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Role of the lattice in the two-step evolution of γ-cerium under pressure

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We report here highly accurate ultrasonic measurements on ultrapure polycrystalline cerium up to 1 GPa. By simultaneously fitting the complete measured data set, bulk and shear moduli have been deduced without any independent input. We observe a maximum in the pressure evolution of the bulk modulus and show that this peculiar behavior can be qualitatively interpreted by taking into account the pressure-induced effects on electron-electron interaction and the anharmonicity of bonding in the γ phase. The vibrational contribution to the total entropy change across the γ to α transition is estimated to be on the order of 15%, highlighting the need to consider the lattice dynamics for an accurate description of the phase transition.

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The understanding of how even small changes in temperature, pressure, or doping alter the correlations between electrons, which in turn tune several fundamental physical and chemical properties, provides a rich experimental and theoretical field. In particular, among the rare-earth metals, the unique properties of cerium have generated a long-standing and broad interest. One of the most intriguing phenomena is the instability of the single $4f^1$ electron along the isostructural (fcc) γ to α phase transition, and the effects that this has on the behavior of Ce. At ambient conditions, γ-Ce is magnetic with a localized moment. Upon compression, it transforms at 300 K and P_T=0.75 GPa to the α phase with loss of magnetic moment (Pauli paramagnetism) and a volume collapse of about 17%.[2] Upon release of pressure, the γ phase is totally recovered at ambient pressure. At higher temperature, the γ to α transition is suggested to end in a critical point at about T_c=600 K and P_c=2 GPa,[1–3] and the extrapolated line of the γ to α boundary seems to terminate at the minimum in the fusion curve. To date, two types of mechanism have been proposed to describe the electronic instability that drives this transition. The Mott transition model (within which the $4f$ electron is considered localized and not binding in the γ phase, and itinerant and binding in the α phase) was first put forward but, the Kondo-Volume-Collapse (KVC), where the *spd-f* hybridization is the dominant effect, has also been suggested. Despite the important number of experimental[4] and theoretical[5–10] studies, the discussion on the validity of these two different pictures remains open.

Only recently, a few studies have started to explicitly point out the need of carefully considering the lattice contribution to fully understand the driving mechanism of the γ to α transition.[3,11–13] In fact, while the key role played by entropy on the physics of the γ to α phase transition is by now quite well-established (see for instance Ref. 10 and 14), the relative importance of spin and lattice contribution is still under debate, with studies suggesting that vibrational entropy changes across the transition can account for about half of the total entropy change[12] and others suggesting that the lattice contribution is negligible.[3,11,15] Still, from an experimental point of view, the lattice properties of Ce have been neglected compared to the electronic responses, and only few experimental studies[3,12,16] explicitly address the differences in lattice and vibrational properties of γ- and α-Ce. Early ultrasonic investigations[16] report a large softening of the longitudinal sound velocity from ambient pressure up to the γ to α transition, while, above the transition, the α phase presents a more classical behavior. Unfortunately, in this study,[16] no data were collected across the phase change itself. Furthermore, the low-purity sample used in this study (98.5%) has led to questions as the role of impurities. Indeed, depending on the amount and type of impurities, samples have shown the transition at different pressures or have shown no transition at all.[17] Furthermore, the extraction of sound velocities and bulk and shear moduli from the travel time measurements is not straightforward, especially in the cases like Ce, where an obvious mechanical instability occurs under pressure. Accordingly, their conclusions might have been affected by mixing results of studies carried out under different hydrostatic conditions and on samples with of different quality. Thus, in this Brief Report, we present results from an ultrasonic study of elasticity of both γ and α phases of Ce. We observe a maximum in the bulk modulus at 0.1 GPa, which is explained through a simple model of the phase transition once both electron-electron interaction and the anharmonicity of bonding in the γ phase are taken into account. Furthermore, we derived the vibrational entropy change across the transition, which, although smaller than the spin contribution, cannot be neglected.

The cerium ingot (99.99%, Johnson Matthey Co., Ltd.) used in this work has been scraped with a diamond file in a glove box under stream of dry nitrogen to remove all surface oxides. Then, a Ce rod (4-mm diameter and 15-mm length) was produced by melting in a home-made crucible using a triarc furnace under high-purity argon atmosphere, the sample being finally kept in a quartz tube sealed under secondary dynamic vacuum.

With the aim of confirming and extending the previous work, we closely tracked both the longitudinal and shear velocities across the phase transformation. We probed the γ phase approaching the transition, as well as the recovered phase when downloading the pressure, and extracted all elastic data (sound velocity, moduli, and attenuation) using a recently developed self-consistent numerical method.[18]

The complete set of experiments has been carried out using several cylinders cut from the same initial ultra pure Ce rod. Samples were prepared with plane parallel surfaces, optically polished and flat to 1 μm. The parallelism was better than 1°. All sample preparation works have been carried out under nitrogen atmosphere in order to avoid any oxidation of the sample. The final material was then kept in ultrapure penthane oil and loaded like this into the experimental volume.

