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The effect of high pressure upon the valence transition in $EuPd_2Si_2$

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Abstract. The so-called 'valence transition' in $EuPd_2Si_2$ has been observed using energy-dispersive synchrotron x-ray powder diffraction at elevated pressures and is centred at 8 kbar. The estimated increase in valence at the transition is 0.2, and is associated with crossover of 4f and 6d/s bands.

1. Introduction

There are many mixed-valence compounds in which an element exists simultaneously in two different stable valence states. Thus, Fe_3O_4 is more accurately represented as $(Fe^{II})(Fe^{III})_2O_4$, and $CsAuCl_3$ as $Cs_2[Au^{I}Cl_2][Au^{III}Cl_4]$.

In solid state physics the term 'mixed valence' is commonly used in an entirely different sense, and the field is further confused by application of the synonyms 'mixed configuration', 'fluctuating valence', and 'fluctuating configuration'. These terms describe complex electronic band structure effects in materials in which at least one of the components may adopt more than one electronic configuration.

The band structure of such a solid may be represented by a linear combination of the two notional 'parent' configurations:

$$\Psi(\text{Total}) = a_k \varphi_1 + b_k \varphi_2.$$

Then, if these two electronic configurations are thought of as different valence states, the material is aptly described as of 'mixed valence', although it is clear that all the atoms of the element in question in that solid have the *same* electronic configuration. The term 'homogeneously mixed valent' is often used to describe these systems, in contrast with 'inhomogeneously mixed valent' materials such as Fe_3O_4.

With variation of temperature or pressure the electronic levels of the material will be changed and it follows that a_k and b_k will take different values. Thus, a change of valence is deemed to have occurred. An 'average valency' R is defined by

$$R = \sum |a_k|^2 \Big/ \sum |b_k|^2$$

where the summation is over the occupied part of the conduction band (Varma 1976). As the temperature or pressure is varied, the accompanying changes in a_k and b_k

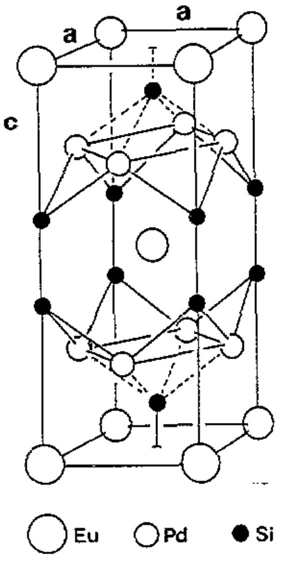

Figure 1. The crystal structure of $ThCr_2Si_2$.

and therefore also in *R* are sometimes regarded as constituting a 'continuous valence transition'.

Of particular interest in this connection are solids in which d and f levels are in close proximity as these show many unusual effects as bands are brought into resonance with each other. The 4f electrons remain essentially atomic in character, whereas the 6d/s electrons are highly delocalized. Hence, as 'tuning' proceeds with change of temperature or pressure, there is progressive transfer of charge from the f to the d/s band which effectively increases the valence of the rare-earth atoms.

1.1. $EuPd_2Si_2$ and related materials

A series of materials MRh_2Si_2 and MPd_2Si_2 exists (M is a lanthanide) with the $ThCr_2Si_2$ structure $I4/mmm$, $Z = 2$), figure 1 (Rossi *et al* 1979). This structure type is notable in that the magnitude of the lattice constant *a* is set primarily by the size of the lanthanide ion, whereas *c* is mainly determined by the Pd/Si skeleton (Ballestracci 1976).

The compound $EuPd_2Si_2$ is of particular interest in that it shows a lattice volume anomaly with respect to the other lanthanide isomorphs, and a strong temperature anomaly near 150 K in several physical properties. In particular, low-temperature x-ray powder diffraction using monochromatic radiation showed that the *a* parameter reduces as *T* approaches zero (Sampathkumaran *et al* 1981a, b), in response to the shrinkage of the europium ion as its average valence increases. We have studied the effect of pressure at ambient temperature upon the lattice parameters of this compound in the expectation that the same valence transition would be observed.

