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Phase Transitions and Neutron Scattering

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ABSTRACT

A review is given of recent advances in neutron scattering studies of solid state physics. I have selected the study of a structural phase transition as the best example to demonstrate the power of neutron scattering techniques. Since energy analysis is relatively easy, the dynamical aspects of a transition can be elucidated by the neutron probe. I shall discuss in some detail current experiments on the 100K transition in $SrTiO_3$, the crystal which has been the paradigm of neutron studies of phase transitions for many years. This new experiment attempts to clarify the relation between the neutron central peak, observed in energy scans, and the two length scales observed in recent x-ray diffraction studies where only scans in momentum space are possible.

INTRODUCTION

Over the years the neutron scattering techniques, in particular, triple axis spectrometers have played a major role in dynamical studies of structural phase transitions. The 100 K transition in $SrTiO_3$ is one of the most extensively studied. This was the first example of the zone boundary soft mode condensations1) and was studied in 1969. Following this, the central peak was discovered by Riste et al2) in 1971 and Shapiro et al3) subsequently characterized it in great detail. Recently a series of x-ray investigations4),5) reported the new phenomena of two length scales in $SrTiO_3$: (1) the "narrow" q peak only observable near T_c, and (2) temperature dependent thermal diffuse peaks originating from the soft modes. Similar two length scales were also reported6),7) for $KMnF_3$ and $RbCaF_3$. These observations prompted the current neutron scattering experiment8) in order to clarify the relation between the x-ray and neutron observations.

Fig. 1 demonstrates an example of energy scans of $SrTiO_3$, which consists of the soft mode peak at $\Delta E = \omega_\infty$ and the sharp central peak at $\Delta E = 0$. The renormalized soft-mode frequency ω_0 is related to ω_∞ by a coupling constant δ^2

$$\omega_0^2 = \omega_\infty^2 - \delta^2 \qquad (1)$$

under certain assumptions,[3] the integrated intensities of these three peak structures are given by

$$\int S(\vec{q},\omega)d\omega=\int S(q,\omega)_{cent}d\omega+\int S(q,\omega)_{phonon}\,d\omega$$

$$\frac{1}{\omega_0^2}=\frac{\delta^2}{\omega_0^2,\omega_\infty^2}+\frac{1}{\omega_\infty^2} \qquad (2)$$

It is the renormalized frequency ω_0 which goes to zero at T_c causing a divergence in the central peak and total integrated intensity (Fig. 1).

