Pressure-Induced Valence Change in Cerium Phosphide

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The pressure-volume relationship for cerium monophosphide (CeP) has been determined to 200-kbar pressure. In this range the substance maintains the NaCl-type structure and exhibits abnormal compression. From the data we conclude that there is an electronic transition involving a change in the valence state of Ce from 3^+ towards the 4^+ state near 100-kbar pressure. Qualitative observations of the reflectivity of CeP under pressure support the valence transition. CeP under high pressure may be expected to exhibit superconductivity.

It has been shown that a number of divalent rare-earth monochalcogenides, such as SmS and EuO, undergo a pressure-induced electronic transition.[1-3] In SmS a discontinuous change in the valence state of samarium from the 2^+ towards the 3^+ state occurs at about 6.5 kbar, and this valence transition is found to be isostructural (NaCl-type remaining NaCl-type). We report in this paper the discovery of an isostructural transition accompanied by a large volume change (~ 8%) at about 100 kbar, in the monopnictide CeP. This transition involves a change in the valence state of Ce from 3^+ towards the 4^+ state. Although valence states intermediate between 3^+ and 4^+ have been reported for Ce in some intermetallic compounds[4] (crystallizing in cubic Laves phases), this is the first time a clear-cut valence change under the influence of direct pressure, akin to that of metallic Ce, is being reported in a compound involving Ce. The observed transition pressure would rule out any possibility of a valence change at atmospheric pressure in either CeP or CeAs, as proposed in some studies[5-7] to explain certain anomalous features in the low-temperature behavior of these compounds. It is expected that CeP at high pressure should be a superconductor, by analogy to ZrN, ZrP, ThN, and ThP.

The monopnictides of rare earths, which are compounds with nitrogen, phosphorus, arsenic, antimony, and bismuth, crystallize in the NaCl type structure[8] and the rare-earth ion is normally in the trivalent state. In this series the compounds involving cerium are of particular interest, because the cerium ion may be expected to undergo a pressure-induced valence transition from the 3^+ towards the 4^+ state. In fact in CeN the Ce ion is near the quadrivalent state and exhibits an anomalously small lattice constant compared to the otherwise smoothly decreasing lattice-parameter variation in going from La to Lu nitride (see Fig. 1). However, in all the other monopnictides, the Ce ion is in the trivalent state. Also, in metallic cerium, a valence change has been observed in which the one $4f$ electron is delocalized and becomes a $5d$ electron, thus causing a change in the valence state of Ce from

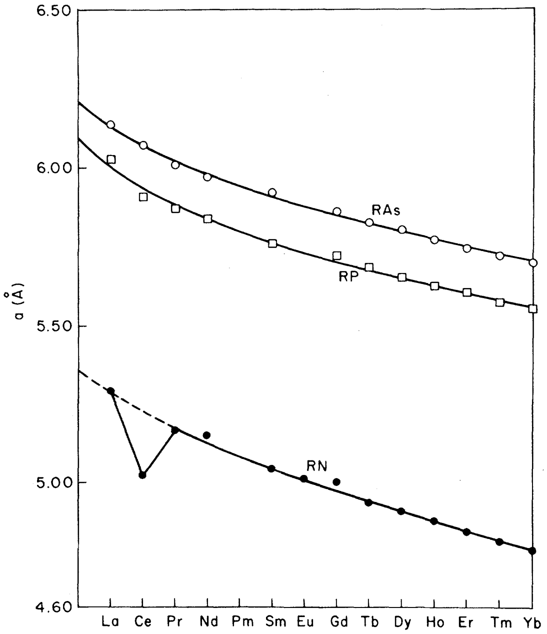

FIG. 1. Lattice parameter of the rare-earth monoarsenides, phosphides, and nitrides.

the 3^+ state towards the 4^+ state.[9] It was this possibility that primarily motivated our present study of CeP under pressure.[10]

When a valence transition occurs, the lattice parameter undergoes an anomalous decrease with pressure, due to the collapse in the size of the rare-earth ion. This can be strikingly seen in the compression curves of these substances[2] and hence high-pressure x-ray diffraction techniques have been used extensively to detect such transitions. We have therefore obtained the pressure-volume relationship of CeP to about 200 kbar. We see clear evidence for the valence transition near 100 kbar. These results will be presented and discussed in this paper.

