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Studies of the pressure dependence of the charge density distribution in cerium phosphide by the maximum-entropy method

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Abstract

The physical properties relating to 4f electrons in cerium phosphide, especially the temperature dependence and the isomorphous transition that occurs at around 10 GPa, were studied by means of x-ray powder diffraction and charge density distribution maps derived by the maximum-entropy method. The compressibility of CeP was exactly determined using a helium pressure medium and the anomaly that indicated the isomorphous transition was observed in the compressibility. We also discuss the anisotropic charge density distribution of Ce ions and its temperature dependence.

1. Introduction

Cerium phosphide (CeP) is one of the heavy-fermion materials being intensively studied, because of the variety of its physical properties related to Ce 4f electrons. For example, CeP shows complicated magnetic phase diagrams in the temperature versus magnetic field and temperature versus pressure [1]. The magnetic phase is a Γ_7 and Γ_8 ordering; these are crystal field splittings of the 4f electron state. CeP crystallizes into an NaCl-type structure at ambient pressure and shows a structural transition to CsCl-type structure at 25 GPa [2]. It is well known that, before the structural phase transition, an isomorphous transition occurs at around 10 GPa and this transition is accompanied by an anomaly in the compression curve [3, 4]. Cerium 4f electrons seem to contribute to this transition. Although pressure-induced excitation from localized states to delocalized states and valence fluctuation have been considered [3], the cause of the isomorphous transition has not been clarified.

We performed an x-ray powder diffraction experiment using synchrotron radiation with a diamond anvil cell to study the behaviour of Ce 4f electrons. The maximum-entropy method (MEM) [5] proved a useful technique for deriving CDD maps from powder diffraction data. The computer code 'MEED' was used for the CDD study by means of the MEM. First, we re-examined the anomalous compression under quasi-hydrostatic conditions using a helium pressure medium and a high-energy x-ray beam (38.3 keV). Secondly, we considered the temperature and pressure dependences of the 4f electrons in the CDD maps. Our powder sample was carefully prepared, in view of the above.

2. Experimental procedure

CeP was prepared by reaction of stoichiometric amounts of Ce and P at around 850 °C for 70 h. It is important for the MEM to obtain precise intensities of the x-ray diffraction. The sample for the MEM analysis was prepared by grinding for 30 min in an Ar atmosphere and Fluorinert was used as the pressure medium. The sample for the compressibility measurement was ground for 5 min in an Ar atmosphere. The powder ground for 5 min was put in toluene solution. After 50 min, we picked up the top clear part of the toluene solution. The selected powder was processed to a pellet and the pellet was enclosed in the gasket hole with a helium pressure medium. Powder x-ray diffraction experiments were conducted at SPring-8, at the bending magnet beamline BL04B2 (38.3 keV) and the undulator beamline BL10XU.

3. Results and discussion

Figure 1 shows the x-ray diffraction patterns together with results of the Rietveld analysis at RT, 2.7 GPa and 18.5 K, 1.1 GPa measured at the SPring-8 beamline BL10XU. Although peak broadening caused by strain of the powder sample was observed, probably due to the long duration of the grinding process, the Debye–Scherrer patterns were uniform, without spots. The R_I- and R_{WP}-factors of the Rietveld analysis were $<3\%$ and were small enough for us to produce CDD maps in both cases. In order to improve the Rietveld analysis, the (100) direction of preferred orientation was considered at both temperatures. CDDs in the (100) plane of CeP are shown in figure 2. Ce charge spreads out to phosphorus ions at both temperatures. This anisotropy is more pronounced at RT than at 18.5 K. This anisotropy in the CDD at RT is consistent with the CDD derived from the x-ray diffraction data for single-crystal CeP by Shobu *et al* [6]. The temperature dependence of the CDD around P was slight. Since Γ_7 is the ground state and Γ_8 is an excited state of the 4f electron, Γ_8 is a more probable state at high temperature and high pressure. According to quantum theory, the wavefunction of Γ_8 spreads out to the phosphorus ions, while Γ_7 spreads out avoiding the phosphorus ions. Γ_8 seems to affect the strong anisotropic electron charge density at RT, 2.7 GPa. At 18.5 K, 1.1 GPa, Γ_7 seems dominant, which is consistent with the phase diagram determined from the neutron scattering. But the anisotropic shape of the CDD does not directly represent 4f electrons: 6s and 6p electrons which hybridize with 4f electrons seem to appear in the CDD map, because the 4f electrons are in a localized state and located in the core region within a 1 Å diameter.