A classical piston-cylinder apparatus was used to generate a hydrostatic pressure up to 1 GPa in the chamber where the sample holder is completely immersed in the pressure transmitting medium (pure penthane remains fluid up to 1.2 GPa). The pressure was measured using a manganin gauge. The estimated uncertainty on pressure was about 0.02 GPa. The ultrasonic system was a pulser receiver sending a signal of adjustable frequency (fixed at 5 MHz in this work) to a 4-mm diameter copper electrode in contact with the surface of the transducer to provide the excitation field. The same transducer was used for both sending and receiving the ultrasonic pulses. Further details of the high-pressure setup can be found in Ref. 18.

We employed the classical pulse-echo overlap method using a signal cross-correlation section between two consecutive echoes in order to measure the travel time t. To determine the sound velocities $v(P)$, the elastic moduli $\rho v_L^2(P)$, $\rho v_T^2(P)$ (where ρ is the sample density), and the bulk modulus B with the maximum precision and reliability, the longitudinal (transverse) travel times have been measured over three (2) different experiments. The whole set of experimental data has been fitted to the dynamical equations $v=2d/t$ (where d is the sample length) and $B=\rho(v_L^2-4/3v_T^2)$ for every pressure using a reverse Monte Carlo method. The basic idea can be described as the following. Assuming that length and density are known at a given pressure P, all velocities and elastic moduli can be directly deduced from the ultrasonic measurements. Using these P values, and the travel times measured at a pressure $P+\Delta P$, the length and the density of the sample at $P+\Delta P$ can be computed. These values are then used to deduce a first approximation of the elastic moduli at the new pressure $P+\Delta P$. The values of the latter are then used as starting points in an iterative process, until convergence is reached. Since the variation in the sound velocity is mainly due to that of the elastic moduli, its dependence on length and density being only second order, this process is robust. Accordingly, the elastic moduli $\rho v_L^2(P)$ and $\rho v_T^2(P)$ and hence the bulk modulus B have been obtained from the only travel time measurements under pressure, without any further independent input, (except for the well-known volume reduction of 17% across the phase transition). In contrary to what is usually done, the use of an equation of state previously determined to extract the pressure-induced length and density variation is not required in this method. Results for the pressure dependence of longitudinal and shear moduli are given in Figs. 1 and 2, respectively.

We observe a significant softening of the longitudinal modulus up to the γ- to α transition pressure (0.75 GPa), whereas the shear mode increases almost linearly with $d\rho V_T^2/dP=1.17$. The transition is reversible, with a complete recovery of the γ phase at 0.56 GPa. Moreover, the present work clearly points out that the pressure derivative of the longitudinal mode is not negative at ambient pressure (inset of Fig. 1). The same behavior is also observed in the pressure dependence of the bulk modulus $B(P)$ (Fig. 3).

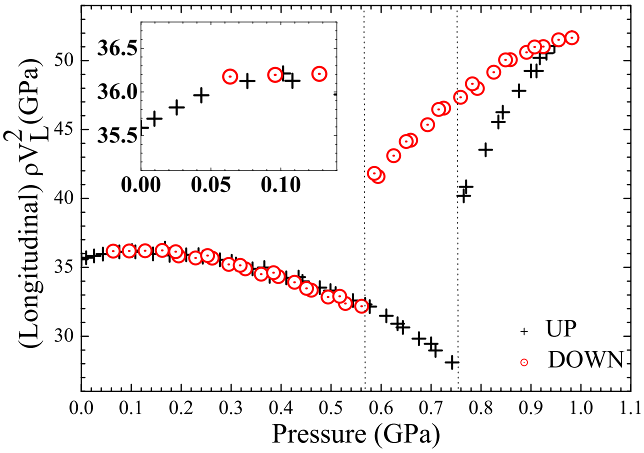

FIG. 1. (Color online) Pressure dependence of longitudinal modulus ρv_L^2 in polycrystalline Ce. The uncertainties in pressure and modulus are within the symbol size. Inset: zoom of the low-pressure region, where the longitudinal modulus reaches a maximum.

