Lowering of the spatial symmetry at the $\gamma \rightarrow \alpha$ phase transition in cerium

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Using time-differential perturbed angular correlation spectroscopy we have measured the electric field gradient (EFG) at ^{111}Cd probe nuclei in solid Ce in a pressure range up to 8 GPa. Covering various allotropic phases of Ce, we find that the value of the EFG in the cubic α phase is almost four times larger than in the cubic γ phase and close to values in the noncubic phases α' and α''. These results together with the differences in time modulation of the spectra are interpreted as evidence for quadrupolar electronic charge-density ordering and symmetry lowering at the $\gamma \rightarrow \alpha$ transition while the lattice remains face-centered cubic.

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Solids built up from lanthanides [rare earths (REs)] and their compounds exhibit a broad range of unusual electronic, magnetic, and structural properties. These properties, known as valence fluctuations and heavy-fermion phenomena, are due to the partly occupied inner $4f$-electron shells of the lanthanide atoms. Hybridization of the localized $4f$ states with the conduction electrons leads to strong correlation effects[1] (charge and spin fluctuations). Among the lanthanides Ce with a single $4f$ electron offers the simplest initial situation but still displays many unusual properties.[2] Most intriguing is the transformation under pressure[3] between two face-centered-cubic (fcc) phases called γ-Ce and α-Ce. While γ-Ce is stable at room temperature (T) and ambient pressure (P), it transforms to α-Ce at P of 0.8 GPa. This so-called isostructural phase transition $\gamma \rightarrow \alpha$ is accompanied by a 16% volume collapse.[2] The magnetic susceptibility follows a Curie-Weiss law in the γ phase and is quasi-T independent in the α phase.[4] At high P (5 GPa) α-Ce transforms to monoclinic α''-Ce (structure $C2/m$) and at even higher P (7.5 GPa) to orthorhombic α'-Ce (α-U structure).[5] The isostructural nature of the $\gamma \rightarrow \alpha$ transformation is apparently at variance with the Landau[6] theory of phase transitions which would require a change in space-group symmetry. Since the establishing of the fcc structure for both phases,[7] various microscopic theoretical scenarios have been proposed. Two theoretical models are well represented in the literature. A Mott-transition scenario propagates the concept of a localized nonbonding state of the $4f$ electron in γ-Ce and an extended and itinerant bonding state in the α phase.[8] The driving mechanism is the lowering of the cohesive energy due to charge fluctuations. Spin fluctuations are the driving force in the Kondo volume collapse (KVC) model of the $\gamma \rightarrow \alpha$ transition.[9,10] The model is based on the spin-1/2 Kondo problem and its relation to the Anderson Hamiltonian.[1] The volume dependence of the Kondo temperature T_K is used to obtain the equation of state, the P-V phase diagram and a critical point similar to the liquid-gas phase transition. Qualitatively, the model is supported by modern dynamical mean-field theory calculations.[11] Despite much effort, both models are debated and there is no consensus.[12] A common feature is the absence of any symmetry breaking at the transition as would be required by the Landau theory.[6] On the basis of thermodynamic data it was suggested[13] that the $\gamma \rightarrow \alpha$ transformation is a first-order phase transition which becomes of second order beyond a tricritical point. Therefore α-Ce should have a distorted lattice with lower symmetry than γ-Ce. However a distorted lattice has been discarded by x-ray diffraction experiments.[14,15] Nonetheless considerable anomalies in the lattice degrees of freedom are present at the $\gamma \rightarrow \alpha$ phase transition. Early ultrasound measurements[16] show a pronounced decrease in the longitudinal sound velocity. Recent neutron and x-ray diffraction experiments under pressure[14] clearly demonstrate the importance of lattice vibrations. In particular, a softening of the bulk modulus B_T (equivalently of the elastic constant c_{11}) is found with increasing pressure in the γ phase. Angle-dispersive x-ray diffraction results[15] exhibit a minimum of B_T along the $\gamma \rightarrow \alpha$ phase boundary line. These results have been used[14,15] to suggest an extension of the KVC model. We show below that they are consistent with the coupling between electronic and lattice degrees of freedom inherent in the quadrupolar electronic charge model on a compressible fcc lattice.

