

05.1-42

A Crystallographer's Approach to the Mechanism of Magnetic C/IC Phase Transitions

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Rare earth and rare earth intermetallics reveal a series of magnetic structures, starting from pure helix whose propagation vector may or not lock in at definite commensurate values. Within a Hamiltonian model which incorporates a competition between exchange interactions and magnetocrystalline effects (anisotropy, magnetostriction, applied field), it is possible to explain that any incommensurability between the periods of exchange and magnetocrystalline order leads to a singularity in the energy. A strategy is defined to construct the phase diagram. Application to ReBe_{13} intermetallics is discussed in detail and possible generalisations to other magnetic or structural phase transitions are discussed. The method that is used is strongly connected to the crystallographic behaviour of the system, which enables a very simple understanding of the occurrence of transitions.

05.1-43

PHASE TRANSITION STUDIES OF POLY-CRYSTALLINE SAMPLES OF YbBr_2 BETWEEN 20°C AND 900°C USING A CURVED POSITION SENSITIVE DETECTOR. By B. Baumgartner, Technische Hochschule, Institut für physikalische Chemie, Darmstadt, Fed. Rep. of Germany.

YbBr_2 undergoes a number of interesting phase transformations, the kinetic studies of which were made with a curved Stoe position sensitive detector in conjunction with the Stoe focusing powder diffractometer (1).

A novel type of an adjustable high temperature attachment for SiO_2 -glass capillaries was developed, which consists of a carefully machined cylindrical heating element of graphite, having a central hole for the rotatable capillary and for thermocouples and equatorial holes for the convergent monochromatic $\text{Cu-K}\alpha_1$ X-ray beam (from a curved Ge-monochromator) and for the reflected X-rays. The heating element was operated with 4 V and up to 250A at 900°C. The current connectors and the metal housing of the attachment are water cooled when operated above 300°C and the chamber was flushed with nitrogen during operation to avoid oxidation of the heating element. The temperature was programmed and controlled to better than $\pm 1^\circ\text{C}$.

With the equipment the kinetics of the phase transitions of YbBr_2 have been studied and some interesting results including metastable phases will be presented.

(1) E.R. Wölfel A novel curved position sensitive proportional counter for X-ray diffractometry. J. Appl. Cryst. (1983) 341-348

05.1-44

PHASE TRANSITIONS AND DELOCALIZATION OF 5f ELECTRONS IN ACTINIDE METALS. By U. Benedict, Commission of the European Communities, Joint Research Centre, European Institute for Transuranium Elements, Postfach 2266, D-7500 Karlsruhe 1, Fed. Rep. Germany.

The 5f electrons of the metals Pa, U, Np and Pu are "delocalized" (or "itinerant"). This means that they are of band type, hybridize with the other conduction electrons and thus contribute to the metallic bonding. In contrast, the metals Am, Cm, Bk and Cf, which follow in the actinide series, are characterized by sharp 5f levels and are said to have "localized" 5f electrons which do not participate in the metallic bond.

The delocalization of 5f (and 4f) electrons correlates to two phenomena of crystallographic interest:

1) The interatomic distances decrease with respect to the "localized" configuration. Thus, the atomic volumes of the elements Pa to Pu are considerably lower than those of the other actinides. This is due to the extra contribution to the metallic bonding from the 5f-band electrons, while in the localized configuration this bonding is absent (B. Johansson, H.L. Skriver, J. Magn. Magn. Mat. 29, 1982, 217-229.)

2) Crystal structures of low symmetry appear. U, Np and Pu have a number of orthorhombic and monoclinic structures while the other actinides (with the exception of the body-centred tetragonal Pa) have close-packed cubic and hexagonal structures, at normal pressure and temperature. The appearance of low-symmetry structures is rationalized by a marked directionality of the hybridized orbital, though a quantitative explanation has not yet been given.

Pressure favors delocalization and hybridization of f electrons. Thus, the low-symmetry α -uranium type structure (orthorhombic, Cmc) was successively observed under pressure in Ce (W.H. Zachariasen, F.H. Ellinger, Acta Cryst. A33, 1977, 155-160), in Am (R.B. Roof et al., Science 207, 1980, 1353-1355), in Pr (G.S. Smith, J. Akella, J. Appl. Phys. 53, 1982, 9212-9213; W.A. Grosshans, Y. K. Vohra, W.B. Holzapfel, J. Phys. F: Metal Phys. 13, 1983, L147-149) and very recently in Bk and Cf (U. Benedict, J. R. Peterson, R.G. Haire, C. Dufour, J. Phys. F: Metal Phys. in press). In addition, monoclinic structures were observed under pressure in Ce and Am. The pressures, at which these low symmetry structures form, increase in the series: Ce about 5 GPa, Pr about 20 GPa in the lanthanide series, Am about 10 GPa, Bk about 25, Cf 41 GPa in the actinide series. In the actinide series, the volume decrease accompanying the transition increases with increasing 5f occupation: small in Am, $\sim 12\%$ in Bk, and $\sim 16\%$ in Cf.

The dhcp-fcc transition, which occurs under pressure in the earlier lanthanide metals, is also observed in Am (J. Akella, O. Johnson, W. Thayer, R.N. Schock, J. Less Common Metals 68, 1979, 95-97), in Bk (R.G. Haire, J.R. Peterson, U. Benedict, C. Dufour, J. Less Common Metals, in press) and in Cf (J.R. Peterson, U. Benedict, C. Dufour, I. Birkel, R. G. Haire, J. Less Common Metals 93, 1983, 353-356). These observations confirm the lanthanide-like character of these heavier actinides (i.e. localized f-electrons). Furthermore Cf shows another parallel to the lanthanides: the fcc phase, with further increasing pressure, is distorted (U. Benedict, J.R. Peterson, R.G. Haire, C. Dufour, J. Phys. F: Metal Phys., in press) in a similar way as the fcc phases of Pr, La and Y (W.A. Grosshans, Y.K. Vohra, W.B. Holzapfel, Phys. Rev. Letters 49, 1982, 1572-1575). In particular, Cf and Pr have the same structural sequence dhcp-fcc-distorted fcc- α -uranium type with increasing pressure. The transition pressure for the dhcp-fcc transition in the actinide series increases with increasing atomic number (Am: 5 GPa, Bk: 7 GPa, Cf: 17 GPa); this is also the case with the earlier lanthanide metals.