Appropriate amounts of Ce filings (prepared in inert gas) and red phosphorus pieces (~ 20 mesh) were sealed in an argon-flushed evacuated quartz tube and reacted gradually at 500°C for 24 h, 700°C for 24 h, 700–950°C for 8 h. The tube was removed periodically and checked for free phosphorus. If found, the tube was shaken vigorously for mixing and particle breakdown and the reaction was continued. The reacted material was then compressed into a pellet, resealed in quartz as before, and refired at 1000°C for 2 to 3 days. The pellet was then wrapped in tungsten foil, placed in a tantalum crucible and fired at 1700°C for 8 h. The NaCl structure of the compound and the lattice constant appropriate for CeP ($a = 5.909$ Å) were verified by taking x-ray powder patterns of the material.[8] The pressure-volume relationship was determined using a diamond-anvil high-pressure x-ray-diffraction apparatus.[11] Silver was used as a pressure calibrant. The diffraction patterns of the substance plus that of silver were recorded on a film in the Debye-Scherrer geometry. A fine focus molybdenum tube was used to generate x rays and Mo $K\alpha$ radiation was used. To get a pattern with good intensity, an exposure of 50 h was required, with the x-ray tube operating at 45 kV and 20 mA. The lattice parameters of the substance as well as silver were measured and from this data the volume at pressure was computed. The pressure generated was computed from the volume of silver, using the Birch equation of state.[12] The pressure dependence of the volume of silver has been verified in previous studies against the pressure-volume relationship of sodium chloride,[13] which has been calculated using Dekker's theoretical equation of state.[14]

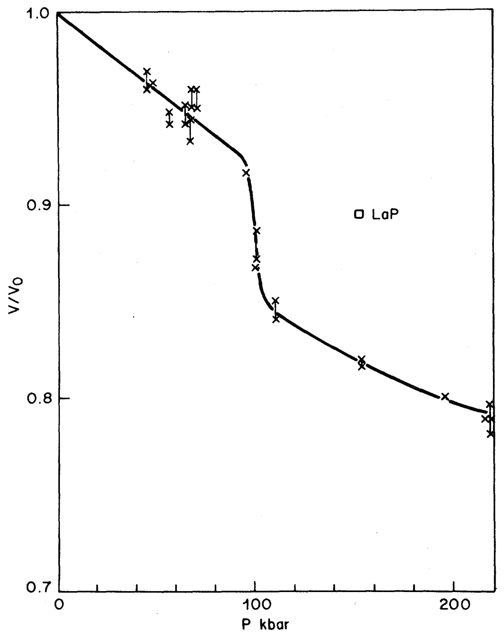

FIG. 2. Pressure-volume relationship for CeP. One V/V_0 determination for LaP is shown in the figure, for comparison.

The data are shown in Fig. 2 where the X axis is pressure in kilobars and the Y axis is the relative volume V/V_0 at pressure (V_0 is the volume at atmospheric pressure). The vertical bars connect V/V_0 data calculated from the averaged lattice parameter obtained from all the observed Debye-Scherrer lines in one case, and in another case obtained only from the (420) line of CeP. We believe these points define the error limits in the volume measurements. We estimate the error in pressure measurements to be of the order of ± 20 kbar in the pressure range above 100 kbar and about 10 kbar in the lower range. The data exhibit an abnormal region of compression around 100 kbar, the volume collapsing very rapidly within a very narrow pressure interval. No change in crystal structure is observable, the NaCl-type structure persisting up to 220 kbar, the limit of the present study. We attribute this abnormal compression without change of crystal structure to the collapse of the CeP lattice due to a change in the valence state of the Ce ion from the 3^+ state towards the 4^+ state. In Fig. 2 we also show the V/V_0 for LaP at about 150 kbar pressure, for comparison. The volume change of CeP above 100 kbar is anomalously large compared to both LaP and TbP, thus strengthening our conclusion regarding a valence change in CeP.

The abnormal compression that we have found in CeP is similar to that observed in the Sm monochalcogenides, where the valence state of Sm changes from the 2^+ state towards the 3^+ state. From the present data it is not possible to conclude with certainty whether the transition occurs discontinuously or continuously in CeP. However we believe it may be discontinuous. We have also seen some qualitative evidence for the electronic transition in the reflectivity change in a diamond-anvil x-ray camera. When pressure is applied, CeP powder appears to change from a silvery gray color to a purple color at high pressure, which we believe is related to $4f$-electron delocalization in cerium. Striking color changes have been observed at the valence transition in many divalent monochalcogenides.[15]

The fact that Ce in CeN is tending towards quadrivalency is very clear from the lattice parameter data in Fig. 1. Further, the valence transitions in the Sm monochalcogenides as well as EuO indicate that the pressure of transition decreases in going from telluride to sulfide to oxide (in EuO). A similar trend may be expected for the Ce monopnictides. In cerium nitride, cerium is already near the quadrivalent state.[16] In CeP moderate pressure is able to effect the valence change. If this trend continues in the series, the pressure of transition should increase in the sequence $\mathrm{CeP} < \mathrm{CeAs} < \mathrm{CeSb} < \mathrm{CeBi}$.

