Low temperature x-ray diffraction study on phase transitions

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Abstract. By using the low temperature x-ray diffraction (LTXD) we investigated several phase transitions which accompany with the crystal distortion. In our present report we will mainly discuss the integrated intensity (I.I.) of the x-ray spectrum. The temperature dependence of I.I. can be expressed by the Debye-Waller factor. As a precursor effect of the crystal phase transition, the softening of the lattice occurs. Due to the softening of the lattice, the I.I. drastically decreases down to the crystal phase transition temperature. We observed this effect in many materials. Here we will show some of them, iron pnictide superconductor SmFe₀.₉₂₅Co₀.₇₅AsO, and magnetic ordering compounds PrCu₄Ag and Nd₂Ti₂O₇.

1. Introduction

In the study of the phase transition which accompany with crystal distortion, the low temperature x-ray diffraction (LTXD) is essential technique. Not only to determine the crystal structure, but LTXD also gives the information about the lattice vibration. When the atom of the crystal is fluctuating, let the position of atom nominally at \( r_j \) contain a term \( r(t) = r_j + u(t) = r_j + u_0 \sin(\omega t) \). Then the structure factor of the x-ray diffraction can be expressed as \( F_j \exp(-iG \cdot r_j) \exp(-iG \cdot u_0 \sin(\omega t)) \). Here we use the formula \( \exp[iy\sin\theta] = \sum J_n(y)\exp[in\theta] \), here \( J_n(y) \) is a Bessel function. Then we can obtain \( F_j \exp(-iG \cdot r_j) \sum J_n(G \cdot u_0)\exp[in\omega t] \). When \( n = 0 \), this structure factor gives the Bragg reflection. Other \( n \neq 0 \)
terms give the diffuse scattering which gives the rather broad background spectrum. The structure factor for the Bragg reflection, taking into account only \( n = 0 \) term, can be expressed by the Debye-Waller factor,

\[
I = I_0 \exp \left( -\frac{k_B T \sin^2 \theta_B}{M \omega^2} \right)
\]

where \( I_0 \) is the scattered intensity from the rigid lattice, \( \theta_B \) the scattering angle, \( M \) the mass of the atom and \( \omega \) the frequency of the oscillator. Here thermal effect was introduced as \( \frac{1}{2}M \omega^2 \langle u(t)^2 \rangle = \frac{3}{2}k_B T \) \[1\]. Even at absolute zero temperature \( T = 0 \) K, the intensity \( I \) is less than \( I_0 \), due to the quantum zero point motion. At rather high temperature the intensity \( I \) is rather small. At very low temperatures, the intensity becomes nearly temperature independent. When the other fluctuation, such as critical fluctuation near the phase transition temperature and/or the quantum critical fluctuation occurs, the intensity again decreases with decreasing temperature. As a precursor effect of the crystal phase transition the softening of the lattice occurs. Due to the softening of the lattice, the I.I. drastically decreases down to the crystal phase transition temperature.

On the other hand the shape of the Bragg reflection does not change due to the fluctuation. Only the rather broad diffuse scattering spectrum can be added to the background of the Bragg reflection spectrum. Therefore the FWHM does not change due to the fluctuation of the lattice.

2. Experimental procedure

Low temperature X-ray diffraction (LTXD) measurements for powder specimens were performed using the RINT 2500 system, Rigaku Co. An X-ray beam was generated by a rotating Cu anode. The powder specimens were used and cooled by a \(^4\)He gas circulating cryo-cooler and can be cooled down to about 10 K. Below 1 K, a \(^3\)He-\(^4\)He dilution refrigerator, the modified Kelvinox-VT of Oxford Instr. Co. was used\(^3\). The temperature stability is better than 0.1% during the LTXD measurements. At several temperatures entire profiles of reflection peaks were measured with a step size of 0.01° and a step-counting of 6 s and refined by the Rietveld method using the reported crystal structure. For some reflection planes X-ray diffraction measurements with a step size of 0.005° and a step-counting time of 60 s were performed to accumulate more counts at certain temperatures. From the observed profile the \( d \) value of the reflection peak, the integrated intensity (I.I.) and also the full-width-at-half-maximum (FWHM) were obtained. In the analysis the profile was fitted to a Pseudo-Voigt function.

