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Comparison between the neutron central peak and the x-ray quasi-Bragg peak in pure $KMnF_3$

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High-resolution x-ray and neutron-scattering experiments have been performed on the same sample of $KMnF_3$ in order to compare the temperature behavior of the neutron "central peak" and of the x-ray "quasi-Bragg" peak. It is found that the peak intensity of both the central and quasi-Bragg peaks evolves similarly as $(T-T_c)^{-\gamma}$ with $\gamma_{CP}=1.34\pm0.08$ and $\gamma_{QBP}=1.26\pm0.04$. This result, together with considerations about experimental conditions, strongly suggests that the central peak and the quasi-Bragg peak are the same feature even if they are not observed in the same range of temperature.

I. INTRODUCTION

Over the past two decades, a great deal of effort has been put into studying critical phenomena at structural phase transition[1,2] (SPT) with a renewed interest coming from the recent discovery of high-T_c superconductors which are known to undergo SPT. Among the points which still remain unclear are the presence and the origin in the inelastic light and neutron-scattering spectra of an elastic component, the so-called central peak (CP), which appears to diverge at the phase-transition temperature T_c.

First discovered by Riste *et al.*[3] in $SrTiO_3$ and subsequently in other perovskites,[4–6] the CP has now been observed in a variety of different systems[7–9] and has almost become a general rule for all SPT. Its origin is controversial although it is now generally believed that the CP is in many, if not most instances, defect related. This statement is strongly enhanced by the fact that, even in nominally pure crystals such as $SrTiO_3$ grown by different techniques, the CP strength can be drastically modified for different crystals while the soft-mode behavior basically remains the same.[10,11] Similarly, it has been shown[12] in KH_2PO_4 that annealing can suppress the CP. Although there is sufficient evidence suggesting that defects in nominally pure solids give rise to the CP, the nature of the defects remains a mystery.

The recent observation, by means of high-resolution x-ray scattering of a "quasi-Bragg" peak (QBP) in a series of different perovskites,[13–17] has raised new interest in the understanding of the central peak origin and leads to the obvious question: is the CP identical to the QBP? It has been argued that, since the QBP is observed over a much smaller range of temperature than the CP, its origin might be different.[15] However, as for the CP, it has been shown that defects also play a major role in the observation of the QBP.[14]

In an attempt to compare the CP and the QBP, we report in this paper a high-resolution x-ray scattering experiment using synchrotron radiation and an inelastic neutron-scattering experiment performed in the same crystal of nominally pure $KMnF_3$. This compound is known[18] to undergo, at 187 K, a slightly first-order transition from a cubic O_h^1 ($Pm3m$) phase to a tetragonal phase with $D_{4h}^{18}(I4/mcm)$ space group. The transition is driven by the slowing down of the triply degenerated R_{25} soft mode which involves alternating rotations of MnF_6 octahedra around the $\langle 001 \rangle$ cubic axes. First studied by Gesi *et al.*,[19] the critical neutron scattering in $KMnF_3$ was studied by Shapiro *et al.*[4] with a better energy resolution and they evidenced the presence of a CP which was observed up to 40 K above T_c. The high-resolution x-ray scattering experiments[13–17] performed with a rotating anode have shown that the QBP is only observable in a very narrow region $(T-T_c)<1$ K. However, it must be noted that, with the low-resolution mode, the range over which the QBP is observed is greatly increased to nearly 10 K. For this reason, it was worthwhile to reinvestigate the QBP measurement by means of synchrotron radiation which has the double advantage to providing high resolution and high flux.

II. EXPERIMENT

The neutron-scattering measurements were performed on the H9 triple-axis spectrometer situated at the cold neutron facility at the Brookhaven National Laboratory High Flux Beam Reactor. Pyrolytic graphite crystals were used to monochromate the incident beam and to analyze the scattered beam. Higher-order contamination was eliminated by using a Be filter. The incident and scattered beams were collimated with 60′-30′-20′-40′ soller slits and scans were performed at a fixed incident energy of 4 meV. The contribution of incoherent scattering

was measured and subtracted from all the data. The crystal was mounted with a vertical [110] zone axis in a cryogenerator and inserted in a helium-filled aluminum can to ensure a better thermal contact. Temperatures were controlled to better than 0.02 K. Typical energy and q (longitudinal, transverse, vertical) resolutions were 0.1 meV and $10^{-2}\times(1.5\times10^{-2})\times10^{-1}$ Å^{-3}. X-ray scattering experiments were performed on the X22B beam line at the National Synchrotron Light Source. Single Ge(111) crystals were used to select a 1.377 Å wavelength from the white beam. The scattered beam was analyzed with a (200) Ge analyzer. The typical resolution was 4.5×10^{-3} Å^{-1} in the longitudinal and 3.5×10^{-3} Å^{-1} in the transverse directions in the vicinity of the (0.5, 0.5, 2.5) R point.