In some recent low-temperature studies at atmospheric pressure, anomalous features in the magnetic susceptibility,[5,6] thermal expansion,[7] and resistivity have been reported for CeAs, and in the magnetic susceptibility[5] of CeP. A small fractional change in the valence state of Ce from the 3^+ to the 4^+ state has been proposed to explain these anomalies. Myers and Narath[17] measured the NMR shift (Knight shift) of ^{31}P and ^{75}As in CeP and CeAs and found that the shifts did not track with the bulk susceptibility. Since the thermal-expansion behavior for CeAs is continuous in the region where the Knight shift is anomalous, they concluded that a valence change is not involved in these compounds at low temperatures. They suggested that a nonlinear change in the hyperfine couplings with temperature may account for the observed anomaly in the NMR shifts. Argument against valence change has been further strengthened in a recent NMR study under pressure in CeP and CeAs by Weaver and Schirber.[18] These authors find that their results do not support either the valence-change idea, or the nonlinear change in the hyperfine coupling as the cause of the anomalous NMR shifts. They have suggested that an electronic transition arising out of a sharp feature in the electron density of states may be responsible. The pressure of transition of 100 kbar observed in the present study very definitely suggests that the $4f$ electron is too strongly bound to Ce for any valence change to occur at atmospheric pressure at low temperature in the case of CeP. A valence change would be even more untenable in CeAs since much higher pressure would be needed to delocalize the $4f$ electron in the latter compound. Thus the present study strengthens the suggestion made in the NMR investigations.

The rare-earth monopnictides with the exception of perhaps Yb compounds are semimetallic.[16,19,20] In Ce monopnictides with the delocalization of one $4f$ electron from cerium, the metallic character should increase and the $4f$ level should rise above the Fermi level. When the $4f$ level is devoid of all electrons, there should be no local moment on cerium. This would then favor superconductivity and therefore we may expect CeP to be a superconductor at high pressure, by analogy to other tetravalent isostructural monopnictides (ZrN, ZrP, ThN, ThP).[21]

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Evidence for Macroscopic Vortex–Porous-Disk Interaction in Helium II†

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We describe measurements of the liquid-helium-flow behavior of Millipore (porous) disks. Our findings lead us to hypothesize a novel effect: Quantum vortices, "destroyed" when the superfluid passes through the porous material, deposit their angular momentum causing an observable, macroscopic torque on the disk. Many different aspects of our data are shown to be in excellent agreement with this model. We present measurements of the temperature and speed dependence of the vortex-induced torque.

We have been investigating the liquid-helium-flow behavior of Millipore[1] (porous) disks (originally in connection with the λ-point anomaly[2] and surrounding controversy[3,4]). In the course of this investigation[5] we have found an unexpected effect which we believe is caused by the interaction of quantum vortices with the porous disk. Although inadvertently encountered in connection with the anomaly, we emphasize that *the phenomenon discovered bears little or no relation to the anomaly.*[6] *In fact, the anomaly and associated equipment serve only as a base upon which this new effect is superposed.*[7]

In our work we have employed two different Millipore disk materials (500 Å and 5 μm pore size), each of 0.28 cm diameter. We have also explored two different situations of liquid-disk interaction: (1) stationary disk immersed in rotating helium, and (2) disk rotated—or swept around—through stationary helium. The disk was suspended (fiber constant 0.68 × 10^{-5} dyn cm/deg) at a fixed distance of 1.84 cm from the axis of a vertical 5.0-cm (i.d.) cylindrical container. The disk equilibrium angle was 45° to the flow direction for both cases and deflections from equilibrium were measured by a galvanometer-type optical setup (with a synchronized flash for the rotating-disk measurements) as described in previous work.[2,8,9] Both the temperature and speed dependence of the torque were studied; the current equipment does not permit varying the radial distance of the disk from the axis. In the case (1) the speed was fixed at 2 rpm.

To facilitate the discussion we utilize an arrow up (↑) or down (↓) to denote the vertical rotation vector *of either disk or chamber*, where ↑ or ↓ signifies counterclockwise or clockwise rotation respectively (when the apparatus is viewed from above). We point out that the same (classical) *relative rotation state* is achieved for the chamber rotating in a given sense or the disk in an opposite sense. Throughout the figures these sets of relative rotation states will be characterized by using a common curve symbol, either a solid or dashed line.

The contrast between the response of the disk for the cases where the liquid is rotating and where the disk is rotating is shown in Figs. 1(a) and 1(b) respectively (for the 500-Å disk), where disk angular deflection from equilibrium is plotted versus temperature. The vertical axis has been scaled so that unit deflection corresponds to the value expected for *ideal flow* (pure potential) about a solid disk of the same dimensions via the