Structural Phase Transitions in Yttrium under Pressure

Y. K. Vohra,[a] H. Olijnik, W. Grosshans, and W. B. Holzapfel
Experimentalphysik, Universität-Gesamthochschule Paderborn, 4790 Paderborn, Federal Republic of Germany

(Received 17 August 1981)

The 4*d* transition metal yttrium was studied at pressures up to 34 GPa by energy dispersive x-ray diffraction. The crystal-structure sequence hcp→Sm-type→double-hcp was observed with increasing pressure. This sequence is well known for the regular trivalent lanthanide metals with decreasing 4*f*-electron number and under high pressure. Its observation in yttrium is conclusive experimental evidence that these structural transitions result simply from changes in *d*-band occupancy ($s \to d$ transfer) without any significant participation of *f* electrons.

PACS numbers: 64.70.Kb, 61.55.Fe

The crystal-structure sequence hcp → Sm-type → double-hcp → fcc is observed for regular trivalent lanthanide metals both for decreasing atomic number from right to left across the lanthanide series and for increasing pressures.[1-4] Johansson and Rosengren[5] suggested a generalized phase diagram for rare-earth elements and found an empirical correlation between the crystal structure of the lanthanides and the fraction of the atomic volume occupied by ion core. This correlation was later quantitatively interpreted by Duthie and Pettifor[6] in terms of *d*-band occupancy and its variation with relative volume of the ion core. It was suggested that the number of *d* electrons per atom in the conduction band (N_d) determines the relative stability of various crystal structures through the bonding contribution U_d^{bond} to the cohesive energy. The observed sequence hcp → Sm-type → double-hcp → fcc for the lanthanides was explained by an increase of N_d from 1.5 to 2.7. Similarly, the hcp → bcc → hcp → fcc structural trend across the transition-metal series had been explained previously[7] by a comparison of U_d^{bond} for different crystal structures at various *d*-band occupancies. Also, the stability of the ω phase in Ti, Zr, Hf, and their alloys had been related to the *d*-band occupancy and its change under pressure.[8] The present experiment was performed to see whether one can simulate the lanthanide crystal-structure sequence in yttrium, in which no *f* electrons are present ($N_d \sim 1.5$), by applying pressure. The conditions are particularly favorable since Y, because of its large *sp* core, should show the largest $s \to d$ transfer under pressure within the 4*d* transition-metal sequence.[9] Also, at extreme pressures, it is expected to become an almost pure 4*d* metal ($N_d \sim 3$).

The metal Y like scandium crystallizes in the hcp phase at ambient conditions. Earlier high pressure and low temperature studies on Y show the onset of superconductivity at about 10 GPa[10] and possible occurrence of new crystallographic modifications.[11] Also, the shock-wave studies on Sc and Y indicate a sluggish low-pressure phase transformation.[12] In the present investigations, Y was studied by energy dispersive x-ray diffraction using a diamond anvil cell with ruby manometer.[13] Figure 1(a) shows the diffraction pattern of Y in the hcp phase at a pressure of 8.9 GPa. Around 10 GPa, new features in the diffraction pattern indicate the onset of a sluggish transition to the Sm-type structure. At 15 GPa, this transformation is almost complete; Fig. 1(b)

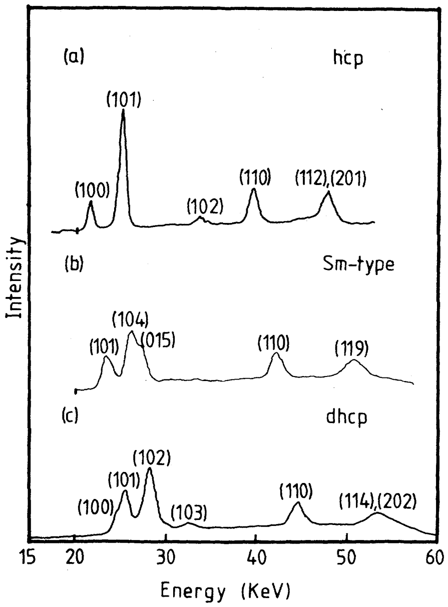

FIG. 1. Energy dispersive x-ray diffraction pattern of yttrium under various pressures (a) at 8.9 GPa with hcp indexing; (b) at 21.3 GPa with Sm-type indexing; and (c) at 33.7 GPa with double-hcp indexing.

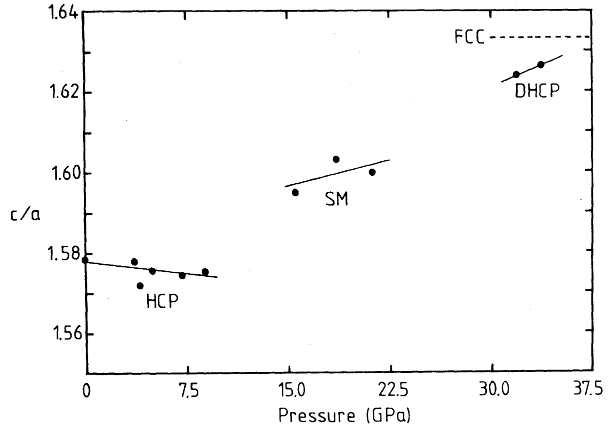

FIG. 2. The normalized c/a ratio for the three phases of Y. The c/a ratio for the Sm type has been scaled by $\frac{2}{9}$ and that of the double hcp by $\frac{1}{2}$. The ideal c/a ratio of 1.633 for the fcc phase is scaled by $\frac{2}{3}$ in the hexagonal representation.

shows the diffraction pattern of Y at 21.3 GPa in the Sm-type phase. At 25 GPa, new features in the diffraction pattern indicate another phase transition. The pure diffraction pattern of this phase at 33.7 GPa is shown in Fig. 1(c) with an indexing of diffraction lines corresponding to double-hcp structure.

