Dynamics of cubic-tetragonal phase transition in KNbO₃ perovskite

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The low-energy part of the vibration spectrum in KNbO₃ was studied by cold neutron inelastic scattering in the cubic phase. In addition to acoustic phonons, we observe strong diffuse scattering, which consists of two components. The first one is quasi-static and has a temperature-independent intensity. The second component appears as quasi-elastic scattering in the neutron spectrum indicating a dynamic origin. From analysis of the inelastic data we conclude that the quasi-elastic component and the acoustic phonon are mutually coupled. The susceptibility associated with the quasi-elastic component grows as the temperature approaches T_C.

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ABO₃ perovskites form a class of important materials, in part because of potential technical applications but also as fundamental interest in the physics of phase transitions [1, 2]. At sufficiently high temperatures many of these perovskites have O₃\(^3\) cubic symmetry and structural phase transitions can take place as the temperature is lowered. Well-known examples are e.g. the cubic-tetragonal phase transition in SrTiO₃ (T_C \(\approx 105\) K) or in BaTiO₃ (T_C \(\approx 425\) K) (for a review see Ref. [3]). There are, however, ABO₃ perovskites which were less studied. An example is the first-order cubic-tetragonal phase transition in KNbO₃ which occurs at T_C \(\approx 683\) K when cooling the crystal from above the transition temperature [4].

The mechanism of the cubic-tetragonal (CT) phase transition in KNbO₃ is still controversial. Whereas well-defined soft phonon modes with frequency varying with temperature have been detected in many materials close to T_C [1 - 3], only an over-damped excitation has been observed in cubic KNbO₃ with neutron scattering and it was suggested that the nature of the C-T phase transition in that compound is similar to the displaceable C-T transition in BaTiO₃ [5, 6]. On the other hand, two coexisting and essentially uncoupled modes are inferred from analysis of optical data in the cubic phase of KNbO₃: a relaxation mode and a soft phonon, with the relaxation process driving the C-T phase transition [7].

We re-investigated the low energy part of the vibration spectrum in KNbO₃ under improved resolution conditions first to try to elucidate the mechanism of the phase transition in this crystal and second to check whether the diffuse scattering found in Ref.[8] is of static or dynamic origin. The inelastic cold-neutron scattering measurements reported here were performed with the three-axis spectrometer TASP, located at the neutron spallation source SINQ (Paul Scherrer Institute, Switzerland). A large single crystal of KNbO₃ (∼ 20 cm\(^3\), mosaic ∼ 80\(^\circ\)) was mounted into an ILL-type furnace. To decrease the level of incoherent background the sample holder was made from pure niobium. The crystal was aligned in the (h k 0) scattering plane. The measurements were performed in the temperature range 727 K - 1030 K. The (002) reflection of pyrolytic graphite (PG) was used to monochromate and analyze the incident and scattered neutron beams, respectively. The spectrometer was operated in the constant final-energy mode with k_f = 1.97\(\AA\)^\(-1\). A PG filter was used to remove higher-order wavelengths. The horizontal collimation was 10′/\(\AA\) - 80′ - 80′ - 80′. With that configuration the energy resolution at zero energy transfer is ∼ 0.4 meV. By monitoring the position and intensity of the (1, 1, 0) Bragg peak, the temperature of the cubic-tetragonal phase transition upon cooling was found at T_C = 684 ± 2 K, in close agreement with published data [4, 6]. The temperature of the sample was controlled by two thermocouples. The temperature gradient through the sample did not exceed 15 K.

Before analyzing the inelastic neutron spectra quan-
where $q_0$ is the position in reciprocal space; $\kappa$ the inverse of the correlation length $\xi$ and $I_0$ yields the integrated intensity. From a fit to the elastic data at $T = 1030$ K we obtain $\xi = 64 \pm 6$ Å. It turns out that the shape and intensity of the diffuse scattering measured in the (2,0,0) Brillouin zone (BZ) does not depend on temperature (see insert of Fig. 2). This is in agreement with the results of Guinier et al. [8] using X-rays and reflects the presence of atomic disorder in the perovskite cell. In KNbO$_3$ atomic disorder yields diffuse scattering along the [100] direction both in the X-ray and neutron diffraction patterns. Here we approximate the line-shape of the diffuse scattering measured along $(1,1,0)$ direction at $\pm 1$ rlu by a Lorentzian profile.