A mechanism of symmetry lowering without lattice distortion (positions of the Ce nuclei still fcc) has been suggested by a scenario of quadrupolar electronic charge-density ordering on a compressible cubic lattice.[17,18] The occurrence of long-range order in α-Ce is due to the orientation of the local $Y_{l=2}^{m=0}$ quadrupolar charge-density components of the valence electrons ($4f+5d6s^2$) of Ce on four cubic sublattices. The space-group symmetry lowering at the transition from the orientationally disordered γ phase to the ordered α phase is $Fm\bar{3}m \rightarrow Pa\bar{3}$, the local site symmetry is C_3 (Fig. 1). It is accompanied by a uniform lattice contraction so that the fcc structure is conserved. Although this latter aspect is "isostructural," the symmetry lowering of the electronic structure is fully consistent with the Landau theory.[6] In reciprocal

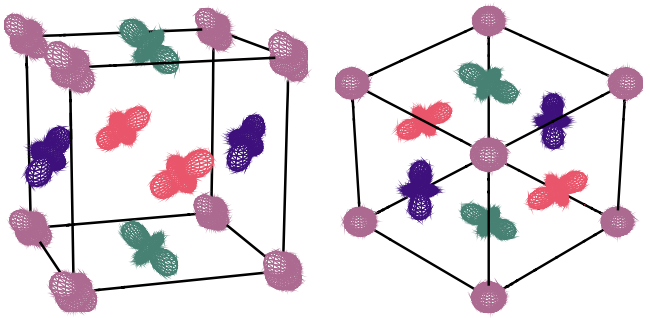

FIG. 1. (Color online) Triple-$\vec{q}$ antiferroquadrupolar ($Pa\bar{3}$) structure of α-Ce proposed by Nikolaev and Michel (Ref. 17). Quadrupoles represent the $l=2$ valence electron ($4f+5d6s^2$) charge-density distribution. Right panel is the view along the [111] cube diagonal demonstrating the trigonal site symmetry (C_3).

space the active electronic mode condenses at the X point of the Brillouin zone and involves the three arms $\vec{q}_X^x$, $\vec{q}_X^y$, $\vec{q}_X^z$ of the star of the wave vector $\vec{q}_X$. One speaks of a triple-$\vec{q}$-antiferroquadrupolar structure ($3\vec{q}$-AFQ). The transition $Fm\bar{3}m \rightarrow Pa\bar{3}$ is not uncommon in molecular crystals. It occurs in o-H_2,[19] in C_{60} fullerite,[20] in α-N_2,[21] etc. A hidden $Pn\bar{3}m$ symmetry change was found experimentally in NpO_2.[22] The $Pn\bar{3}m$ space group represents another triple $\vec{q}$ structure which differs from $Pa\bar{3}$ in the way the threefold axes and electronic quadrupoles are distributed over four sublattices.[23] The problem of measuring the $Pa\bar{3}$ structure directly in Ce is complicated by the fact that the Ce nuclei remain on an fcc lattice. Although the quadrupolar charge-density ordering could be detected by synchrotron radiation, there remain in practice many technical problems which so far have obstructed the experiment.

Here we report on experimental evidence for quadrupolar electronic densities in the α phase of Ce and their absence in the γ phase by using a method of nuclear spectroscopy. Through the electric quadrupole hyperfine interaction (QHI) the electric field gradient (EFG) V_{ij} at a lattice site is directly experienced by a probe nucleus. One determines the nuclear quadrupole frequency (QF) $\nu_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. Here Q is the nuclear quadrupole moment and $0 \leq \eta \leq 1$.[24] QHI in solids is often exploited by nuclear quadrupole resonance and Mössbauer spectroscopy. We use the less common method of time-differential perturbed angular correlations (TDPACs) (Ref. 24) with the ^{111}In/^{111}Cd probe nuclei introduced into the cerium lattice.[25,26] As an advantage measurements can be performed with few impurities and at higher T. In the best cases the accuracy approaches that of nuclear quadrupole resonance.

