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EFG at Sb site of filled Skutterudites

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Abstract

The electronic field gradients are obtained based on electronic bandstructure calculations for filled skutterudites. The LDA+U calculations have revealed that asymmetry parameters are affected from the anisotropic charge density distribution at the rare earth site for $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$, suggesting Sb atoms move in low temperatures.

Key words: electronic field gradients, bandstructure calculations, filled skutterudites
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Filled skutterudites RT_4X_{12} (R=rare earths; T=Fe, Ru, Os; X=P, As, Sb) are well known because of the variety of the interesting physical properties [1]. Such properties are thought to be related to the unique electronic bandstructure [2] and the crystalline electronic field in the rare-earth site [3], which is surrounded by 12 pnictogens. Among them, $PrOs_4Sb_{12}$ is well known as an unusual superconductor with a singlet ground state [4], $PrRu_4Sb_{12}$ is, however, a typical s-wave superconductor also with a singlet ground state [5]. It has been revealed that with decreasing temperature the NQR frequency (ν_Q) for $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ starts to increase around the temperature corresponding to the energy for the first excited level; 10 K and 70 K, respectively. This implies that anisotropic $4f^2$ charge distribution affects the electronic field gradients (EFG) at Sb-site. To study the effect from the $4f$ electrons, EFG are calculated for a several filled skutterudite compounds. EFG can be calculated by using an FLAPW method [6–8]. Moreover, the charge distribution of the singlet $4f^2$ ground state could be taken into account by using the LDA+U method [9].

Filled skutterudites crystallize in a unique bcc structure of a space group $Im\bar{3}$ (T_h^5, #204), where 12 pnictogens, at $24g$ site such as (0, u, v), form a cage of an icosahedron. The lattice parameters used in calculations are listed in Table 1. The EFG at Sb site are obtained based on an FLAPW bandstructure calculation, proposed by Blaha et al. [6]. To get well converged values, about 1,300 LAPWs and 195 sampling k points in the irreducible BZ (3,456 points in the BZ) are used for all calculations. For Sb at (0, u, v), the bc-plane is a mirror plane, so V_{ab} and V_{ca} in EFG tensor are zero, but V_{bc} is nonzero. (Here, we use a, b and c for the crystalographic axes.) One of the principle axes (the z-axis) is parallel to the a axis, and the others are on the bc-plane. After transforming the principle axes, EFG are obtained as V_{zz} and asymmetric parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, as listed in Table 1.

ν_Q is proportinal to $3/(2I(2I-1))QV_{zz}$, where I stands for nuclear spin and Q for nuclear quadupole moment. To convert V_{zz} to ν_Q, we use the Q values for Sb, as in the caption in Table 1, which are determined to reproduce the experimental ν_Q. As seen in Table 1, the Q values for ^{121}Sb and ^{123}Sb could obtain good agreement with the experimental ν_Q not only for similar V_{zz} values of skutterudites, but also for USb_2. Therefore, these Q values seem to b quite reliable. Note that η does not depend on the values I and Q.

To involve the effect from the anisotropic charge distribution of $4f^2$ singlet in Pr, we use the LDA+U method for $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$ [1,10,11]. The LDA+U method used here has the generalized form for the system in which the spin-orbit interaction is involved and U is set as 0.4Ry [9]. For $PrOs_4Sb_{12}$, three other method are used; i) $4f^2$ electrons are treated

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Table 1
The lattice constants a, the internal lattice parameters u and v, the calculated EFG and ν_Q ($^{121}\nu_Q$ for ^{121}Sb and $^{123}\nu_Q$ for ^{123}Sb) and asymmetry parameters η The lattice parameters for skutterudites are obtained in room temperature by K. Oikawa [12]. Nuclear quadrupole moments $Q = -0.59 \times 10^{-28} m^2$ for ^{121}Sb (I=5/2) and $Q = -0.75 \times 10^{-28} m^2$ for ^{123}Sb (I=7/2) are used to calculate ν_Q. The experimental ν_Q and η are taken from Ref. [13] for skutterudites and from Ref. [14] for USb_2.

material	a (Å)	u	v	Method used	V_{zz} (10^{22} V/m^2)	$^{121}\nu_Q$ (MHz)		$^{123}\nu_Q$ (MHz)		η	
				in calculation	Calc.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
$LaRu_4Sb_{12}$	9.27736	0.34208	0.15837	LDA	-1.9682	42.118	41.171	25.171	24.994	0.3816	0.406
$CeRu_4Sb_{12}$	9.27215	0.34104	0.15773	LDA	-1.9953	42.698	41.358	25.846	25.108	0.3732	0.401
$PrRu_4Sb_{12}$	9.27013	0.34107	0.15723	LDA+U	-1.9752	42.267	41.516	25.585	25.204	0.4341	0.402
$LaOs_4Sb_{12}$	9.30807	0.34140	0.15660	LDA	-2.0159	43.138	43.777	26.113	26.576	0.4503	0.450
$CeOs_4Sb_{12}$	9.30310	0.34043	0.15628	LDA	-2.0329	43.502	43.847	26.333	26.628	0.4523	0.463
$PrOs_4Sb_{12}$	9.30311	0.34050	0.15608	LDA+U	-2.0415	43.686	44.167	26.444	26.810	0.5281	0.459
				4f as core	-2.0429	43.715		26.462		0.4401	
				$4f^0$	-2.0261	43.356		26.245		0.4386	
				LDA	-2.0345	43.535		26.353		0.4590	
USb_2	(Sb_I)			LDA	-2.7971	59.855	60	36.232	37	0	0
	(Sb_{II})			LDA	1.0211	21.851	19.4	13.227	11.8	0	0

as spherical core electrons ("4f as core" in Table 1), ii) Pr is replaced by La with the lattice parameters kept ("$4f^0$" in Table 1), iii) $4f$ electrons are treated as itinerant electrons by using LDA. Remember that the Fermi surfaces of $PrOs_4Sb_{12}$ are well reproduced by the LDA+U calculation [11].

For $LaRu_4Sb_{12}$ and $LaOs_4Sb_{12}$, the calculated EFG reproduce well the experimental ν_Q and asymmetry parameter η. Here parameters such as Q are used for ν_Q, but no adjustable parameters are used for η. When the lattice constant is reduced, EFG increases in general. In fact, ν_Q for Pr is larger than for La. Such a tendency is qualitatively reproduced in calculations. But, the difference of ν_Q is too small to be discussed.

The LDA+U calculations for $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$ show that ν_Q are almost unchanged, but η increase, due to the anisotropic charge distribution on Pr-site. This is because V_{bc} is increased for the LDA+U calculation in both Pr compounds. It should be noted that V_{bc} is directed to the Pr position from (0, u, v). However, the measured η seem to be independent on La, Ce and Pr. Moreover, the recent careful experiment shows that η decreases with decreasing temperatures in $PrOs_4Sb_{12}$ [15]. The discrepancy of η in both Pr skutterudites implies that the internal parameters of Sb site, which are experimentally obtained in room temperatures, are changed in low temperatures, affected by the anisotropic $4f^2$ electrons. It means that Sb moves its position and the cage changes its shape in low temperatures. To confirm it, the calculations with other Sb positions are necessary.

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