We turn now to the analysis of the inelastic neutron scattering spectra. Figure 2 shows an example of a constant-$q$ scan taken at $Q = (2, -0.1, 0)$ and $T = 1030$ K. The spectrum contains an inelastic peak at $h\omega = 4$ meV from the transverse acoustic (TA) phonon and a narrow peak centered around zero energy transfer. To analyze the data quantitatively, we hence modeled the neutron scattering intensity $I(Q, \omega)$ in the following way:

$$I(Q, \omega) = S(Q, \omega) \otimes R(Q, \omega) + B$$

with $A(q)$ given by Eq. 1. The line-shape of the acoustic phonon is given by the usual damped-harmonic oscillator (DHO)

$$\chi_{DHO}(q, \omega) = (\Omega_q^2 - i\gamma_q \omega - \omega^2)^{-1}.$$
In Eq. $\gamma_q$ is the damping and $\Omega_q = \sqrt{\omega_q^2 + \gamma_q^2}$ with $\omega_q = c \cdot q$ [10] is the renormalized frequency of the acoustic phonons. For small values of momentum transfers $q$, a linear dispersion for the acoustic phonon branch is a reasonable approximation and the phonon damping approximately follows a $dq^2$-dependence [11]. The scattering function used to fit the neutron data then reads

$$S(Q,\omega) = S_{CP}(Q,\omega) + \frac{[n(\omega)+1]}{\pi} f_1^2 \chi_{DHO}(Q,\omega) \quad (6)$$

where $Q = q + \tau$ is the neutron scattering vector and $\tau$ a reciprocal lattice vector; $f_1$ is the structure factor of the acoustic phonon. As shown in Fig.2 Eqs. 1-6 parameterize the experimental data in the (2, 0, 0) BZ well. The central peak is resolution-limited and temperature-independent. The acoustic phonon branch has a stiffness $c = 28 \pm 1.3$ meV·Å$^2$ and the damping is small at low $q$, $\gamma_q = dq^2$ with $d = 55 \pm 6$ meV·Å$^2$. In the temperature range $750 < T < 1030$ K no qualitative change in the dispersion of the acoustic phonon was observed for data taken along (2, q, 0) ($|q|<0.15$ (rlu)).

On the contrary, for temperatures below $T=1030$ K an additional component is observed in the inelastic spectra for constant-$q$ scans in the $(1,1,0)$ BZ. For means of comparison, Fig.3 shows two representative neutron scattering spectra measured in the $(1,1,0)$ BZ at $T=1030$ K and $T=727$ K, respectively. At $T = 1030$ K the spectrum consists of two components - a central peak (CP) and a phonon response around $\hbar\omega = 4$ meV. However, as the temperature is lowered to $T=727$ K, additional quasielastic scattering (QE) appears along $(1,1 \pm q,0)$ direction. The intensity of this quasi-elastic scattering grows when approaching $T_C$. From the above discussion we conclude that in the $(1,1,0)$ BZ, the inelastic neutron spectra consist of three contributions: a central peak, quasi-elastic and phonon scattering. To describe the quasi-elastic scattering we introduce a Debye-like relaxation function

$$\chi_{q-el}(q,\omega) = \frac{\chi(0,T)}{1 + q^2/\kappa^2} \frac{(1-i\omega/\Gamma_q)}{\Gamma_q}, \quad (7)$$

$\chi(0,T)$ is the temperature dependent static susceptibility; $\kappa$ the inverse of the correlation length and $\Gamma_q = \Gamma_0 + Dq^2$. Taking into account the quasi-elastic scattering modifies the neutron cross-section to

$$S(Q,\omega) = S_{CP}(Q,\omega) + \frac{[n(\omega)+1]}{\pi} [f_1^2 \chi_{DHO}(Q,\omega) + f_2^2 \chi_{q-el}(Q,\omega)], \quad (8)$$

However, the scattering function given in Eq. 8 fails in reproducing the experimental data in the $(1,1,0)$ BZ for $T<1030$ K. For example Fig. 2 shows an inelastic spectrum at $T=727$ K and $Q=(1,1.075,0)$ where a qualitative change in the phonon line-shape accompanied by a shift in the position of the phonon peak is observed. These two effects suggest that coupling between the quasi-elastic component and the acoustic phonons becomes important as the temperature approaches $T_C$.