2. Experimental procedure

$EuPd_2Si_2$ was prepared in a furnace with excess of europium and annealed at 1100 K for a week. EDXRPD measurements were made on the SERC Daresbury Laboratory

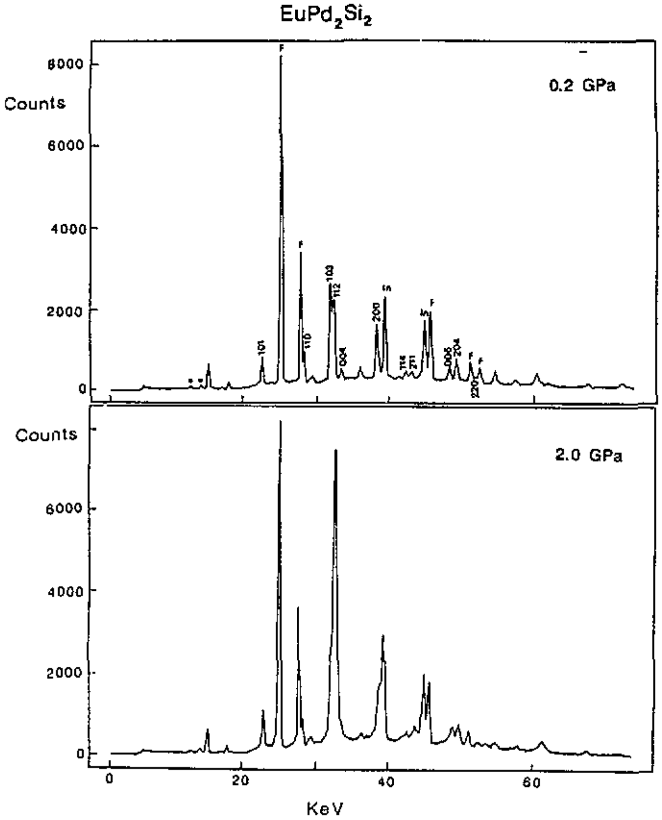

Figure 2. EDXRPD patterns for $EuPd_2Si_2$ at (*a*) 2 kbar, (*b*) 20 kbar.

synchrotron radiation source (Station 9.7) with the sample in a diamond anvil cell. The pressure-transmitting fluid was 4 : 1 methanol : ethanol, and the ruby fluorescence shift was used as the pressure scale. Bragg peak positions were determined using the GENIE data analysis package, and lattice parameters calculated using VARVEC.

3. Results and discussion

Good quality data were obtained, figure 2, and successfully indexed on the basis of the $I4/mmm$ cell with $a = b = 4.237$ and $c = 9.851$ Å (Rossi *et al* 1979). Observed d_{200} values were then used to deduce the values of a at various pressures, figure 3. These values vary smoothly, showing a steady contraction of a centred near 8 kbar.

At about 20 kbar the lattice constants of $EuPd_2Si_2$ are almost identical to those of isomorphous $SmPd_2Si_2$ in which samarium is trivalent, suggesting that the europium ion approaches the trivalent state at high pressure. The volume reduction of 3.4% at the valence transition is equivalent to a decrease of the europium ion radius of 0.0385 Å. Assuming a linear relationship between valence and atomic radii ($Eu^{2+} = 1.17$, $Eu^{3+} = 0.947$ Å), the valence increase of europium at the transition is about 0.2.

We conclude that both pressure and temperature changes induce the same valence transition in this material.

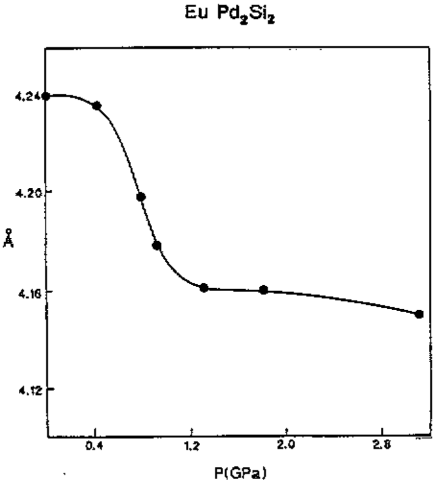

Figure 3. Variation of lattice parameter a with pressure for $EuPd_2Si_2$ where a is calculated from d_{200} data.

Acknowledgments

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