An accurate description of the evolution with pressure of the bulk modulus, in particular approaching the phase transition, is of great interest as this provides crucial information on the coupling between electronic and lattice degrees of freedom. Neutron and x-ray diffraction results at high pressure and 300 K have shown that the softening of the bulk modulus follows a power-law with an exponent around 0.5, as expected for Gaussian fluctuations.[12] This strongly suggests that electron-phonon coupling is at the origin of the instability of the γ phase under pressure. In our case, the pressure-induced vanishing of B may be fitted to a power-law $(P-P_C)^\alpha$ between 0.45 and 0.75 GPa, with P_C=0.92 and

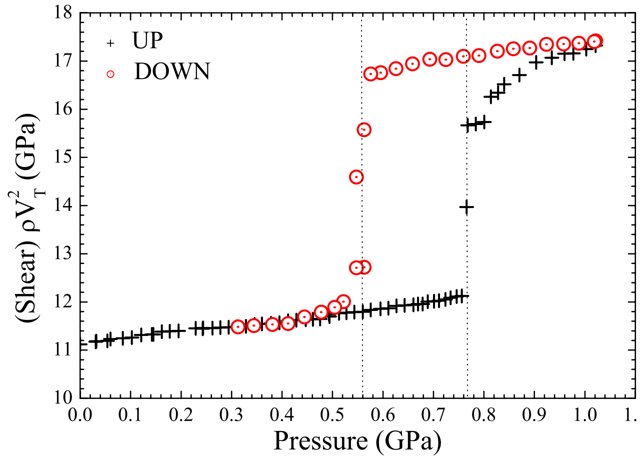

FIG. 2. (Color online) Pressure dependence of shear modulus ρv_T^2 in polycrystalline Ce. The uncertainties in pressure and modulus are within the symbol size.

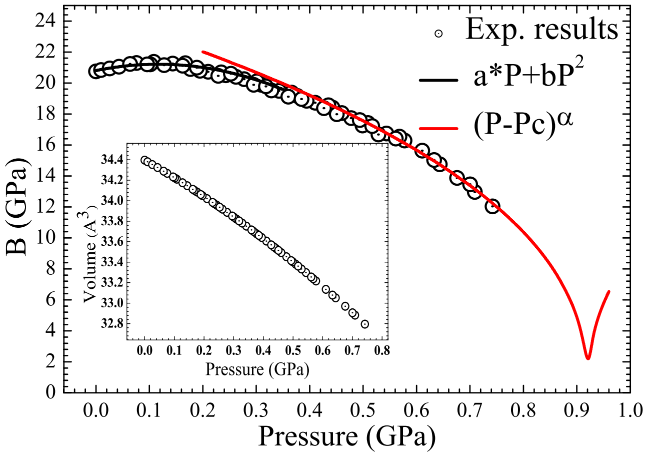

FIG. 3. (Color online) Pressure dependence of the bulk modulus B in polycrystalline Ce. Inset: equation of state $V(p)$ of Ce at 300 K deduced from the $B(p)$ ultrasonics data.

$\alpha = 0.42$, in good agreement with Ref. 12. Below this range of pressure, the softening of B does not match any power law but can rather be fitted using a simple second-order polynomial fit with a maximum of B at a pressure of 0.10 ± 0.01 GPa.

This peculiar evolution of the bulk modulus can be understood using a Murnaghan equation of state and a model taking into account the hybridization effect on the electron interaction.[14,19,20] In the framework of Ref. 19, the total free energy $F(V)$ is written as a sum of the energy of the noninteracting system $F_0(V)$—taken as parabolic—and a stabilization free energy ΔF [see Eq. (5) of Ref. 19]. In this formulation, at high volume (low pressure), the system exhibits a normal behavior. Then, as the pressure increases, the contribution of ΔF to the bulk modulus is negative, so the bulk modulus decreases. This behavior—corresponding to Eq. (6) of Ref. 19—is shown on Fig. 4 and is derived from the free energy shown in the inset. Note that the existence of two inflection points in the free energy requires that $B(V)$ has two nodes. A more recent calculation solves explicitly the interaction of the electrons within dynamical mean-field theory[21] and a similar behavior is obtained for the sound velocity.

Here, we simply generalize the model of Ref. 19 by using a Murnaghan equation of state for $F_0(V)$. Nonharmonic effects in $F_0(V)$—which can be expressed through $B' = \frac{\partial B}{\partial P}$—are in principle non negligible, especially in the range of volume covered by the transition. A value of $B' = 3$ is given by the LDA+U method (see Ref. 22 for computational details), which is sufficient to describe the high volume phase of cerium.[22,23] However, as the parameters given by LDA+U are only qualitatively correct, this is only an indication that B' has to be taken into account. Using, for example, $B' = 0.5$, we obtain an increase in the bulk modulus derived considering only $F_0(V)$, as reported in Fig. 4 (dotted red line). As a consequence, when the full free energy is used, including both $F_0(V)$ and ΔF, we obtain a maximum in the bulk modulus. The physical interpretation is straightforward: when cerium is compressed, it first feels the anharmonic effects—due to the repulsion of filled electronic shells—and then the stabilization plays its role.