The method exploits an anisotropic intensity distribution of γ rays emitted from an ensemble of the excited nuclear states of probe ^{111}Cd atoms (171–245 keV cascade). The cascade proceeds via the 245 keV level with the half life $T_{1/2}=84$ ns, nuclear spin $I=5/2$, and the nuclear quadrupole moment $Q=0.83$ b. The precession of nuclear spins in a static electric crystal field changes the alignment of the ensemble with time, which is observed by measuring the γ-ray anisotropy [see Eq. (2) below]. The initial alignment is prepared by populating the excited states with the electron capture decay of the 2.8 d ^{111}In isotope. The ^{111}In activity was produced via the ^{109}Ag$(\alpha,2n)^{111}$In reaction by irradiating a silver foil with the 32 MeV α beam. After that the nuclear ^{111}In/^{111}Cd probes were introduced into the cerium lattice by melting cerium powder (about 500 mg of 99.99% Ce) with a small piece of the irradiated silver foil ($\leq$0.1 mg) in a special chamber under P of 8 GPa.[25] The TDPAC measurements were performed on polycrystalline samples of cerium metal at room T using a four-detector spectrometer equipped with a small size hydraulic four arm press with a capacity up to 300 ton.[27] The high P up to 8 GPa was produced in a calibrated "toroid"-type device with NaCl as P-transmitting medium, Ref. 26. Nonhydrostaticity of the transmitting medium was checked by measuring the ^{111}Cd-TDPAC spectra of silver (fcc) under high P and observed to be negligibly small.

The angular time correlation is given[24] by

$$G_{22}(t;\nu_Q,\eta,\Lambda) = s_{20} + \sum_{n=1}^{3} s_{2n} \cos(\omega_n t) e^{-\Lambda_n \omega_n t}. \qquad (1)$$

Here t is the time delay, s_{2n} are the amplitude coefficients, and ω_n are the angular precession frequencies ($n=1,2,3$ for $I=5/2$) related to the energy differences between levels split by the QHI. The frequencies are functions of ν_Q, i.e., of the EFG V_{zz} and of the asymmetry parameter η. Λ (or σ) is the half width of the QF Lorentzian (Gaussian) distribution accounting for oscillatory damping.

Recording the delayed coincidence spectra at angles $\pi/2$ and π between detectors, $N(\pi/2,t)$ and $N(\pi,t)$, one obtains the usual angular anisotropy

$$R(t) = 2\frac{N(\pi,t) - N(\pi/2,t)}{N(\pi,t) + 2N(\pi/2,t)}, \qquad (2)$$

which is the TDPAC spectrum. The P evolution of the TDPAC spectrum of ^{111}Cd in Ce is given in Fig. 2. Experiments have been carried out at room T and covered four phases of elemental cerium: γ, α, α'', and α'. It can be shown[24] that $R(t) = -A_{22}Q_2G_{22}(t)$, where $G_{22}(t)$ is the perturbation factor, Eq. (1), $Q_2 \approx 0.80$ is the solid-angle correction, and $A_{22} = -0.17$ is the unperturbed angular correlation coefficient for the γ-γ cascade of ^{111}Cd. The EFG parameters are determined from a least-square fitting of the TDPAC spectra in accordance with Eq. (1).

Extensive TDPAC data are presently available for the ^{111}Cd impurity, for which the EFG as a function of T and P has been determined in several RE metals.[28,29] The majority of RE metals crystallizes in hexagonal structures implying a nonzero EFG. In particular, the hexagonal β phase of cerium has been thoroughly investigated by Forker *et al.*[30]

In the cubic symmetry the EFG tensor vanishes. Therefore one expects $\nu_Q = 0$ if both γ and α-Ce are assumed to have the same cubic site symmetry. Instead there are marked differences in the value of ν_Q and in the time modulation of the TDPAC spectra of γ and α-Ce (Fig. 2). At ambient P and T corresponding to γ-Ce the fitting gives $\nu_Q = 3.0(5)$ MHz ($\eta = 0$). At high pressure we find $\nu_Q = 11(1)$ MHz. The TDPAC spectrum of γ-Ce [Fig. 2(A)] is very close to the one of Ref.

