Materials Science

4C, 9C/2006G050

Valence fluctuation compounds, R_4As_3, studied by a resonant x-ray scattering technique

Hironori NAKAO*, Keisuke NAKATSUKA, Daisuke BIZEN, Tetsuya MURATA, Takeshi MATSUMURA, Kazuaki IWASA, Youichi MURAKAMI, Akira OCHIAI
[1]Department of Physics, Tohoku University, Sendai 980-8578, Japan

Introduction

Valence fluctuation (VF) is one of the anomalous phenomena in rare earth compounds. The VF state was vigorously studied by Mössbouer spectroscopy, NMR, x-ray absorption spectrum and so on, and the time correlation of the VF state was discussed. [1] On the other hand, the spatial correlation of the valence of cations has not been investigated by diffraction techniques so far. R_4As_3 (R=Yb and Eu) indicate the typical VF behavior, and also show a transition between the VF phase and a charge ordered phase at Tco. [2] Therefore, the valence state can be systematically studied from the static ordered state to the thermally fluctuated state. In present study, we have investigated the valence state in R_4As_3 by using a resonant x-ray scattering (RXS) technique, which is a quite suitable technique for the study of charge ordered state.

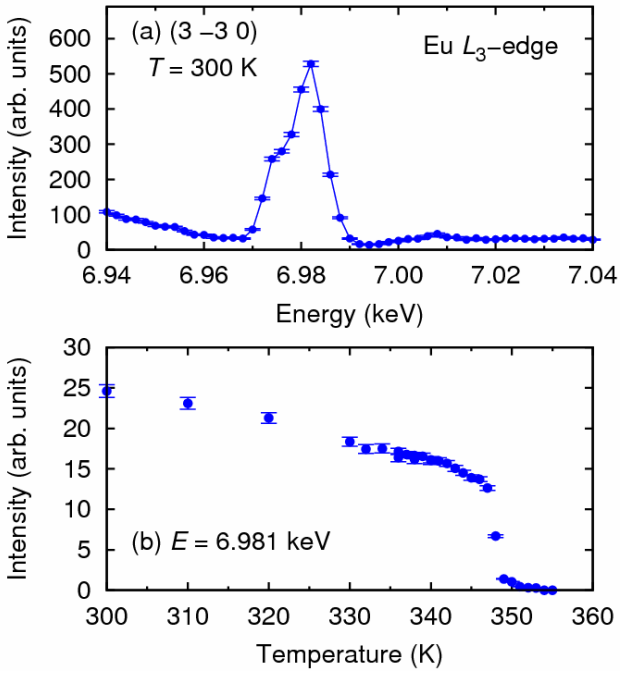
Experiments

High-quality Yb_4As_3 and Eu_4As_3 single crystals were grown as in Ref. [2]. Small crystal of Eu_4As_3 was sealed in glass capillary with Ar gas to prevent the oxidation. The RXS experiments were performed using four-circle diffractometers at beam lines 4C and 9C of the Photon Factory. The incident beam was monochromatized by a pair of Si(111) crystals, giving an energy resolution about 2 eV, and focused by a bend cylindrical mirror. The x-ray energy near the Yb L_3-edge (~8.94 keV) and Eu L_3-edge (~6.98 keV) was used for the RXS experiments. A closed cycle He cryostat (10~320 K) and a N_2-gas flow cryostat (100~370 K) were used for the temperature control.

Results

First, the charge ordering (T<Tco~290K) in Yb_4As_3 is precisely evaluated by the RXS technique [3]. The RXS results were consistent with the reported charge ordered (CO) structure. [4] Moreover, we have estimated the valences of two inequivalent Yb sites, +2.25-δ and +2.25+3 δ, and the fully charge ordered state with δ=0.25±0.02 was elucidated. Through the RXS experiments of Yb_4As_3, we have examined the validity of the RXS technique for the charge ordering in 4*f*-electron systems.

Eu_4As_3 is a similar VF compound, which show the CO phase transition at Tco~348 K. However, the CO structure was still not clear. In order to reveal the CO structure, we searched the resonant signal at several forbidden reflection positions. The energy dependence of the scattering intensity at (3 –3 0) is show in Fig. (a). The resonant signal reflecting the different anomalous scattering factor of Eu^{2+} and Eu^{3+} was clearly observed. The temperature dependence of RXS intensity at (3 –3 0) is also shown in Fig. (b). The intensity disappears above Tco. These are direct evidences of the charge ordering in Eu_4As_3.



The short range ordering reflecting the thermally fluctuated valence state was also searched above Tco. However, we found the unexpected strong critical scattering near Tco, and the intensity highly depends the surface treatment. The similar critical scattering was reported in the case of $SrTiO_3$, so called skin effect. [5] Further study is needed to make clear it.

References

[1] O. Berkooz et al., Solid State Commun. **6** (1968) 185; S. Takagi et al., J. Phys. Soc. Jpn. **62** (1993) 2861; N. Mori et al., Physica B **230-232** (1997) 630.
[2] A. Ochiai et al., J. Phys. Soc. Jpn. **59** (1990) 4129; M. Shirakawa et al., J. Phys. Soc. Jpn. **72** (2003) 2893; A. Ochiai et al, J. Phys. Soc. Jpn. **72** (2003) 3174.
[3] H. Nakao et al, AIP Conf. Proc. **850** (2006) 1175.
[4] U. Staub et al. Phys. Rev. B **71** (2005) 75115.
[5] K. Hirota et al., Phys. Rev. B **52** (1995) 13195.
* nakao@iiyo.phys.tohoku.ac.jp