PRESSURE INDUCED TRANSITIONS IN SOME RARE-EARTH COMPOUNDS

J. Leger, K. Oki

To cite this version:

J. Leger, K. Oki. PRESSURE INDUCED TRANSITIONS IN SOME RARE-EARTH COMPOUNDS. Journal de Physique Colloques, 1984, 45 (C8), pp.C8-149-C8-152. 10.1051/jphyscol:1984827. jpa-00224327

HAL Id: jpa-00224327
https://hal.archives-ouvertes.fr/jpa-00224327

Submitted on 1 Jan 1984

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
PRESSURE INDUCED TRANSITIONS IN SOME RARE-EARTH COMPOUNDS

J.M. Leger and K. Oki

E.R. 211, C.N.R.S., 92190 Meudon, France

Abstract - The pressure-volume dependence has been measured for CeTe, CeSb, LaSb and CeBi by x-ray diffraction on polycrystalline samples in a diamond anvil cell up to 25 GPa. All these compounds undergo first order polymorphic transitions under high pressure. From the comparison of the bulk moduli of the cerium and lanthanum compounds and from the variation of the Ce-X distance at the transition a continuous electronic transfer has been inferred in CeTe and CeBi in the f.c.c. phase followed by a back discontinuous variation at the crystallographic transition; no such a behaviour was found in CeSb.

INTRODUCTION

In cerium mono-pnictides or chalcogenides the cerium electronic transition which has already been observed in CeP /1/ and CeS /2/ is expected to be induced by higher pressures when the atomic number of the anion increases as the 4f level moves towards higher binding energies. However no evidence for an electronic transition has been found in CeAs /3/ up to 30 GPa and the volume change at the NaCl -> CsCl crystallographic transition occurring at 16 GPa can be accounted for by a stable trivalent cerium ion with six and eight coordination numbers.

The 4f electron is even more tightly bound in the remaining cerium monopnictides but nevertheless CeSb and CeBi exhibit unusual magnetic properties /4/ which actually result from their semi-metallic character. Band calculations /5/ indicate that a small amount of p holes exist at the zone center while the electrons of 5d(T2g) character are concentrated at the zone boundary. The mixing interaction between the 4f electrons and the anion p band increases in the series and accounts for the anomalous properties of CeSb and CeBi although the 4f electrons are further away from the Fermi level.

Among the cerium monochalcogenides, CeTe exhibit unusual magnetic properties /6/; below 2K a type II antiferromagnetic order appears but the cerium moment is only one third the expected value for a T2 doublet ground state.

Pressure-volume measurements on CeSb, CeBi and CeTe could then reveal any electronic transitions as they are coupled to large volume variations. In addition the comparison of the bulk moduli of the cerium and lanthanum compounds can also reveal any anomalous behaviour as the Kondo coupling in cerium monochalcogenides lowers the bulk modulus /7,8/; the p-f mixing in cerium monopnictides is expected to produce such an effect as the physical basis is the same.

On leave from Kyushu University, Kasuga-shi, Fukuoka 816, Japan
EXPERIMENTAL

The volumes were determined by x-ray powder diffraction under high pressure. The experiments have been carried out in a modified diamond anvil cell of the lever arm type. The incident x-ray beam was produced by a molybdenum fine focus tube operated at 45 kV and 9 mA; the Zr filtered radiation was collimated by crossed slits 0.10 mm wide. The 2θ diffraction angle allowed was 40°. Good diffraction patterns were obtained within 24 hours.

The samples were obtained by crushing small single crystals and were mixed with silicon grease as the pressure transmitting medium and with CsCl, NaCl or Au used as the pressure standard.

A liquid pressure transmitting medium has not been used because liquids freeze in the 4-15 GPa range and introduce large perturbations in the pressure distribution which could be misleading when phase transitions are looked for. When determining P-V relationships in diamond anvil cells, the presence of possible uniaxial stress components must always be taken into account as the low shear strength pressure transmitting medium can possibly extrude from between the higher strength sample particles allowing them to bridge the anvils and thus to develop large anisotropic stresses. It has been shown /9/ that the low pressure data should be discarded and the initial volume is then treated as a third unknown parameter. This effect was found to be weak for the compounds studied here.

RESULTS AND DISCUSSION

CeTe exhibits a quite anomalous compression curve. Actually, its bulk modulus, $B_0 = 52.8$ GPa, is lower than that of LaTe, 55 GPa, in opposition to the expected trend since the bulk modulus of isostructural and isocharged compound should vary as $B_0 \propto \sqrt{V_0}$ where $V_0$ is the unit cell volume and $\gamma$ is close to one for ionic solids, and to 5/3 for free electron metals and covalent solids. In addition the first pressure derivative of the bulk modulus is very high, +13.6, and very far from four, the usual value.

A first order crystallographic transition occurs at 8 GPa from the NaCl to the CsCl-type structure, but the volume jump, 8.5 %, is then anomalously low; it is markedly smaller than the value found for PrTe (11 %) which undergoes the same transformation. At the transition, the Ce-Te distance increases by 0.17 Å, but this is too much to come only from the increase of the coordination number, usually 0.11 - 0.12 Å. Then a part of this increase of the size of the cerium ion comes from an associated electronic transition. Assuming a linear relationship between valence and ionic radius, the valence is then calculated to decrease by approximately 0.3 at the transition /10/. The low value of the magnetic moment at normal pressure and the pressure-volume relationship of CeTe can be accounted for by considering that, at normal pressure, CeTe is just at the border line between a magnetic and a non magnetic Kondo state. The Kondo coupling gives a negative contribution to the bulk modulus and a first or second order transition results depending on temperature. In CeTe, the NaCl structure becomes unstable under pressure and transforms into a CsCl structure where the Ce-Te increased distance leads to a smaller Kondo coupling reflected in the volume dependence observed at high pressure: the bulk modulus of the CsCl phase is higher and its first pressure derivative is strongly reduced.