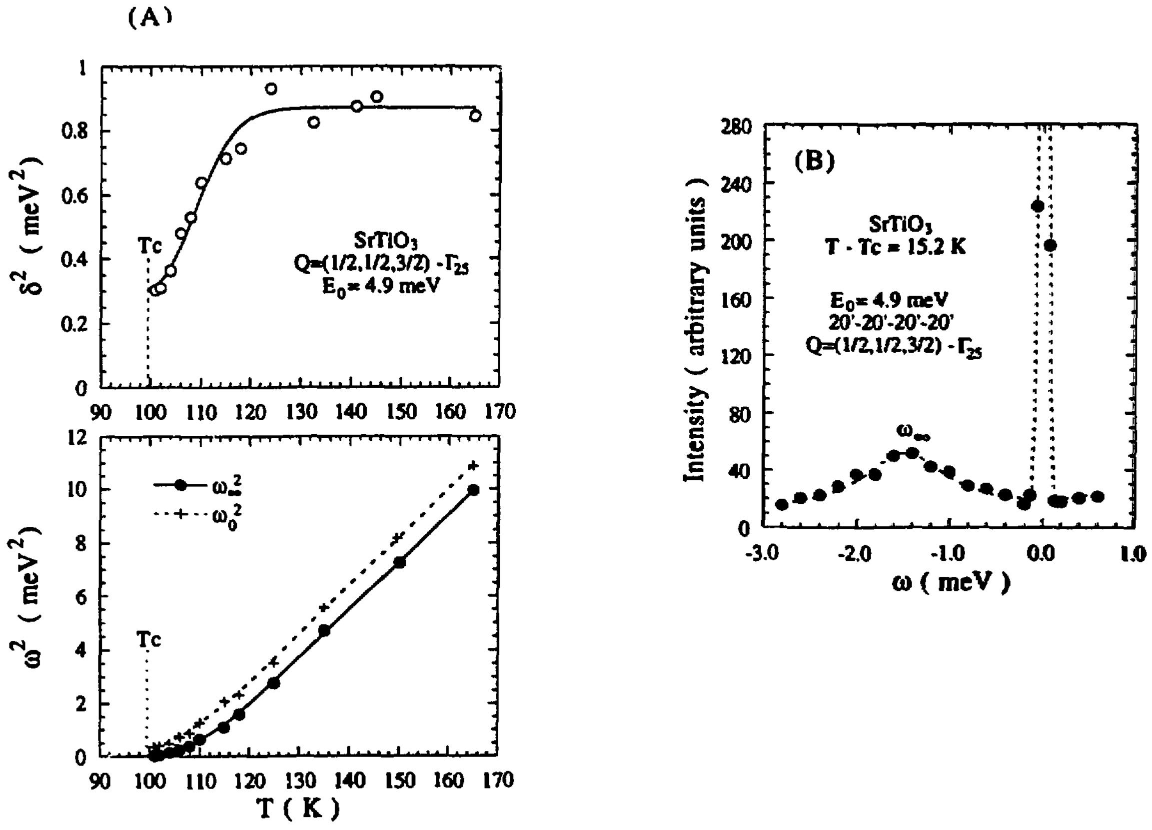

Figure 1

Fig. 1 (A) temperature dependence of ω_∞^2, ω_0^2 and δ^2 near th 100K transition in SrTiO$_3$ (B) Neutron profiles of side-band ω_∞ and central peak around ω = o. After Shapiro et al.[3]

Recent high resolution x-ray studies revealed a narrow and broad peak centered at the zone boundary position as shown in Fig. 2 Andrews[4] reported

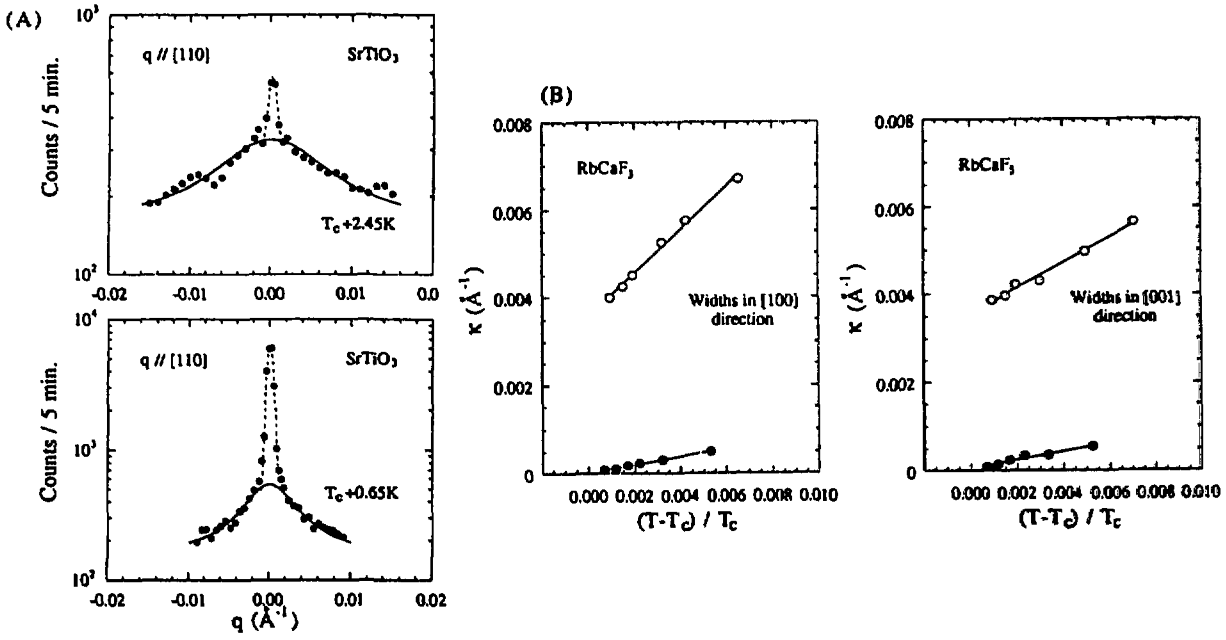

Figure 2

Fig. 2 (A) two length scales observed by Andrews[4] for SrTiO$_3$. (B) Anisotropy of short length scale and isotropy of long length scale observed by Ryan et al7 for RbCaF$_3$