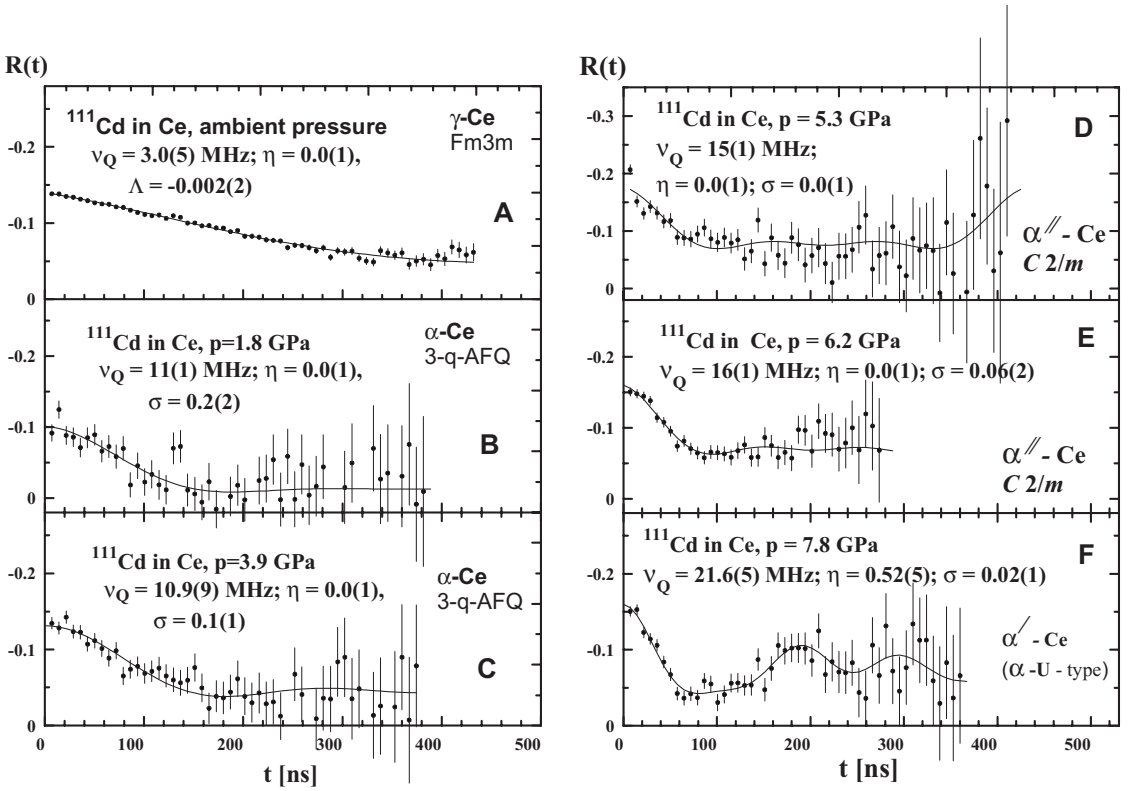

FIG. 2. Room-temperature TDPAC spectra of ^{111}Cd in cerium under pressure. In pressure experiments the spectra contain a nonzero background component, which appears because of the scattering within a thin disk of Ce (Ref. 31) and pressure-transmitting media (Ref. 26). The value of the background depends on specific activity of ^{111}Cd probes during measurements.

30 with the same value of ν_Q. We attribute the nonzero EFG (instead of the ideal $\nu_Q=0$) to static random strain fields[32] which are generated by the substitutional Cd^{2+} ions (volume difference with Ce^{3+} 12%). Due to the elastic anisotropy of the crystal the strain fields couple to the electronic quadrupoles and cause local orientational freezing. Such EFG are found in all cubic metals. In addition, in γ-Ce there can be some small area of frozen quadrupoles because our samples were prepared under high P and T. Some spectra are measured for $t<T$, where T is the period of oscillations. However, the results were observed on various samples and were stable and reproducible, and from our experience we are confident that the fitted parameters are correct.

