X-ray measurement for the orbital ordering materials

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Abstract

By using our developed x-ray measurement system for powder sample below 1K, we have studied the orbital ordering materials PrPtBi, $Ce_0.75La_0.25B_6$ and $PrPb_3$. The ground state of Pr^{3+} ion in the cubic semiconductor compound PrPtBi, is a non-magnetic Γ_3 doublet. To investigate whether the phase transition at 1.35K is antifrro-quadrupolar (AFQ) or ferro-quadrupolar (FQ) type ordering, we have studied this compound by x-ray measurement. Below the transition temperature we could not observe the splitting of any reflection lines but the full width at half maximum (FWHM) increases with decreasing temperature, which suggests the phase transition at 1.35K is AFQ ordering. In this paper we also report the integrated intensity of (400) reflection as a function of temperature. This is the first experiment to investigate the AFQ ordering using ordinary x-ray diffraction method.

Key words: X-ray Diffraction ; Orbital Ordering

1. Introduction

We studied rare-earth compounds of PrPtBi, $Ce_0.75La_0.25B_6$ and $PrPb_3$ by using the low temperature diffractometer, which recently developed by us [1]. In these compounds it was found that the electric orbital took important roll in their low temperature phases. PrPtBi has the MgAgAs-type crystal structure at room temperature. The crystalline-electric-field (C.E.F.) interaction acting on Pr^{3+} ($4f^2\ ^3H_4$) ion in PrPtBi lift the nine fold degeneracy of the J=4 ground multiplet into one singlet (Γ_1), one doublet (Γ_3) and two triplets (Γ_4, Γ_5). From the analysis of the magnetic susceptibility it is known that the ground state is nonmagnetic Γ_3 doublet and the energy difference between this ground state and the first excited state doublet is about 87.5K [2]. The specific heat measurement shows a large anomaly at 1.35K suggesting the phase transition. From the specific heat and magnetic susceptibiliy measurement [2] it is deduced that the phase transition at 1.35K is not magnetic. The non-magnetic ground state Γ_3 doublet has the quadrupolar moments $O_2^0 = (2J_z^2\text{-}J_x^2\text{-}J_y^2)/\sqrt{3}$ and $O_2^2 = J_x^2\text{-}J_y^2$. Probably this phase transition may arise from the electric quadrupolar ordering. Below the transition temperature 1.35K, whether the phase is antiferro-quadrupolar (AFQ) or ferro-quadrupolar (FQ) type is unknown. To investigate this phase transition at 1.35K, the precise x-ray diffraction measurement was performed between room temperature and 0.32K.

2. Experimental Results and Discussion

PrPtBi samples were prepared by melting stoichiometric amounts of the constituent elements in an arc furnace [2]. The x-ray diffraction data were collected using a Rigaku x-ray diffractometer RINT2000 with a scintillation counter [1]. The powder samples were mounted on a gold plated sample holder made of Oxygen-Free High-Conductivity (OFHC) Cu, at-

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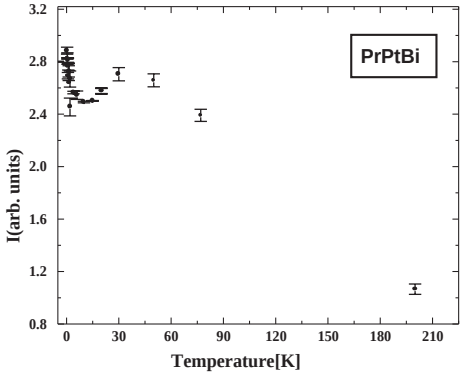

Fig. 1. Intigrated Intensity I as a function of temperature for (400) reflection.

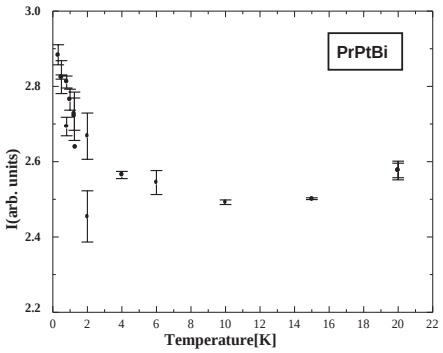

Fig. 2. Intigrated Intensity I as a function of temperature for (400) reflection. Fig. 2 is the enlargement of Fig. 1 in the low temperature ragne.

tached to the mixing chamber of the ^{3}He-^{4}He dilution refrigerator of Oxford Instr. Kelvinox VT, which was modified for x-ray measurement. An x-ray generator with a rotating Cu target was operated at 45kV and 300mA. The diffractometer was operated in continuous θ-2θ mode. In the case of FQ the amount of the crystal distortion in PrPtBi can be estimated from the experimental results of neutron diffraction for other FQ ordered compounds such as HoB_6 [3]. Our x-ray diffractometer has enough resolution to detect this crystal distortion. We also measured the temperature dependence of the lattice constant d, the integrated intensity I and the FWHM of the reflection lines. We could not observe any splitting of the reflection lines at lower temperatures below T_Q. We, however, observed the increasing of FWHM with decreasing temperature below T_Q. Our experimental results suggest that the phase transition at 1.35K must be AFQ ordering. We also observed the very interesting result for the intensity of the reflection line. The intensity for the x-ray reflections is expressed by the Debye-Waller factor

$$I(hkl) = I_0 exp(-k_B T G^2/M\omega^2). \quad (1)$$

Where hkl are the indices of the reciprocal lattice vector G, M is the mass of an atom, ω is the frequency of the oscillation of the lattice and k_B is the Boltzman constant. According to the Debye-Waller theorem in equation (1) the intensity increases exponentially with decreasing temperature. The temperature dependence of the integrated intensity for (400) reflection is shown in fig. 1. Fig. 2, is the enlargement of fig. 1 in the low temperature range. At higher temperature, say about 30K the temperature dependence of the intensity can be explained by the Debye-Waller factor. At lower temperature, however, the intensity variation on temperature, is rather complicated. In the eq. (1), the lattice vibration, that is, the frequency ω , is assumed to be constant expect for T $\cong$ 0. At T $\cong$ 0, the only zero point motion is taken account in eq. (1). At higher temperature, the thermal effect is so large that it smeared out the effect due to the change of the force constant in the lattice, which correspond to the change of the ω value in eq. (1). Below about 30K, the intensity starts to decrease till about 10K, then it again increases with decreasing temperature. This temperature dependence of the intensity at low temperatures must reflect the lattice properties, such as softening and also the phase transition. This must be the first x-ray measurement, which succeeded to observe the elastic properties, at low temperatures.

References

[1] H.Suzuki, S.Naher, T.Shimoguchi, M.Mizuno, A.Ryu and H. Fujishita J. Low Temp. Phys. 128, 1/2 July (2002) to be published. And S.Naher, H.suzuki, M.Mizuno, Y.Xue and H. Fujishita LT23 in this issue.

[2] H.Suzuki, M.Kasaya, T.Miyazaki, Y.Nemoto and T.Goto J. Phys. Soc. Jpn. 66(1997)2566.

[3] A.Donni, P.Fischer, L.Keller, V.Pomjakushin, Y.Nemoto, T.Goto and S.Kunii J. Phys. Soc. Jpn. 70(2001)Suppl.A p. 448-450.