the first observation of two length scales in SrTiO$_3$ (Fig. 2a) and more accurate line width measurements were later presented by McMorrow et al[5]. Fig 2b illustrates similar two inverse correlation lengths[7] κ_{L1} and κ_{L2} for RbCaF$_3$. The broad peaks (κ_{L1}) have Lorentzian profiles and are anisotropic, which reflects the anisotropic slopes of the phonon dispersion curves measured along the (100) and (011) directions about the R point. On the other hand, the narrow peaks (κ_{L2}) have a Lorentzian squared shape and are isotropic. The latter are observable only in a narrow temperature range near T_c $(T-T_c)/T_c \leq 0.05$.

Now, what is the relation between the new narrow peak in q space observed in the x-ray experiment and the central peak in ω space observed in the neutron studies? To clarify this point, it is necessary to characterize more precisely the q dependence of the central peak in terms of a neutron experiment. The soft phonon energy ω_{∞}^{2} follows a dispersion relation (q is measured relative to the zone boundary). This slope α is known to be temperature independent[3]

$$\omega_{\infty}^{2}(q) = \omega_{\infty}^{2} + \alpha\, q^{2} \tag{3}$$

and depend upon direction; namely α = 3200 meV^{2}A^2 for (100) and α = 1000 meV^{2}A^2 for (011) for SrTiO$_3$. Since integrated intensities of phonons are proportional to $1/\omega_{\infty}^{2}(q)$ the inverse correlation length κ_∞ is given by.

$$\kappa_\infty(T)=\sqrt{\frac{\omega_{\infty}^{2}(T)}{\alpha}} \tag{4}$$

The total integrated intensity is proportional to $\omega_0^{-2}(q)$ (Eq. 2) and if we assume δ^2 is q independent, κ_0 is given as:

$$\kappa_0(T)=\sqrt{\frac{\omega_{0}^{2}(T)}{\alpha}} \tag{5}$$

The quantities κ_∞ and κ_0 are calculated from the temperature dependence of ω_∞ and ω_0 measured in ref. 3 and are plotted in Fig. 3 for the [011] direction for SrTi0$_3$. Also shown are the inverse correlation lengths κ_{L1} and κ_{L2} determined by x-ray diffraction[4),5)]. The observed values of κ_{L1} lie between κ_∞ and κ_0, but closer to the latter. As T → T$_c$, both κ_0 and κ_{L2} approaches zero; however κ_0 remains an order of magnitude larger than κ_{L2}. Therefore the small value of κ_{L2} can not be explained by the central peak unless δ^2 is strongly q dependent and decrases rapidly with increasing q. This point can easily be checked by a neutron scattering experiment as described below.

As seen in Fig. 1, the central peak of SrTiO$_3$ can be easily separated out, in energy, from the phonon part, except for a very narrow temperature and q range near T$_c$. Even in these areas, the intensity of the central peak dominates the spectrum and the high resolution neutron study probes essentially only the central peak (Fig. 4) If δ is q dependent, the intensities of the central peak alone are given by (See Eq. 1 and 2).

$$I_{cent} \propto \frac{1}{\kappa_0^2+q^2} - \frac{1}{\kappa_\infty^2+q^2} = \frac{\delta^2}{\left(\kappa_0^2+q^2\right)\left(\kappa_\infty^2+q^2\right)} \tag{6}$$

This equation gives a Lorentzian like profile near Tc where $\omega_\infty^2 >> \kappa_0^2$ and its half width κ_c approaches κ_0 as T → T$_c$. At high temperature limits, it changes into a Lorentzian squared profile with κ_c approaching 0.64 κ_∞. If the basic