Figure 3 shows the x-ray powder diffraction patterns obtained using a helium pressure medium. The data were measured at the SPring-8 beamline BL04B2. The helium pressure medium maintained the quasi-hydrostatic conditions of the sample space and suppressed the peak broadening to $<150\%$ up to 18 GPa. Figure 4 shows the volume compression together with the results obtained by Adachi *et al* [4] using methanol and ethanol solution. It should be noted that the compressibility using the helium pressure medium was less than that when using the methanol and ethanol solution as the pressure medium above 10 GPa. The non-hydrostatic conditions produce uniaxial stress parallel to the incident x-rays, so the d-spacing of the reflection plane, which is almost perpendicular to the incident x-rays, is hard to compress. The isomorphous transition takes place gradually, and the starting and finishing transition

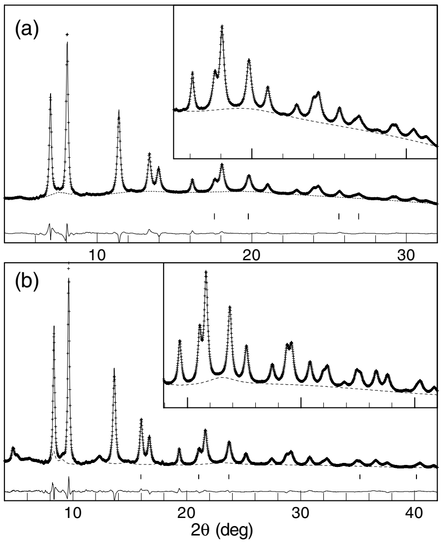

Figure 1. Results of the powder x-ray diffraction experiment and Rietveld analysis (a) at RT, 2.7 GPa, $R_{WP} = 2.3\%$, $R_I = 2.9\%$ and (b) at 18.5 K, 1.1 GPa, $R_{WP} = 2.3\%$, $R_I = 2.8\%$.

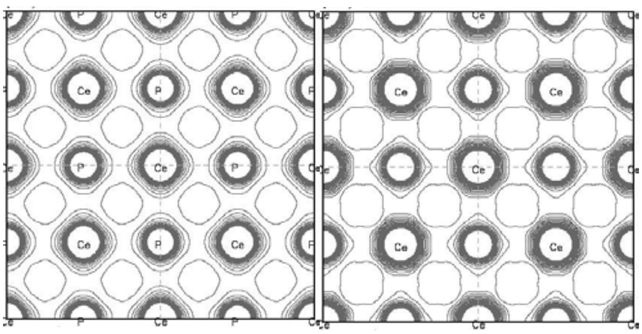

Figure 2. Charge density distribution maps for the (100) plane of CeP derived by the maximum-entropy method. The contours go from 0 to 4.0 e Å^{-3} in intervals of 0.2 e Å^{-3} (a) at RT, 2.7 GPa and (b) at 18.5 K, 1.1 GPa.

pressures were determined as 8 and 12 GPa respectively by checking the inflection points of the compression. The solid curve and dotted curve represent results of fitting a Birch–Murnaghan equation of state before and after the isomorphous transition, respectively. Before the transition, B_0 is 57.3(2.9) GPa and V_0 is 209.5 Å^3. After the transition, B_0 is 64.9(2.7) GPa and V_0 is 198.0(1.1) Å^3. In both fittings, B_0' was fixed at 4.0. In addition to the compressibility, the position of the white line in the x-ray absorption spectra of CeP at the Ce K edge was shifted to around 10 GPa [7], so the electron configuration of Ce should be changed by pressure. As a result of appropriate selection of the particle size, the FWHM of the diffraction peaks was narrow and this condition was maintained above 18 GPa. This is favourable for maximum-entropy analysis in studying 4f electrons in an isomorphous transition. Unfortunately, some spots were observed in the Debye–Scherrer ring. This made it difficult to estimate the exact integrated intensity with an R_I-factor below 8%. The Rietveld analysis was not good enough for us to proceed to a MEM study of the CDD after the isomorphous transition.

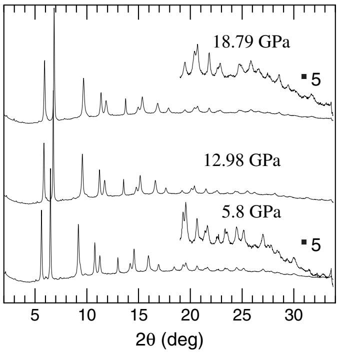

Figure 3. Powder x-ray diffraction patterns obtained using a helium pressure-transmitting medium.

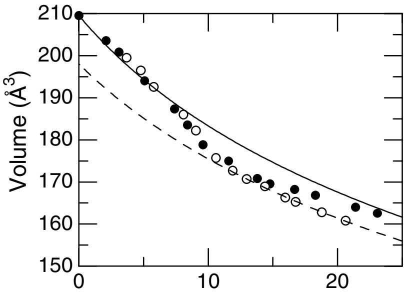

Figure 4. Compressibility measured with a helium pressure medium (open circles) and a methanol and ethanol pressure medium (closed circles). The solid curve and the dotted curve represent Birch–Murnaghan equations of states before and after the isomorphous transition, respectively.

4. Conclusions

We performed x-ray powder diffraction experiments under high pressure on CeP. The anisotropic charge density distribution of Ce ions in the low-pressure region was revealed. Precise compressibilities for low- and high-pressure phases were successfully obtained up to 20 GPa by using a helium pressure medium. From the inflection points of the relative volume change, the transition pressures of the isomorphous transition were determined exactly.

In order to extract 4f electrons after the isomorphous transition from CDD maps, we need to obtain uniform Debye–Scherrer rings without spots under hydrostatic conditions up to 20 GPa. Furthermore, it will be helpful to compare the CDD map of LaP, because the electron configuration of LaP is similar to that of CeP except for the 4f electrons. Since the experimental technique has been established in this experiment, we are now preparing powder x-ray diffraction experiments using a helium pressure medium again.

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