Charge-Ordered Structure of Eu₃S₄

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Introduction

A mixed-valence compound Eu_3S_4 has divalent Eu^{2+} and trivalent Eu^{3+} ions in the ratio 1:2 and is recognized as a unique system including divalent rare-earth ions. The room-temperature phase has a Th_3P_4 structure, where all Eu ions occupy a kind of crystallographic site in a *bcc* lattice. Eu_3S_4 has the transport property as intrinsic semiconductor by a hopping of $4f$ electrons between adjacent Eu sites. The origin of the hopping motion of charge carriers is considered as either thermally activated drift mobility or electron tunneling.

In Mössbauer spectra of $^{151}Eu_3S_4$ below $T = 210$ K, two absorption peaks were observed and interpreted as electron hopping between Eu^{2+} and Eu^{3+} ions [1]. X-ray powder diffraction study found a cubic to tetragonal phase transition, having a 0.4 % distortion in the ratio of a/c in the low-temperature phase. Based on an approach to derive from the Th_3P_4 structure and construct a charge-ordering model between Eu^{2+} and Eu^{3+}, a tetragonal cell was proposed (Carter model) [2]. In the Raman scattering study any new phonon mode was not observed for single crystals of Eu_3S_4, which is inconsistent with the charge order-disorder transition [3].

Thus, the occurrence of the charge ordering in Eu_3S_4 still remains in dispute. The valence-selective structure determination would be the best way to examine the charge order-disorder mechanism. Therefore, the crystal structure of a low-temperature phase of Eu_3S_4 as well as the cation distribution of Eu^{2+} and Eu^{3+} are determined by the valence-difference contrast (VDC) technique with X-ray anomalous scattering [4].

Experimental

X-ray intensity measurements for the VDC crystal-structure analyses were made with a spherical crystal at BL-10A. Slightly longer wavelengths from the minima of f' were selected in order to keep the anomalous scattering effect intense but the absorption effect small.

Measurements of XANES spectra were performed at BL-3A. The program DIFFKK was used to calculate the experimental-base f' values from the f'' ones, with a chemical shift between different oxidation states and a relation of Kramers-Kronig's dispersion.

Results and discussion

The crystal structures of Eu_3S_4 at $T = 300$, 180 and 160 K were determine in the least-squares refinements with the Mo $K\alpha$ intensity data. A Th_3P_4-type $I\bar{4}3d$ structure transforms to a charge-ordered $I\bar{4}2d$ one at $T_c = 188.5$ K. The atomic coordinates at 160 K are $x=y=z=0$ for Eu($4a$), $x=0.3749(3)$, $y=1/4$, $z=1/8$ for Eu($8d$) and $x=0.573(1)$, $y=0.823(1)$, $z=0.448(1)$ for S($16e$).

The occupancy of Eu^{2+} and Eu^{3+} ions was doubly determined with the values of (1) $f'_{Eu2+} = -14.820$ and $f'_{Eu3+} = -12.114$ for $\lambda = 1.6312$ Å and (2) $f'_{Eu2+} = -10.7350$ and $f'_{Eu3+} = -13.625$ for $\lambda = 1.6298$ Å (Table 1). The least-squares structural refinements suggest that the most plausible atomic arrangement is $[Eu^{3+}]^{4a}[Eu^{2+}Eu^{3+}]^{8d}S_4$ (Fig. 1). The charge-ordering scheme is not the Carter model. A half of Eu^{3+} ions occupy the whole $4a$ sites in the $I\bar{4}2d$ crystal structure, while the remaining half of Eu^{3+} ions mix with Eu^{2+} in the $8d$ sites. The scheme is also supported by the energy-dependence of Bragg intensities for 400 and 004 reflections.

Table 1: Results of the site preference on Eu^{2+} and Eu^{3+}.

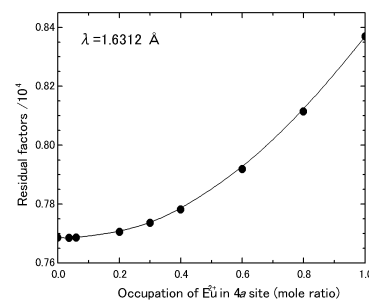| Wavelength	Occup. in $4a$		Occup. in $8d$	
	Eu^{2+}	Eu^{3+}	Eu^{2+}	Eu^{3+}
1.6312 Å	0.04(11)	0.96	0.96	1.04
1.6298 Å	0.00(17)	1.00	1.00	1.00

Fig. 1: Compositional change of the XMCD spectra of $La_{1-x}Sr_xCoO_3$ ($0 \leq x \leq 0.6$) at the Co K absorption edge.

References

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