3. Experimental results and discussions

3.1 Pnictide superconductor \( SmFe_{0.925}Co_{0.075}AsO \)

In all the FeAs-based parent pnictide-oxide compounds, there are a structural phase transition in the temperature range of 100-200 K and an antiferromagnetic (AFM) ordering. Various chemical-doping approaches can suppress the structural phase transition and AFM ordering, and high-\( T_C \).
superconductivity consequently appears. A dome-like $T_c(x)$ curve is widely observed in the Co-doped SmFe$_{1.5}$Co$_x$AsO system. The SmFe$_{0.925}$Co$_{0.075}$AsO compound locates near the quantum critical point of the crystal and magnetic phase transitions. This compound shows the nearly maximum of $T_c(x)$ [2]. We measured the LTXRD of this compound. The temperature dependence of the I.I. measured for (220) reflection is shown in Fig. 1. At high temperatures (not shown here) the I.I. increases with decreasing temperature down to about 30 K. From the maximum value of I.I. at about 30 K, it decreases with decreasing temperature. As shown in the figure it decreases rather sharply below about 10 K and at 4 K it suddenly recovered the value to the nearly maximum value. This result can be understood by the Debye-Waller factor of Eq. 1. The decrease of the I.I. is the softening of the lattice. At 4 K, the crystal phase transition already occurred, that is, the lattice became rather rigid again.

3.2 PrCu$_4$Ag.

The magnetic properties of PrCu$_4$Ag have been investigated by measuring magnetic susceptibility, magnetization, specific heat, thermal expansion, electric resistivity and elastic constant. The ground state of Pr$^{3+}$ (J = 4) in the cubic crystalline electric field of PrCu$_4$Ag was determined to be $\Gamma_5$ triplet. An antiferromagnetic phase transition has been observed at 2.4 K. Though the cubic symmetry of the lattice, the anisotropic magnetic behaviour was observed below about 10 K. It was suggested that a possible quadrupole fluctuation, that is a structural fluctuation can explain this anomalous anisotropic behaviour in magnetic properties [3]. The measured I.I. and FWHM of the (220) reflection are plotted against temperature in Fig. 2 and Fig.3, respectively. The insets show the low temperature part in the expanded scale. Below about 50 K, the I.I. starts to increase drastically till about 10 K, then it decreases rather steeply down to our lowest temperature of 0.7 K. The decrease of the I.I. suggests the softening of the lattice. The FWHM also
increases steeply below about 10 K, suggesting the short-range order of the crystal structure change. Our experimental results strongly support the magnetic experimental results.

3.3 \( \text{Nd}_2\text{Ti}_2\text{O}_7 \)

The ground state of \( \text{Nd}^{3+} \) spins in the monoclinic \( \text{Nd}_2\text{Ti}_2\text{O}_7 \) (NTO) splits into five Kramers doublets in the crystal field associated with the C1 site in \( \text{P}2_1(4) \) space group. The NTO does not show a magnetic transition at least down to 2 K, though the average Weiss temperature \( \theta_W \sim -42.1 \text{ K} \). At low temperatures, especially below about 10 K, ac susceptibility shows the strong field and frequency dependences suggesting the slow spin-lattice relaxation \([4]\). In Fig. 4, the I. I. of the (400) reflection is shown against temperature. The I.I. decreases drastically below about 4 K, suggesting the softening of the lattice. The degenerate ground state should favor the crystal distortion at low temperatures. This fluctuation of the crystal distortion may couple to spins, and can be one of the candidate mechanism responsible for the slow spin-lattice relaxation.

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