The dynamical susceptibility for two coupled excitations was considered in details in Refs. [3, 12, 13] and is given by

$$\chi_{CM}(Q,\omega) = \frac{f_1^2 \chi_1 + f_2^2 \chi_2 + 2\lambda f_1 f_2 \chi_1 \chi_2}{1 - \lambda^2 \chi_1 \chi_2} \quad (9)$$

where $\chi_i \equiv \chi_i(Q,\omega)$, $i = 1,2$ are the dynamical susceptibilities of the uncoupled phonon and QE component,
since in KNbO$_3$ of symmetry. The interaction term is $D_{ij}$ as real constants since in KNbO$_3$ all the atoms are situated on centers of symmetry. The interaction term is $\lambda \equiv \lambda(q, \omega) = (g_r + i\omega g_i)q^2$. Finally, the scattering function reads:

$$S(Q, \omega) = S_{CP}(Q, \omega) + \frac{[n(\omega) + 1]}{\pi} \chi_{CM}''.$$  \hspace{1cm} \text{(10)}$$

In order to obtain a good agreement between Eq. (10) and the neutron spectra, it was necessary to fit the complete set of data (0<q<0.2) taken at a given temperature simultaneously. Figures [1] and [2] show the results of such calculations for T=727 K and T=760 K. We obtain $g_r = 20 \pm 3$ meV$^2$.Å$^2$ and $g_i = 95 \pm 6$ meV.Å$^2$. Introduction of a coupling between the QE and acoustic modes has two consequences. First, Eq. (10) yields a better description of the line-shape of the inelastic neutron spectra. Second, $\chi_{CM}''(Q, \omega)$ is enhanced at low energy transfers. Further, we obtained $\Gamma_0 = 0.19 \pm 0.05$ meV and $D = 44 \pm 4$ meV.Å$^2$ for the damping of QE component. As discussed above, both the CP and the

![FIG. 5: Observed and fitted inelastic neutron intensities taken in the (1, 1, 0) BZ at T=760 K. Fitted curves were obtained with Eq. (10). Intensity is given in a logarithmic scale.](image)

line-shape of the acoustic phonons are temperature independent in the (2, 0, 0) BZ. Hence, to fit the data measured in the (1, 1, 0) BZ as a function of temperature, we fixed the parameters of the CP and the acoustic phonons. The only parameter left to describe the temperature dependence of the neutron spectra is the susceptibility of QE scattering $\chi(0, T)$. As shown in Fig. [3] the intensity of the quasi-elastic component is maximum close to $T_C$ and decreases continuously with increasing temperature. The temperature dependence of $\chi(0, T)$ follows approximately the Curie-Weiss law $\propto 1/(T - T_0)$ with $T_0 = 615 \pm 23$ K in good agreement with the value deduced from dielectric measurements $T_0 = 633 \pm 5.9$ K (Ref. [14]), and $T_0 = 615$ K (Ref. [15]). This suggests that the cubic-tetragonal transition in KNbO$_3$ is driven by the quasi-elastic relaxational excitation. The intensity of the quasi-elastic component is strong in the (1,1,0) zone and has a small intensity in the (2,0,0) Brillouin zone, which indicates that the relaxation mode is due to correlated atomic motion of optical character. However, at all q and temperatures we did not observe that the relaxation mode evolves into an under-damped optic phonon branch. Thus, we conclude that QE scattering in KNbO$_3$ is not due to an usual overdamped soft phonon but is related to disorder in the lattice.

To summarize, we measured the low-energy part of the vibration spectrum of KNbO$_3$ in the cubic phase with inelastic neutron scattering. We find a coexistence of a static and a quasi-elastic component. The static component appears to correspond with static disorder in the cubic cell and is temperature independent in agreement with X-rays results [5]. The quasi-elastic component is coupled with the acoustic phonon branch and its intensity follows the Curie-Weiss law well.

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