Materials Science

4C/2003G196

Valence fluctuated state in Yb_4As_3 studied by resonant x-ray scattering

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Introduction

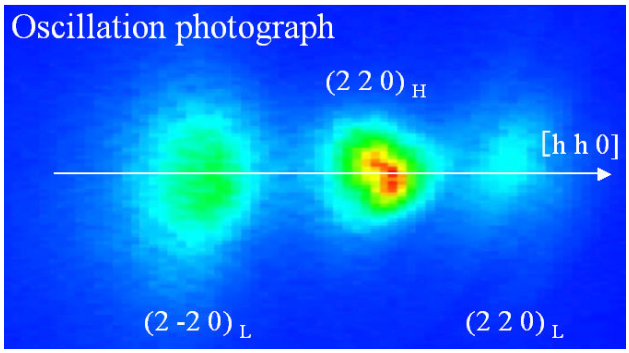
In rare earth compounds, valence fluctuation (VF) is one of the anomalous phenomena due to the instability of 4f electrons, and has attracted much attention. Yb_4As_3, an example of VF compounds, has a cubic anti-Th_3P_4 structure with space group *I*-43d and the lattice constant, a = 8.788Å[1]. Only one kind of Yb ion crystallographically exists in the structure and the valence should be the mean value, +2.25, although the two kinds of valence states, Yb^{2+} and Yb^{3+} in the ratio 3:1, have observed by the x-ray absorption spectra at Yb L_3-edge and the photoemission [2]. As a result, an inhomogeneous mixed valence state of the thermally fluctuated valence is expected at room temperature. At T_{CO} ~ 290 K, there is a first-order structural phase transition from the cubic structure to a trigonal one with space group R3c. In the transition, the magnetic Yb^{3+} ions occupy one of four equivalent [111] directions with the trigonal distortion. The other three directions are shared by the nonmagnetic Yb^{2+} ions. The charge ordering of the Yb ion in Yb_4As_3 has been clearly determined by the resonant x-ray scattering (RXS) technique. The resonant signal at (3 -3 0) reflecting the difference of the atomic scattering factors between Yb^{3+} and Yb^{2+} was observed, and the temperature dependence of the order parameter of the charge ordering was measured [3]. On the other hand, the VF state above T_{CO} has never been measured, although the short-range order of the charge ordering (SRO-CO) is expected by the specific heat [4]. Therefore, we have studied not only the valence state but also crystal structure in the VF state above T_{CO} using RXS and non-resonant x-ray scattering (non-RXS), respectively.

Experiment

High-quality Yb_4As_3 single crystals were grown as in ref.[1]. To observe the strong RXS signal at (3 -3 0) reflection positions, (1 1 0) surfaces were polished with fine emery paper. The diffraction experiments were performed using a four-circle diffractometer equipped with a closed-cycle helium refrigerator at beam line 4C of the Photon Factory. The incident beam was monochromatized by a pair of Si(111) crystals, giving an energy resolution of about 2 eV, and focused by a bent cylindrical mirror. The x-ray energy near the Yb L_3-edge (2p-5d transition energy, ~8.94 keV) was used for the RXS experiments. A Hamamatsu Photonics charge-coupled device (CCD) camera was also used for this experiment.

Results

To elucidate the VF state in Yb_4As_3, the temperature dependence of the valence state of Yb ion and the crystal structure reflecting the valence state were measured by RXS and non-RXS near the T_{CO}. At the T_{CO}, not only lattice constants but also the domain structure drastically change. The chasing the all peak positions and intensities using the scintillation counter is difficult, and needs long experimental time. Therefore, an oscillation photograph method using the CCD camera was selected to measure the overview of the temperature dependence.



The oscillation photograph at *T*=291 K near the fundamental peak (2 2 0) is shown in the figure. The (2 2 0)$_H$ of the cubic structure and (2 2 0)$_L$, (2 –2 0)$_L$ of the trigonal one coexist clearly owing to this first-order phase transition. We have also measured the RXS at (3 –3 0). Finally, it becomes clear that the trigonal structure of the charge-ordering state survives as a SRO-CO in the cubic structure of the charge disordered state. The SRO-CO is expected to be the fully charge ordered state, while it accompanies few atomic displacement due to the charge ordering. The correlation length of the SRO-CO gradually decreases with increasing temperature like a second order transition, and still survives even at 320K. These are first observation of the spatial correlation of the VF state, and this success with typical VF compound, Yb_4As_3, will be crucial in the study of the VF states.

References

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