A large single crystal of $KMnF_3$ was grown by the Czochralski technique by Dr. J. Y. Gesland (L. T. M., Le Mans, France) from highly purified starting materials. A typical pink-colored crystal of volume 8 cm^3 was obtained with well-defined cleaved [100] faces. A small part $1\times1\times0.2$ cm^3 was cleaved from the bulk crystal for the x-ray scattering experiments (no etching was made).

The mosaic spread measured with x rays yielded a value of 0.012°, while the neutrons gave a mosaic $<0.2°$. The lattice parameter at room temperature is 4.1860 Å. The crystal was mounted in a [110] zone allowing access to a $\frac{1}{2}(h,h,k)$ R point.

With neutrons, T_c was obtained by monitoring the scattering at the cubic (0.5, 0.5, 1.5) R point as a function of temperature. It was observed that, due to the large volume of the sample, a minimum time of 40 min was necessary to reach the thermal equilibrium. With x rays, T_c was measured by monitoring the sudden shift in the position of the (0,0,2) Bragg reflection. In both cases, T_c was found to be 186.7 ± 0.1 K.

III. RESULTS

A. Inelastic neutron scattering

In order to investigate the soft-mode and the central-peak characteristics, high-resolution constant-Q scans were made at the (0.5,0.5,1.5) R point at four temperatures corresponding to $T-T_c=3$, 10, 20, and 40 K (see Fig. 1). As evidence in this figure, there is an overdamped soft phonon and a central peak which are clearly separated at the higher temperatures. As $T-T_c$ decreases, the CP intensity increases and the separation be-

