character of this peak is mainly lanthanum d with a small contribution of sulfur p states. A similar situation is found for $LaPd_3B$ and SrPdP, but the peak is below E_F. We assume that this peak is responsible for inhomogeneous mixed valency in the isostructural europium compounds. Also in the A15 superconductors such a peak at E_F leads to a phase transition with a small distortion of the structure. Even though the 4f electrons are the reason for the valence instability, it is the conduction bands that are responsible for its formation. To find further proof of a van Hove singularity of the conduction electrons for inhomogeneous mixed valency we calculated the energy band structure around the Fermi level for La_3S_4, $LaPd_3B$ and SrPdP, shown in Fig. 4. A saddle-point in the vicinity of E_F is found in all the investigated

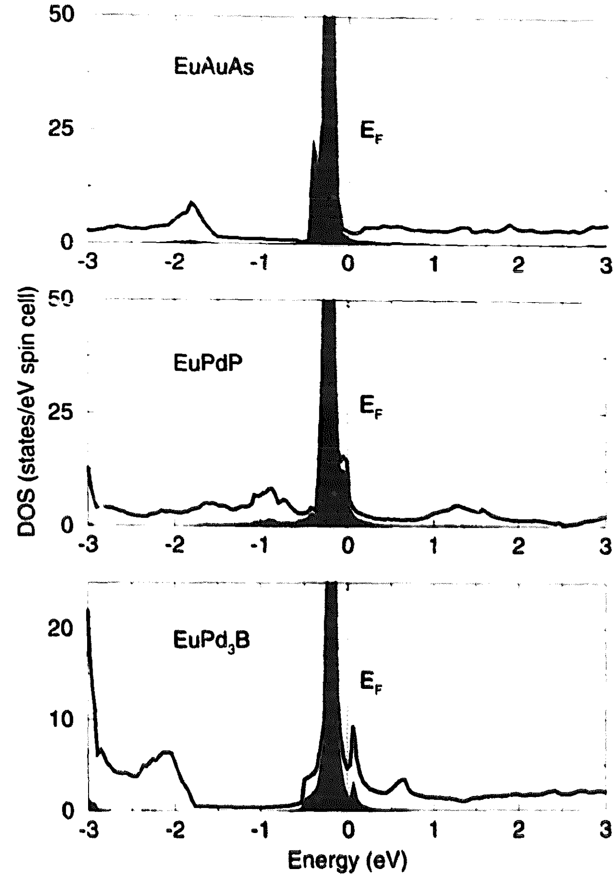

Fig. 2. Self-consistent total DOS of EuAuAs, EuPdP and $EuPd_3B$. The partial DOS contribution from Eu 4f states is shown by the grey shading. The Fermi level is dra[illegible] a dotted vertical line.

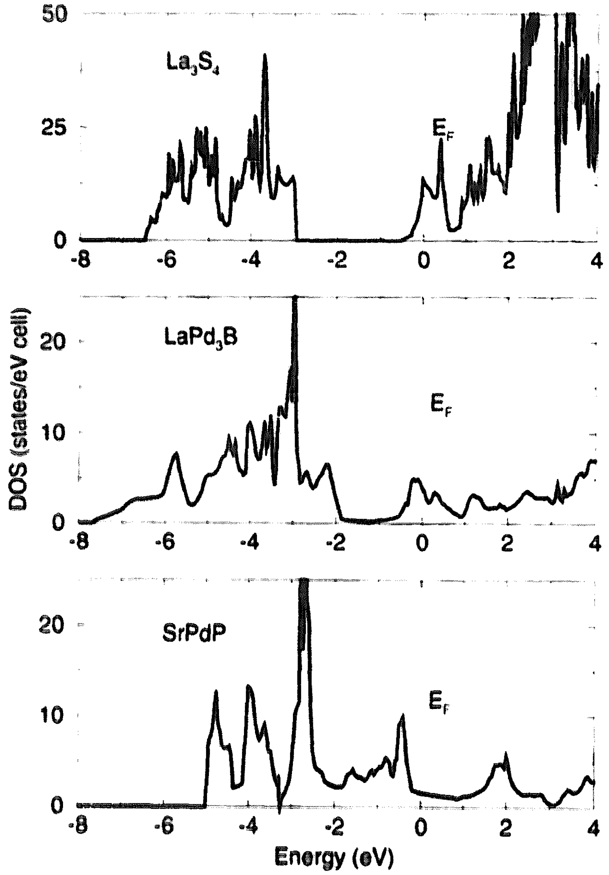

Fig. 3. Self-consistent total DOS of La_3S_4, $LaPd_3B$ and $SrPd_3P$. The Fermi level is drawn as a dotted vertical line.