All the diffraction patterns were affected by basal-plane texture as the c axis is preferentially oriented along the stress direction. A least-squares fit of the diffraction pattern, with use of correlated Gaussian lines with prefixed relative intensities and widths and adjustable a and c, results in the values of c/a which are presented in Fig. 2 for the pure one-phase pattern.

This preliminary evaluation of the data is in agreement with the similar variation of c/a with increasing N_d in the lanthanide sequence and lanthanide alloys at ambient conditions[14] as well as under pressure.[15] Figure 2 also shows an increasing tendency of c/a towards 1.633, the value of an ideal close packing. From this tendency, one can expect that Y may transform to the fcc structure at only moderately higher pressures even at room temperature.

The present study shows that the lanthanide crystal-structure sequence can be simulated by changing the number of d electrons in Y under pressure without any participation of f electrons. Therefore, only the structure anomalies of Ce,[16] Eu,[17] Yb,[18] and Pr[19] at moderately high pressures (below 30 GPa), as well as the anomalies in actinides,[20] must be related to the presence of f character at the Fermi surface. From this point of view, the other "regular" rare-earth elements can be considered just as transition metals with d-band occupancies between 1.5 and 2.7 (at least at moderately high pressures). It appears to be reasonable to discuss the structural stability of the regular rare-earth metals just as a function of $U_d{}^{\text{bond}}$ within a canonical band theory,[21] as has been done for the other transition metals.

Finally, it should be mentioned that no f-electron character is required for the stabilization of the Sm-type phase in lutetium under pressure in contrast to an earlier interpretation[22] of the structural data,[23] and similar experiments on Sc are expected to support this view.

One of us (Y. K. V.) is an Alexander von Humboldt Fellow.

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[a] Permanent address: Neutron Physics Division, Bhabha Atomic Research Center, Trombay, Bombay 400085, India.

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Surface-Enhanced Photoabsorption and Photoyield in Small Spheres

David R. Penn and R. W. Rendell
Electron Physics Group, National Bureau of Standards, Washington, D. C. 20234

(Received 12 June 1981)

Calculations of the photoabsorption and photoyield of small metal spheres are reported for photon energies below the plasmon energy. It is found that the excitation of electron-hole pairs due to the presence of the surface results in (1) enhancements in the photoabsorption rates and photoyields that are typically 10–10^2 and (2) similar enhancements in the threshold photoyields of small spheres relative to plane surfaces in agreement with recent experimental results.

PACS numbers: 78.20.Bh, 79.60.Cn

In recent years the spatial variation of the photon field at the metal surface has been identified as an important element in photoemission experiments.[1-5] This variation is associated with excitation of plasmons and electron-hole (*e-h*) pairs by *p* polarized incident light. Theoretical work has progressed from the inclusion of plasmons via an additional boundary condition[6] to the unified treatment of plasmons and *e-h* pairs with an infinite surface barrier[7-9] to use of a realistic surface potential.[10]

To date almost all calculations have been carried out for plane surfaces. However, small particles (e.g., 15–50-Å radii) are of interest in a number of contexts, particularly in atmospheric physics. Recent experiments by Schmidt-Ott, Schurtenberger, and Siegmann[11] (SSS) have served to focus attention on the very unusual optical properties of such particles. They find that the photoelectric yields at threshold of small particles of Ag, Au, MoO_3, and WO_3 are much larger (~ 10–10^2) than the yields from plane surfaces of the same materials. There has also been evidence that the surface-enhanced Raman effect, currently of great interest, is associated with surface roughness which in a very crude sense can be simulated by spherical particles at the metal surface. Thus the study of small particles may ultimately be relevant to that phenomenon.

In a classic work Mie[12] treated the transverse modes of the sphere. More recently a semiphenomenological paper by Ruppin[13] included the excitation of plasmons in the spirit of Melnyk and Harrison[6] for plane surfaces. The purpose of the present work is to include for the first time *e-h* pair excitations on an equal footing with plasmons and transverse modes. We find that the *e-h* pair excitations can dominate the absorption and photoelectric yield of a small sphere. An examination of the experimentally determined dielectric functions, $\epsilon_1(\omega)$, and the threshold energies of the materials observed by SSS shows that the enhanced photoyields cannot be due to the well-known peak in the optical absorption of a sphere predicted by Mie theory to be at the energy determined by $\epsilon_1(\omega)+2=0$. This is simply because the thresholds for these materials do not lie sufficiently near the "Mie peaks."

The probability per unit time for photoexcitation, P_E, is given by the Fermi golden rule. With the aid of Maxwell's equations it can be reexpressed as $P_E=\int d^3r\, P_E(\vec{r})$, where

$$P_E(\vec{r})=\mathrm{Re}\nabla\cdot[E(\vec{r})\times H(\vec{r})^*], \qquad (1)$$

where $\vec{E}$ and $\vec{H}$ are the total electric and magnetic fields in the solid. This establishes the connection between the quantum mechanical and classical electrodynamic formulations. The optical adsorption is $\alpha=P_E/I_0$, where I_0 is the incident flux. The photoelectric yield at threshold is