Novel Reentrant High Pressure Phase Transition in Lanthanum

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High presure x-ray diffraction experiments with synchrotron radiation in an extended pressure range up to 67 GPa reveal a novel phase transition of La: At about 60 GPa the low pressure fcc structure of La is recovered from the distorted fcc (*d*-fcc) phase. The reappearance of the high symmetry cubic structure at higher pressure implies that the *d*-fcc phase, which also appears in other lanthanides, is not a precursor of the low symmetry structures caused by the so-called f delocalization. A possible mechanism for the reentrant behavior is considered and the phase diagram of La is discussed.

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Under pressure the regular trivalent lanthanide elements show a well-known series of close packed structures [1]

$$\text{hcp}\rightarrow\text{Sm-type}\rightarrow\text{dhcp}\rightarrow\text{fcc}\,.$$

The same sequence is shown by these elements at ambient conditions with decreasing atomic number. According to band structure calculations [2–4], the structural stability of these lanthanide metals is controlled by the d occupation number which decreases with increasing atomic number and increases under pressure due to $s\rightarrow d$ transfer.

Systematic high pressure x-ray diffraction studies in wider pressure ranges [5–8] have revealed one more common structure for the regular lanthanides beyond the fcc phase for the elements La, Pr, Nd, Pm, Sm, Gd, Tb, and Dy. This additional structure has been designated as "distorted fcc" (*d*-fcc) because there are additional superstructure reflections in the fcc diffraction pattern. Though there are many proposals for the structure of the *d*-fcc phase [3,9–11], final agreement has not been obtained. A separate paper is devoted to this question [12].

At still higher pressures the early lanthanides following Ce become "irregular" and form structures of low symmetry [7]. The occurrence of these phases of low symmetry is attributed to the delocalization of $4f$ electrons [13]. However, La has no localized f electrons at ambient conditions. If La remains an *sd* band transition metal up to ultrahigh pressure [14], such structures should not appear in La at high pressure. This question has stimulated the present study.

Energy dispersive x-ray diffraction with synchrotron radiation at HASYLAB (DESY) was used to study the structural behavior of La under pressure up to 67 GPa. The experimental setup with diamond anvil cell and ruby manometer has been described previously [15]. The nonlinear pressure scale [16] was used for the ruby manometer and mineral oil was used as the pressure transmitting medium. The chemical analysis of the La material provided by Gschneidner is given elsewhere [7].

The two phase transitions of La at 2.5 GPa from dhcp to fcc and at 7 GPa to *d*-fcc are well known [6]. It was noticed also previously [6] that the intensity of the superstructure reflections of the *d*-fcc phase increase continuously with increasing pressure. At 26 GPa the superstructure reflections (101), (105), and (113) are well developed (Fig. 1). However, the present study shows that the intensity of these superstructure reflections decreases again at higher pressure (Figs. 1 and 2). At about 60 GPa all three superstructure reflections disappear and the diffraction pattern of the undistorted fcc structure is obtained again. This process is reversible; on lowering the pressure the *d*-fcc phase is recovered. Because this effect is reproducible (four preparations) and reversible and affects all the superstructure reflections, we conclude that this is not an effect of texture but that there is a reentrant fcc phase of La above 60 GPa.

The observed reentrant structural behavior is very exceptional for solid-solid phase transitions. To our knowl-

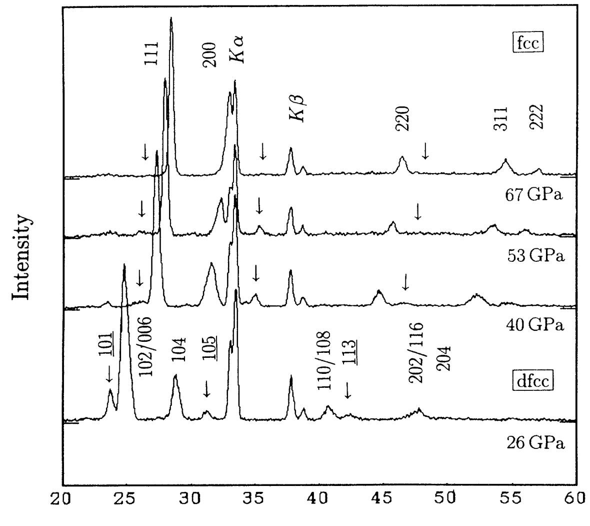

FIG. 1. Energy dispersive x-ray diffraction spectra of La under pressure. Arrows indicate the positions of the superstructure reflections. Hexagonal indexing according to [6]. $2\theta=10.3^\circ$ (10.7° at 26 GPa); $K\alpha$, $K\beta$: x-ray fluorescence of La.