The complicated magnetic phase diagram of CeSb at normal pressure has been accounted for by p - f mixing effects /4/. Under high pressure, the volume variations of CeSb and LaSb are identical leading to equal values for their bulk moduli, in contrast with the trend expected from the unit cell volume. This no variation is attributed to p - f mixing effects; in CeSb the small negative electronic contribution balances the lattice one.

Above 11 GPa, CeSb and LaSb transform into a new structure which is not the usual CsCl-type one, but a largely CsCl distorted structure. The x-ray powder patterns, d spacings and line intensities, have been interpreted by assuming a tetragonal structure with the space group P 4/mmm (c/a = 0.82) (Léger et al., to be published in J. Phys. C.). This structure can be considered as a special case of the FH.I-type structure which is adopted preferably to the CsCl one by less ionic compounds.

At the crystallographic transition the Ce-Sb distance increases by 0.17 Å, the same amount as found for the Ce-Te distance at the NaCl + CsCl transformation. However,
the increase of the Ce-Sb distance cannot be related to a sizable change of the cerium electronic state for two main reasons. Firstly, the coordination number is not well defined in the tetragonal structure as from the peculiar value of the c/a ratio, the next nearest neighbours consist of two kinds of atoms; secondly, the same increase is also found for the La-Sb distance although no valence change of the lanthanum atom can occur. From the study of CeBi (see below), the extra increase of the distance from the classical CsCl structure can be estimated to be 0.04 Å leaving then 0.13 Å for the increase of the cerium radius from a sixfold to an eight-fold coordinated atom. Such a value is close to the expected value, 0.11 - 0.12 Å, for a stable ionic state. So, in CeSb, no sizable electronic change of the cerium atom can be evidenced at the crystallographic transition, although the Ce-Ce distances in the tetragonal structure, 3.24 and 3.95 Å, fall on each side of the often mentioned 3.4 Å value for the threshold of the γ - α transition.

The bulk moduli of CeSb and CeAs, 71 and 69 GPa respectively, are nearly equal although the unit cell volumes are largely different. Such an increase with respect to the expected trend, must originate in the increased covalent bonding in CeSb whereas the behaviour of CeAs and in particular the volume jump at the crystallographic transition is well accounted for by an ionic description.

In CeBi the p-f mixing effects are expected to be more important than in CeSb. The pressure-volume relationship has been determined up to 25 GPa. In the f.c.c. phase, at lower pressure, the bulk modulus of CeBi, 49.6 GPa, is markedly lower than that of LaBi, 55 GPa. Above 14 GPa, the NaCl structure has disappeared and two structures of close unit cell volumes coexist: a tetragonal structure, as found for CeSb, of the P 4/mmm space group, and the usual CsCl-type structure. At this transition the volume jump is small and the Ce-Bi distance increases by as much as 0.20 Å from the NaCl to the CsCl type structure and 0.24 Å from the NaCl to the tetragonal structure. The analysis of the NaCl-CsCl transformation can be performed as well as in the case of CeTe and from a linear relationship between valence and ionic radius a back electronic transfer by ≈ 0.45 is calculated at the transition (Léger et al., submitted to J. Physique). The p-f mixing lowers the bulk modulus of the NaCl type phase and a second order transition results in this case. At the crystallographic transformation the increase of the Ce-Bi distance reduces the p-f mixing coupling and a reentrant
behaviour results.

CONCLUSION

The cerium monopnictides display a large variety of behaviours. CeN is already metallic at normal pressure and cerium is close to the tetravalent state but in the remaining members of the series cerium is always trivalent at normal pressure. Under pressure CeP undergoes a pure discontinuous electronic transformation at 11.5 GPa while CeAs and CeSb do not show any evidence of an electronic transition up to 25-30 GPa. Increased covalent bonding occurs in CeSb and CeBi and the pressure-volume relationship of CeBi indicates some continuous electronic transition in the low pressure phase followed by a back discontinuous change at the crystallographic transition at 13 GPa.

Among the cerium monochalcogenides, only the pressure-volume dependences of CeS and CeTe have been determined. CeS undergoes a discontinuous pure electronic transformation at 13 GPa while CeTe shows a continuous transfer starting from normal pressure up to 8 GPa where a back discontinuous electronic transition occurs at the crystallographic transformation.

In both series, cerium behaves in the same way: with small anion, a discontinuous electronic transition occurs under pressure (CeS, CeP); with large anions, no electronic transition is observed up to at least 25-30 GPa (but experiments are not reported for all the chalcogenides). Finally with the largest anions, a continuous electronic transition occurs under pressure beginning already at normal pressure (CeTe, CeBi). The crystallographic phase transitions which occur under high pressure increase the cerium-anion distance and smaller d-f or p-f coupling results leading to reentrant behaviours and reduced effects are then observed in the high pressure phase.

REFERENCES