

On the valence instability in CeAl₂

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Abstract. This paper reports the observation of an isostructural electronic phase transition in CeAl₂ near 77 Kbar pressure at ambient temperature. The present volume compression data obtained under truly hydrostatic pressure conditions gives a clear indication of the first order nature of this phase transformation.

Keywords. Valence transition; high pressure; concentrated Kondo system.

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1. Introduction

The cubic Laves-phase compound CeAl₂ has been extensively studied in recent years (Croft *et al* 1981 and references therein). In analogy with the high volume, local magnetic moment phase of Ce (γ -Ce), the ambient pressure phase of CeAl₂ is generally considered as γ -like. The role of Kondo effect in this γ -like phase has been well characterized (Steglich *et al* 1979, 1980). It would suffice here to mention that in these γ -like Ce systems, including CeAl₂, there is a strong antiferromagnetic $4f$ electron-conduction electron exchange interaction leading to some interesting magnetic properties. Neutron diffraction studies on CeAl₂ have clearly established that it has a sinusoidally modulated antiferromagnetic structure (Barbara *et al* 1977). The moment reduction in such a modulated structure has been again explained as due to the existence of a singlet ground state resulting from the negative exchange between the $4f$ electron of Ce³⁺ ion and the conduction electrons. Prior to this neutron diffraction work, the absence of magnetic order at low temperatures as inferred from several measurements had led some authors to conclude that CeAl₂ is a valence fluctuating compound similar to α -Ce. On the other hand the lattice parameter data and the value of the magnetic moment of the Ce-ion at ambient pressure as deduced from the high temperature part of the magnetic susceptibility are all characteristic of a tri-positive Ce ion with $4f^1$ configuration (Hill 1970; Walker *et al* 1973).

Probst and Wittig (1978) found that the room temperature resistance of CeAl₂ passes through a faint maximum around 60 Kbar pressure which they attributed to a continuous electronic transition with pressure just like in Ce above the critical point. However, these authors had noted that since their measurements were on powdered samples in a Bridgman anvil set up, a small discontinuity in the R-P characteristic might have escaped detection. Croft and Jayaraman (1979) first reported the existence

of an isostructural transition with a volume discontinuity of the order of 4% near 65 Kbar pressure. These authors further noted that the transition is associated with a change over from a concentrated Kondo system to a strongly mixed valence state above 65 Kbar. Recently Vedel and co-workers (1986) have reported that there is no volume discontinuity near 65 Kbar but the compression curve exhibits an anomalous softening of the CeAl_2 lattice over the entire pressure range of 200 Kbar.

In this communication, we report some new measurements on the compression behaviour of CeAl_2 upto 120 Kbar under truly hydrostatic pressure conditions. The present data gives clear evidence for a discontinuous volume collapse of the order of 1% near 77 Kbar.

2. Experimental technique

The high pressure x-ray diffraction technique employed in the present investigation has been described elsewhere (Syassen and Holzapfel, 1978). In brief, the pressure apparatus is a boron carbide anvil cell adapted to a conventional powder diffractometer. The main advantage of the boron anvil technique is that a liquid pressure transmitting medium like the 4:1 methanol-ethanol mixture can be filled along with the sample in a small hole (0.3 mm in diameter, 0.5 mm deep) at the tip of the boron carbide anvil. The sample is intimately mixed with NaCl which acts as a marker substance and then filled into the hole along with the methanol-ethanol mixture. A maximum pressure of about 120 Kbar could be routinely generated in this set up. X-ray diffraction measurements are performed in the Debye-Scherrer geometry with photon counting techniques. A collimated beam of MoK_α radiation which has an absorption length of 8 mm for B_4C material impinges on the hole containing the sample, marker and pressure transmitting fluid. During the measurement, the high pressure anvil set up is oscillated around the axis of the goniometer in order to reduce the effect of finite grain size. The position of a diffraction peak is determined by a least-squares fit of a Gaussian line to the measured intensity data and since measurements are carried out on either

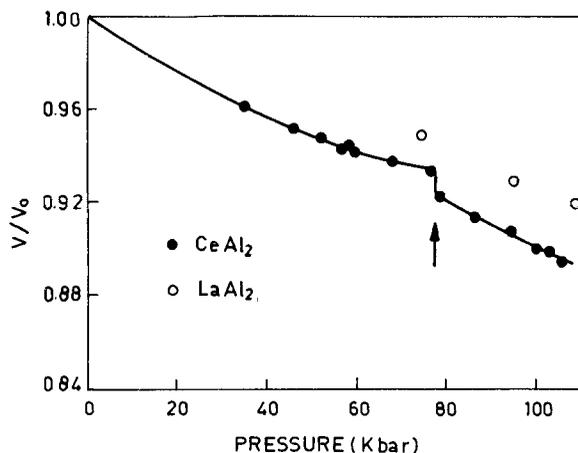


Figure 1. Reduced volume V/V_0 (V_0 =volume at 1 bar) versus pressure for CeAl_2 (closed circles) and LaAl_2 (open circles). Position of arrow gives the transformation pressure for the first order iso-structural phase transition.

side of the primary beam, the diffraction angle for a given (hkl) reflection is taken as the average of the peak positions.

3. Results and discussion

The pressure-volume data for $CeAl_2$ at room temperature is given in figure 1. The NaCl scale of Decker *et al* (1972) has been used for pressure calibration. Also shown in the figure is the compression data on $LaAl_2$ which is a typical trivalent rare-earth dialuminide compound with no valence instability. It is clear from figure 1 that there is a first order phase transition near 77 Kbar and the present data shows that there is a volume change of only 1% at the transformation pressure. From the previous data of Croft and Jayaraman (1979), it is not possible to specify the order of the transition and they had deduced that a volume collapse of the order of 4% occurs at the isostructural phase transition. The present experimental data is in disagreement with the data of Vedel and co-workers (1986) who found no volume discontinuity in the entire pressure range of 200 Kbar.

We believe that the isostructural phase transition in $CeAl_2$ near 77 Kbar is very similar to the γ - α transition in elemental cerium. However the small volume discontinuity near room temperature suggests that the γ -like- α -like phase boundary in the P-T plane terminates at a critical point with the critical temperature not far above the ambient temperature.

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