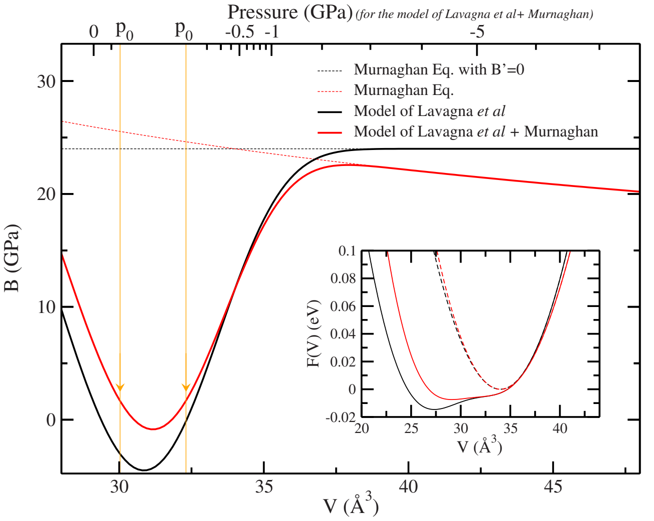

FIG. 4. (Color online) Bulk modulus $B = -V\frac{\partial^2 E}{\partial V^2}$ as a function of volume from the model of Ref. 19 with a Murnaghan equation of state for $F_0(V)$. The thermodynamical ideal transition pressure, computed with the double tangent construction on the free energy, is shown on the pressure axis by vertical lines. The corresponding volumes are indicated by arrows: the area of transition is between these two volumes. Inset: corresponding free energies as a function of volume.

Finally, from our measured sound velocities, we can estimate the Debye temperature for the two phases just above and below the transition (respectively, $\theta_D^\gamma = 132.8$ K and $\theta_D^\alpha = 142.9$ K) and hence[12,24,25] the vibrational entropy change per atom $\Delta S_{\mathrm{vib}}^{\gamma-\alpha} = 3k_B ln(\theta_D^\alpha / \theta_D^\gamma)$. We obtain $0.22k_B$, in reasonably good agreement with previous ultrasound measurements[16] ($0.32k_B$), and in excellent agreement with a recent theoretical work[13] ($0.22k_B$), but our result is significantly lower than $0.75k_B$, a value obtained from neutron and x-ray diffraction studies.[12] Irrespective of this discrepancy, possibly due to the uncertainties associated to the estimation of the vibrational entropy from thermal displacement, our results definitively confirm that the lattice contribution to the total entropy change across the transition, $\Delta S_{\mathrm{tot}}^{\gamma-\alpha} = 1.5k_B$, although smaller than the spin contribution, cannot be neglected. This conclusion cast doubts on the model fit used to interpret recent x-ray diffraction measurements[3] on Ce. Moreover, our pure Ce results differ to what has been proposed[15] for $Ce_{0.9}Th_{0.1}$ which demonstrates that although the same isostructural γ to α transition occurs in both systems, a small change in the doping leads to a significant vibrational entropy difference.

In conclusion, we performed high-pressure ultrasonic pulse-echo measurements on high-purity polycrystalline cerium across the isostructural (fcc) γ to α phase transition. The travel time and the acoustic velocities have been determined as a function of pressure at ambient temperature, and the hysteresis cycles has been quantified along the transition line through measurements in increasing and decreasing sweeps. Special effort was made to eliminate the errors traditionally associated with pulse-echo overlap measurements. In particular, the treatment of the signal of the echoes as well as the travel times analysis have been performed with great care, enabling a highly accurate determination of the moduli as a function of the pressure without any input from independent literature equation of state. Our results clearly provide experimental insight into the high-pressure properties of γ-Ce and the vanishing of the longitudinal elastic modulus (and consequently of the bulk modulus) along the γ to α boundary at 300 K. We report a maximum in the pressure evolution of the bulk modulus and show that this peculiar behavior can be interpreted according to a simple model, taking into account the effect of electronic hybridization on the electron-electron interaction and using a Murnaghan equation of state. Such observation clearly indicates that below 0.1 GPa γ-cerium behaves as commonly expected, and is not yet mechanically on the verge of the transition. Accordingly, investigation of cerium properties at ambient conditions have limited value for the understanding of the γ to α transition. Moreover, the present work proposes a straightforward way to accurately determine the relative importance of spin and lattice contribution to the entropy change across the transition, suggesting $\Delta S_{\mathrm{vib}}^{\gamma-\alpha}/\Delta S_{\mathrm{tot}}^{\gamma-\alpha} \sim 15\%$. Finally, it is important to stress that this study has been performed at ambient temperature and hence well below the critical end point of the γ to α transition, where the purely electronic transition concept expects the bulk modulus to vanish according to the mean-field law. A very interesting question thus concerns the behavior of the Ce longitudinal sound velocity near the thermodynamic conditions of the critical point.

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