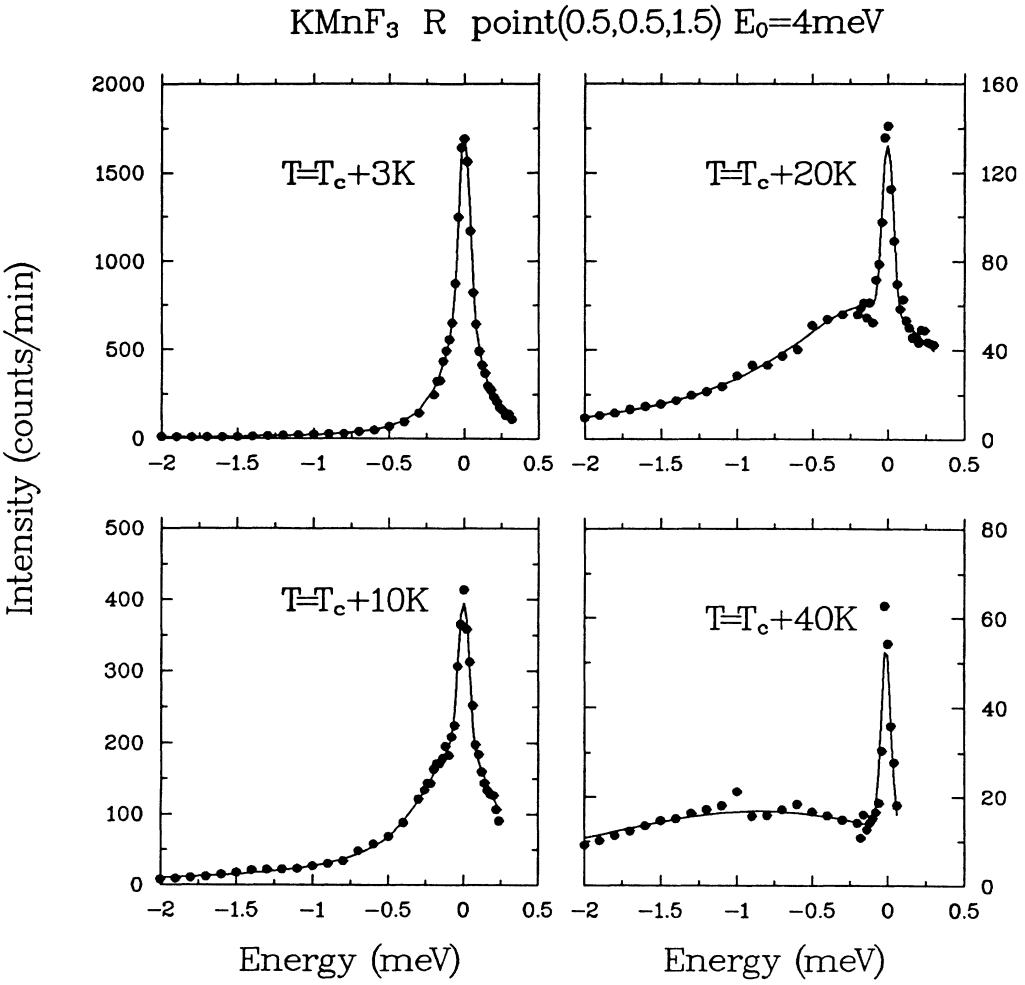

FIG. 1. Neutron constant-Q scans at the (0.5,0.5,1.5) R point of the Brillouin zone showing the presence of the overdamped phonons together with the CP at various temperatures.

tween the phonon and the CP becomes less apparent.

As previously presented in a detailed manner in Ref. 4, a scattering cross section which separates the respective contributions of the central peak and of the phonon side bands can be written as follows (for the limit $k_B T \gg \hbar\omega$):

$$S(\mathbf{q},\omega)=S(\mathbf{q},\omega)_{\rm ph}+S(\mathbf{q},\omega)_{\rm CP}$$

with

$$S(\mathbf{q},\omega)_{\rm ph}=\frac{k_B T}{\pi}\frac{F_{\rm in}^2(Q)\Gamma_0}{[\omega_\infty^2(\mathbf{q},T)-\omega^2]^2+\omega^2\Gamma_0^2},$$

$$S(\mathbf{q},\omega)_{\rm CP}=\frac{k_B T}{\pi}\frac{\delta^2(T)}{\omega_0^2(\mathbf{q},T)\omega_\infty^2(\mathbf{q},T)}e^{-\omega^2/2\sigma^2}$$

with

$$\omega_\infty^2(T)=\omega_0^2(T)+\delta^2(T)$$

and where k_B is the Boltzmann constant, Γ_0 is the damping constant, ω is the energy transfer, $F_{\rm in}(Q)$ is the inelastic structure factor for the soft mode, ω_∞ is the quasiharmonic frequency of the phonon, ω_0 is the renormalized frequency of the phonon, and σ is an energy width much smaller than that of the resolution function.

In the expression of $S(\mathbf{q},\omega)$, the q dependence is entirely contained in the anisotropy of the phonon frequency and the dispersion coefficients measured by Gesi *et al.*[20] were used to describe the anisotropy in the calculation. The data analysis is greatly complicated because of the overdamped nature of the soft mode and it is necessary to reduce the number of adjustable parameters in the cross section. We have assumed that the central peak response is simply given by a very narrow Gaussian having a temperature-dependent height $H(T)$ such as

$$S(\omega)=\frac{k_B T}{\pi}H(T)e^{-\omega^2/2\sigma^2}$$

with σ being much smaller than the HWHM of the resolution function.

For a particular setting of the spectrometer $(\mathbf{q}_0,\omega_0)$, the measured intensity can be calculated through the convolution of the scattering cross section with the four-dimensional resolution function $R(\mathbf{q}-\mathbf{q}_0,\omega-\omega_0)$ of the apparatus

$$I(\mathbf{q}_0,\omega_0)=A\int\int\frac{k_f}{k_i}S(\mathbf{q},\omega)R(\mathbf{q}-\mathbf{q}_0,\omega-\omega_0)d\mathbf{q}\,d\omega\ ,$$

where k_f and k_i are the initial and final values of the wave vector of neutrons, A is a scale factor which takes into account the volume of the crystal and other independent coupling parameters.

The first step in the calculations was to determine the damping constant Γ_0. This was achieved at T_c+20 K without serious difficulties since, at this temperature and with the high-instrumental resolution in energy, it was possible to clearly separate the CP and the phonon so that the obtained parameters are unique. The agreement between the calculated damping constant and that ob-

TABLE I. Results of the fit to the data according to the phenomenological formalism described in the text. The phonon frequency ω_∞, the scale factor A, and the CP intensity $H(T)$ are given for various temperatures.