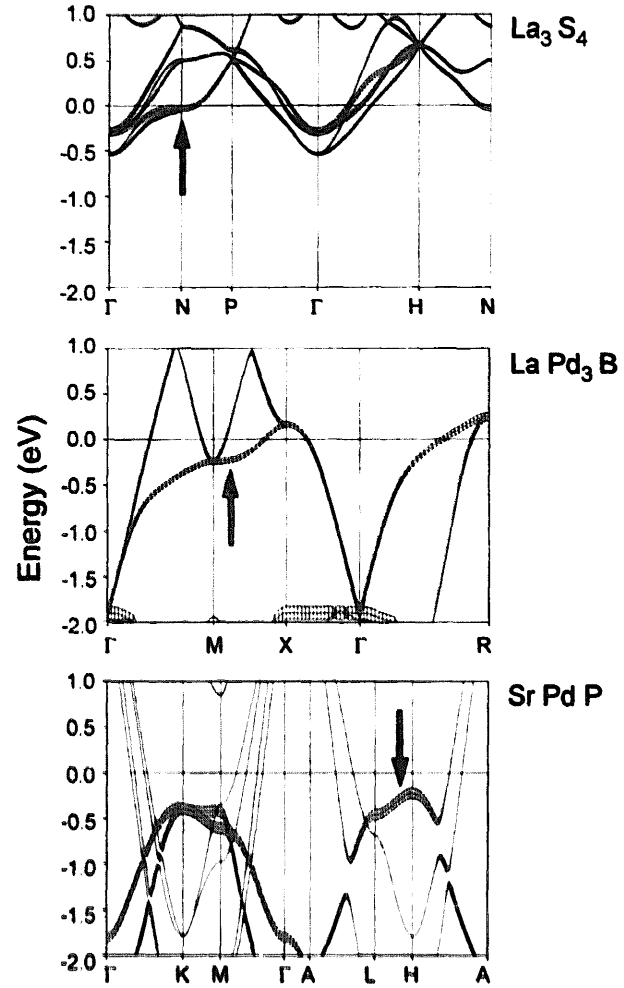

Fig. 4. Self-consistent energy band structure of La_3S_4, $LaPd_3B$ and $SrPd_3P$ around the Fermi level. The zero energy is taken at the Fermi level and the van Hove singularities are marked by arrows.

compounds. The cause for the formation of the saddle-point is the bonding situation of these compounds which will be discussed in detail elsewhere. In the case of the europium compounds, a second saddle point close to the Fermi level exists, which is caused by the interaction of the 4f electrons with the conduction band.

5. Conclusion

The valence of europium in divalent, homogeneous and inhomogeneous mixed valency compounds can be determined by photoemission with synchrotron radiation. The more itinerant character of homogeneous mixed valency compounds can be seen clearly in the broadening of the $4f^6$ final state multiplet and the sharp Fermi cut-off of the $4f^7$ states compared with divalent compounds. In inhomogeneous mixed valency compounds the shape of the Fermi edge shows a logarithmic behaviour. There are also 4f states in the vicinity of the Fermi level and the $4f^7$ final state no longer has core character. LMTO band structure calculations show that a van Hove singularity of the conduction electrons are responsible for the valence instability in inhomogeneous mixed valency compounds. If the van Hove singularity coincides with E_F, superconductivity will be observed provided there are no f electrons. Therefore La_3S_4 is a superconductor and it must be possible to induce superconductivity in $LaPd_3B$ and SrPdP via hole doping.

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