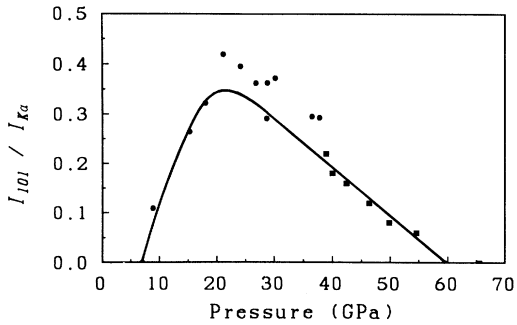

FIG. 2. The integrated intensity of the superstructure reflection (101) of *d*-fcc La scaled to the La $K\alpha$ fluorescence intensity. ●, data extracted from measurements by Grosshans [23]; ■, this work, with increasing and decreasing pressure.

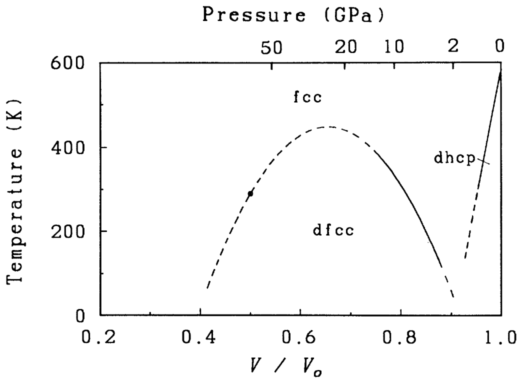

FIG. 3. Tentative phase diagram of La. Phase boundary dhcp-fcc (solid line) from [24]; phase boundary fcc–*d*-fcc (solid line) from [25] (resistance measurements) and [7] (x-ray diffraction); ●, this work.

edge there is only one single example for an element which may have a pressure-induced reentrant phase transition, namely, Pu [17,18]. However, in Pu as in other reentrant materials (Rochelle salt, for instance [19]), the structures involved are much more complex. Therefore, one may ask how such a simple structure as fcc may develop a reentrant behavior at all. For the other lanthanides the intermediate character of the *d*-fcc phase is most likely masked by the onset of the so-called *f* delocalization which leads to structures of low symmetry.

The reappearance of the high symmetry cubic structure at higher pressure in La implies that the *d*-fcc phase is *not* a precursor of the low symmetry structures. Hence, there should be no remarkable 4*f* contribution to the stability of the *d*-fcc structure of La and the other lanthanides. However, band structure calculations [20, 21] for the fcc La indicate that up to four Lifshitz singularities are passed when La is compressed to $V/V_0=0.5$. The structural instability of fcc La may be related to these singularities where the Fermi surface topology changes [6,22]. On increasing temperature the Fermi surface and the Lifshitz singularities become blurred and hence such structural distortions are expected to vanish at high temperatures. These considerations and the present data from Fig. 2 strongly support a phase diagram of La as given in Fig. 3 which takes into account the reentrant behavior. If this phase diagram is correct, the new fcc high pressure phase of La is the same as the well-known fcc phase at ambient conditions. The parabolic interpolation between the experimental data at low pressure (solid line in Fig. 3) and the reentrant transition at high pressure yield a maximum temperature of the *d*-fcc phase well below the melting point of La which should be around 1000 K in this pressure range. There are some interesting thermodynamical implications for this maximum point. The phase transition fcc→ *d*-fcc is believed to be of second order [6,7,25]. For second-order phase transitions there is no latent heat and no change of density at the phase transition and the slope of the phase boundary dp/dT is given by the Ehrenfest relations

$$\frac{dp}{dT}=\frac{\Delta C_p}{TV\Delta\alpha}=\frac{\Delta\alpha}{\Delta\kappa}\,.$$

Because dp/dT becomes infinite at the maximum temperature of the *d*-fcc phase, the difference of the thermal expansions $\Delta\alpha$ and the difference of the compressibilities $\Delta\kappa$ of the two phases must vanish at this point. This implies that it is hard to detect the phase transition in the vicinity of the maximum by volume measurements because even the differences of the derivatives of the volume should vanish. But the transition can be estimated by extrapolating to zero intensity of the superlattice reflections. High pressure high temperature experiments are planned to verify the proposed phase diagram. This very special phase diagram of La may also stimulate further theoretical studies on structural stabilities of the lanthanide elements.

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