From the structural data we know that the TDPAC spectra at pressures 1.8, 3.1, 3.9, and 4.4 GPa should be identified as belonging to the α phase, Figs. 2(B) and 2(C). They are consistent and from fitting we obtain for $P=1.8$ GPa $\nu_Q=11(1)$ MHz [$V_{zz}=0.54(4)\times10^{21}$ V m^{-2}] and a uniaxial local site symmetry ($\eta=0$). Furthermore, the values of ν_Q and V_{zz} are close to the TDPAC parameters for β-Ce [$\nu_Q=12.5(7)$ MHz and $V_{zz}=0.61(4)\times10^{21}$ V m^{-2} (Ref. 30)], and other noncubic phases of cerium, Fig. 3. The observed values of QF and EFG for α-Ce unambiguously rule out the cubic symmetry and indicate a hidden quadrupolar order in this phase as predicted by the quadrupolar electronic charge-density model.[17]

The ^{111}Cd TDPAC spectra at pressures 5–8 GPa are shown in Figs. 2(D)–2(F). They show two changes characteristic of two other phase transformations. An increase in the quadrupole frequency at 5.3 GPa without the change in the asymmetry parameter ($\eta=0$) is induced by the modification of the Ce crystal structure from the simple cubic symmetry (α-Ce) to the monoclinic α'' phase. From Figs. 2 and 3 one sees that the monoclinic $C2/m$ structure is preserved up to 7.5 GPa. The spectrum at 7.8 GPa refers to the orthorhombic (α-U) structure.[5] The assignment is corroborated by a large value of $\eta=0.52$, typical for the α-U symmetry. (For elemental uranium in the α phase $\eta=1$.[33])

Figure 3 presents the overall pressure dependence of QF

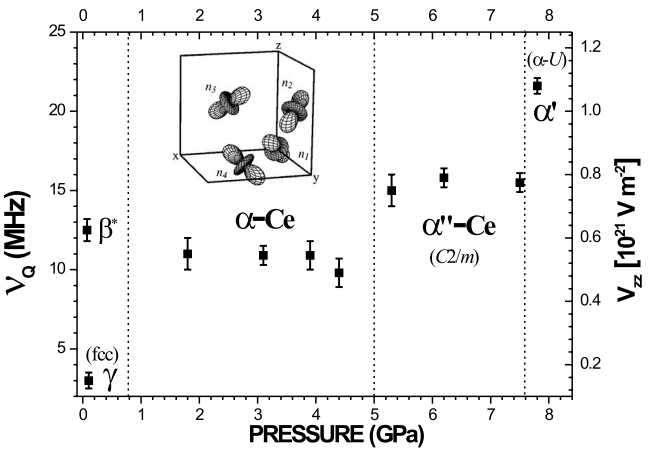

FIG. 3. Pressure dependence of EFG (V_{zz}, right scale) and the nuclear QI frequency (ν_Q, left scale) of ^{111}Cd in cerium lattice sites. * data for β-Ce are from Forker *et al.*, Ref. 30.

and EFG in Ce. At the phase transition boundaries QF and EFG change discontinuously indicating the first-order character of the transitions. Earlier, the stepwise behavior of QF with changes in the crystal structure was observed for a number of rare earths.[28,29]

In conclusion, our TDPAC experiments (Fig. 3) detect an appreciable EFG in α-Ce comparable with EFG for noncubic phases (β, α''), which border α-Ce in the P-T phase diagram. This finding rules out the $Fm\bar{3}m$ symmetry in α-Ce and evidences in support of a $3\vec{q}$-AFQ order suggested by Nikolaev and Michel.[17] With further pressure increase, the evolution of the TDPAC spectrum follows other phase transitions in cerium: $\alpha \rightarrow \alpha''(C2/m)$ and $\alpha'' \rightarrow \alpha'$ (α-U structure).

We close with two comments on the relations of the quadrupolar electronic order model with other degrees of freedom, a first one on lattice dynamics and a second one on magnetism. The fcc lattice contraction accompanying the AFQ ordering at the $\gamma \rightarrow \alpha$ transition is driven by the coupling of pairs of quadrupolar order parameter components $\vec{\rho}$ with opposite wave vector at the zone boundary to the longitudinal lattice displacements $\vec{u}$ at the zone center.[17] This coupling accounts for the linear increase in the transition temperature with pressure.[17] It is the quadrupolar analog of the compressible Ising model[34] and leads to a softening of the elastic constant c_{11} (Refs. 14–16) at the γ-α transition. For magnetic effects the quadrupolar model is not necessarily in contradiction with the Kondo effect, which may be responsible for the quenching of the magnetic moments in α-Ce. Further investigations are needed.

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