Ytterbium: Transition at High Pressure from Face-Centered Cubic to Body-Centered Cubic Structure

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Abstract: *Pressure of 40,000 atmospheres at 25°C induces a phase transformation in ytterbium metal; the face-centered cubic structure changes to body-centered cubic. The radius of the atom changes from 1.82 to 1.75 Å. At the same time the atom's volume decreases by 11 percent and the volume, observed macroscopically, decreases 3.2 percent.*

We present here data on a pressure-induced phase transformation from a close-packed structure to a nonclose-packed arrangement of atoms. When identical spherical atoms are stacked in honeycomb-like layers in which every atom touches six neighbors in its own layer and, in addition, touches three atoms in the layer above and also three atoms in the layer below, the total space (including voids between the spheres) occupied by a large number of atoms will be at a minimum. Such arrangements in which each atom touches 12 adjacent atoms are called closest-packed structures. Identical spherical atoms arranged in any other fashion will occupy a larger total volume.

At room temperature and pressure atoms of the metal ytterbium (Yb) are arranged in a closest-packed structure known as face-centered cubic (FCC). The FCC structure is shown in Fig. 1 by the conventional "unit cell" where only the centers of the atoms (dots) are shown. A basic dimension of the FCC unit cell is the length of the cube edge which, for Yb, is 5.481 Å at 25°C, and 1 atm. this corresponds to a radius of 1.940 Å for the metallic Yb atom. We have discovered a phase transformation occurring in Yb at 25°C, 40,000 atm, wherein the FCC phase transforms into a body-centered cubic (BCC) phase[1]. The BCC unit cell is also shown in Fig. 1. In this structure each atom touches eight surrounding atoms.

The nature of the transition was elucidated with the aid of a high-pressure x-ray diffraction apparatus which consists of a tetrahedral anvil press[2] to which x-ray goniometers have been attached. Primary x-rays are directed into the specimen (contained in a lithium hydride-amorphous boron tetrahedron) through a tiny axial hole in one of the triangular anvil faces. Diffracted x-rays ("powder" pattern) exit through gaskets formed between the sloping anvil shoulders and then, after passing through collimating slits, pass into the counter tubes.

The fraction of total space occupied by voids (spaces between the spheres) in FCC-closest packing is 26 percent, whereas the fraction of space taken up by voids in the non-closest-packed BCC structure is 32 percent. Offhand, therefore it would appear impossible for pressure

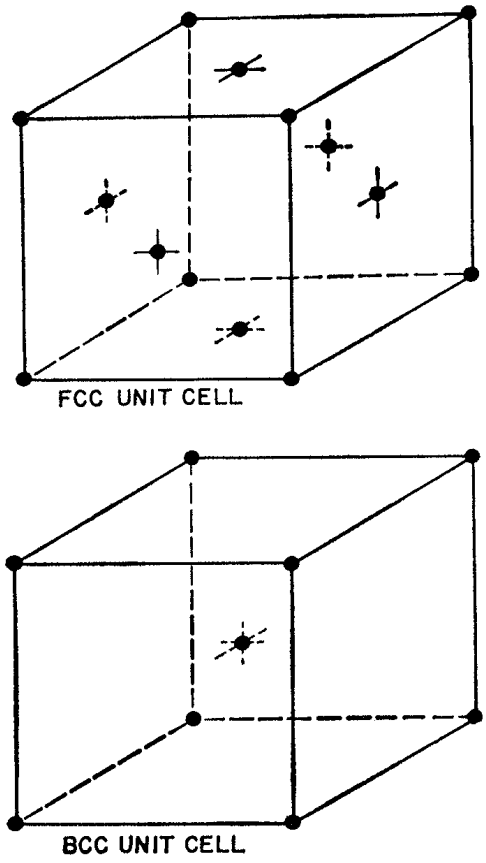

Fig. 1. Face-centered cubic (FCC) and body-centered cubic (BCC) space lattices.

to affect a transformation from the FCC to the BCC structure. Unit-cell data obtained from the tetrahedral x-ray press, however, make it possible to explain what has taken place. Calculation of the radii of the atoms from these data gives r = 1.82 Å for the FCC modification at 40,000 atmospheres and r = 1.75 Å for the BCC form at the same pressure. Calculation of volume changes from these values for the radii shows that an individual, spherical Yb atom shrinks in volume by 11 percent during the transition from FCC to BCC. This is even more interesting in view of the fact that the overall, macroscopic volume change at the transition is only 3.2 percent. Of course, the change to BCC structure is responsible for the greater decrease in the volume of the individual atoms.

A look at a chart of the values for the metallic radii plotted against the atomic numbers for the rare-earth atoms (Fig. 2) throws additional light on the nature of the transition. Note that most of the values for the radii of the rare-earth atoms fall very close to a straight line which represents

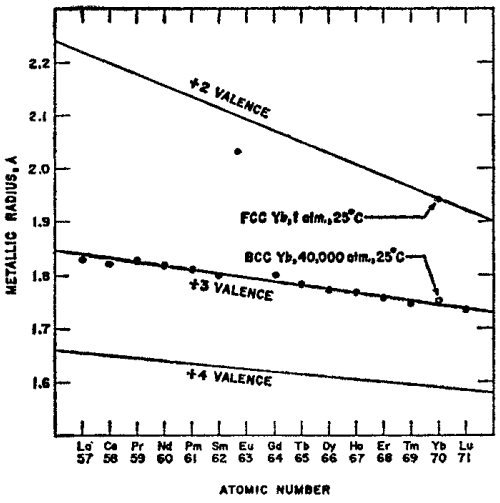

Fig. 2. Values of metallic radii of rare earths plotted against atomic numbers.

a valence of +3. Europium (Eu) and Yb having anomalously large radii, deviate significantly from the line. The valence of Yb is +2. However, the value of the metallic radius of BCC Yb (1.75 Å) at 40,000 atm is very close to the line where the valence in +3. Thus under the conditions of high pressure Yb has become a "normal" rare-earth metal! The electronic structure of the rare-earth elements is unique in that, as the charge on the nucleus increases in passing from element of atomic number 58 to atomic number 71, the balancing electrons fill in the inner, incomplete 4*f* subshell. The probable electronic configuration for the "outermost" shell of Yb is $4f^{14}\ 5d^{0}\ 6s^{2}$—a situation in which the 4*f* and 6*s* levels are completely filled and the 5*d* is empty. Since this is the case, it seems logical to conclude from our data on atomic radii that the transition from FCC to BCC in Yb is "electronic" in nature and is accompanied by the promotion of a 4*f* electron to the 5*d* level. In the solid, the two 6*s* electrons and the single 5*d* electron would enter the valance band; thus a valance of +3 would be the result.

When an atom changes its valence, it becomes a "different" atom with different bonding properties. Consequently, after a valence change the crystal structure may be entirely different from that of the untransformed material. We anticipate that additional high pressure x-ray diffraction research will show that the electronic transition from close-packed to non-close-packed structure will be found to occur in many substances if they are subjected to sufficiently high pressures.

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References and Notes

[1] This is undoubtedly the same transition as the electrical-resistance transition previously reported to occur at 60,000 atm. P. W. Bridgman, *Proc. Amer. Arts. Sci*. **83**, 1 (1954).
[2] H. T. Hall, *Rev. Sci. Instr*. **29**, 267 (1958).
[3] Supported by U.S. Army Research Office, National Science Foundation, and Alfred P. Sloan Foundation grants.
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