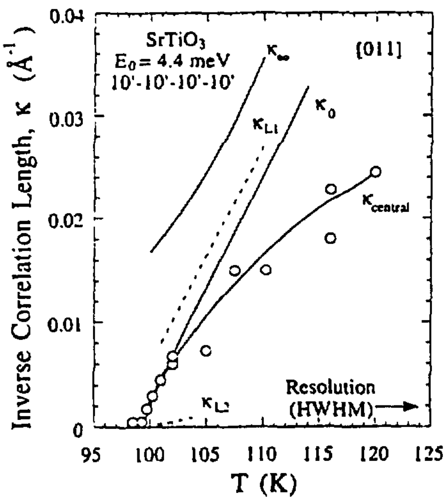

Fig. 3

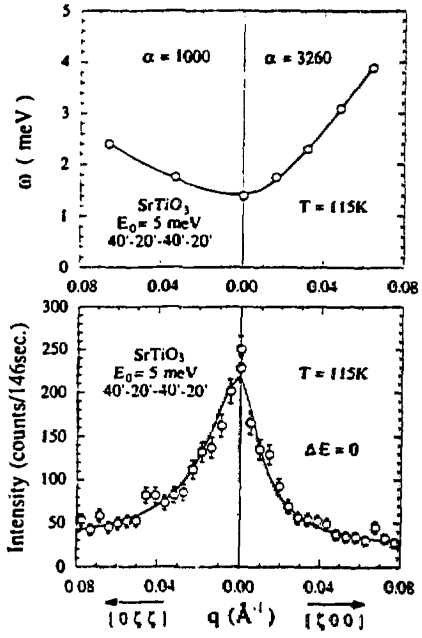

Fig. 4

Fig. 3 The inverse correlation length κ's derived for $SrTiO_3$. Open circles are current high resolution neutron data[8].

Fig. 4 Anisotropy of phonon dispersions observed for $SrTiO_3$. The lower figures illustrate similar anisotropy reflected in the central peaks at $\Delta E = 0$. These are results of the current joint experiment[8] with Cowley, Matsuda and Shapiro.

assumption of q independent δ^2 is correct, the observed profile of the central peak should reflect the anisotropy of κ_∞ is in the q space.

This key point is clearly demonstrated in Fig. 4, the data obtain at 115K. Moreover the observed line widths $\kappa_c(T)$ are in reasonably good agreement with the prediction of Eq. 6. The data taken near T_c with the better resolutions revealed the same characteristics. The highest resolution obtained so far employed $4.4E_i$, 10' collimation throughout with a PG(002) monochromator and analyzer. The resolutions (FWHM) are 0.003-0.004 Å^{-1}, depending upon the direction of the scan. These values are only a factor of two or three larger than the x-ray resolution used in Fig. 2. We can now conclude that the central peak is an integral part of soft phonon cross sections over a wide range of temperature (up to 180 K) and q (up to 0.1 Å^{-1}) and corresponds most closely with κ_{L1}

measured with x-rays. It does not correspond to the narrow q peak $\kappa_{1,2}$ in the x-ray profiles.

Can we conclude that the narrow component is missing in the neutron central peak profile? If so, the narrow peak must be highly localized in the near surface region or the "skin" of the crystal (a few microns) and can be detected only by x-rays. The answer is probably yes. But in order to be positive, it would be highly desirable to carry out neutron measurements with q resolution nearly identical to those of x-ray. This is actually possible for the current study, since the $SrTiO_3$ crystal has a nearly perfect mosaic width of 7 seconds of arc9). Combined with a perfect Ge(220) analyzer, one can reach the resolution of $0.001Å^{-1}$. This experiment, which is expected to be low counting, is now being planned.

What is the current physical picture of two length scales? The most attractive one is to assume two types of excitations7); one is the ordinary soft phonon within the framework of cubic lattice vibration. Impurities may create the central peak to modify the spectral weight. Another excitation of long length scale is a very different type of excitation into a tetragonal "embryo", near T_c. This has a finite size, is isotropic; and with the size growing as T approaches T_c. Most likely these "embryos" are highly populated near the surface so that it is more sensitive to x-rays.

The 100 K transition in SrTiO, is second order and the tetragonal distortion below T_c is extremely small. $KMnF_3$ and $RbCaF_3$ both show first order transitions and the lattice distortion at T_c are 1.0009 and 1.0002 respectively[6,7], within the detectable range of high resolution x-ray technique. There has been some experimental evidence presented 6),7) that the narrow component just above T_c does not appear at the cubic R points but at the q point corresponding to the low temperature superlattice Bragg position. The lattice distortion is sufficiently large for $KMnF_3$ and can be detected by high resolution neutron measurements10). In this case, the narrow peak should appear at a position slightly shifted from the central peak maximum; which would considerably enhance the detectability 10).

Very recently, similar two peak structures are observed for magnetic critical scattering of Ho by Thurston et al11). In this case, neutrons see both broad and sharp components and x-ray see only the narrow one. Further study of other structural and magnetic phase transitions would reveal how common these two length scales are near T_c.

ACKNOWLEDGEMENT

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