T (K)	ω_∞ (meV)	A	$H(T)$
T_c+3	0.645±0.008	16.8±0.7	119±8
T_c+10	0.95±0.01	19.1±0.8	21.7±1
T_c+20	1.33±0.01	19.4±0.8	7.9±0.4
T_c+40	1.96±0.02	18.6±0.7	3.6±0.2

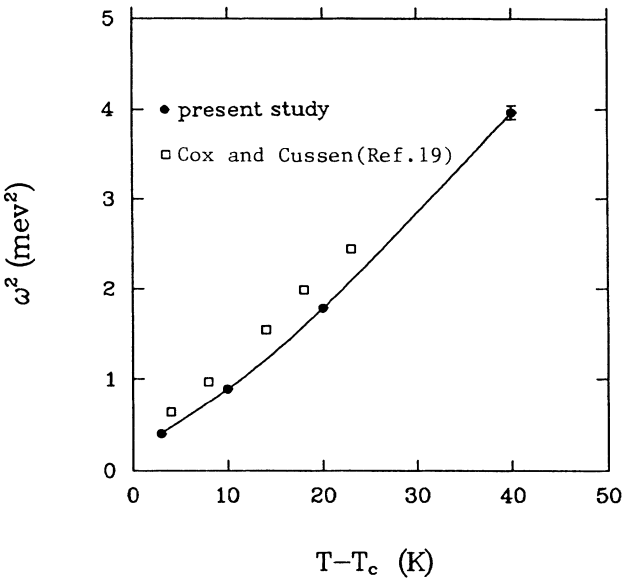

FIG. 2. Evolution of the phonon frequency as a function of temperature showing the agreement between our calculated data and those obtained by Cox and Cussen (Ref. 19) (the solid line is a guide to the eye).

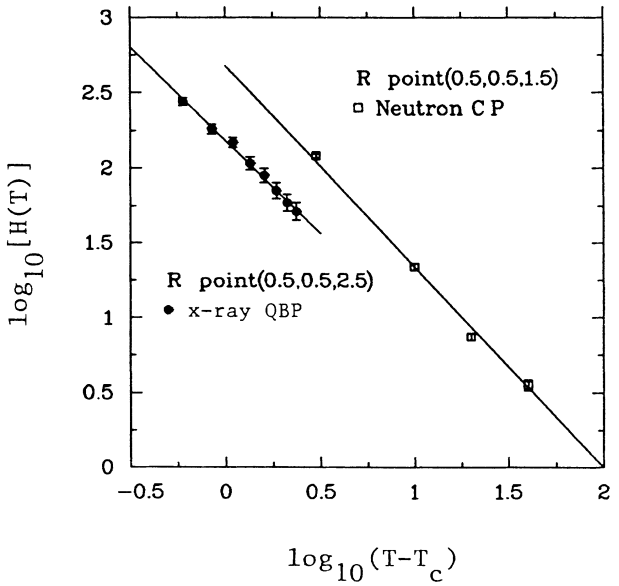

FIG. 3. Log-log plot of the CP (open squares) and of the QBP (solid circles) intensity vs $(T-T_c)$ showing the similarity between the temperature behavior of the CP and of the QBP; the solid lines are least-squares fit to the data.

tained at high temperature by Gesi *et al.*[20] is good and leads to $\Gamma_0=3.3$ meV (to be compared to 3.4 meV in Ref. 20). Γ_0 was held at this fixed value and three parameters, namely the scale factor, the CP height, and the phonon frequency of the R_{25} soft mode were allowed to vary for subsequent temperatures. The results of the fits are summarized in Table I. It can be seen that the overall scale factor is nearly constant and, as shown in Fig. 2, the phonon frequencies are very similar to those recently obtained by Cox and Cussen[19] in the doped material $KMn_{0.99}Mg_{0.01}F_3$. This is a good indication that substitutional impurities do not affect the temperature behavior of the phonon frequencies but mainly the transition temperature as theoretically evidenced by Dvorak and Glogar[21] and experimentally by Hastrings *et al.*[11] in $SrTiO_3$. Let us note, however, that these frequencies differ markedly from those obtained in $KMnF_3$ by Gesi *et al.*[20] who did not take into account the presence of the CP.

The CP intensity is plotted on a logarithm scale as a function of $\ln(T-T_c)$ in Fig. 3. The straight line is a fit to a power law

$$H(T)=A(T-T_c)^{-\gamma}$$

with $\gamma=1.34\pm0.08$. This result is considerably less than the exponent $\gamma=2.0$ recently obtained over the same range of temperature by Cox and Cussen[19] in $KMn_{0.99}Mg_{0.01}F_3$. This discrepancy is likely related to the fact that, in this latter case, the system contained substitutional impurities. This statement is enhanced by the results of similar measurements performed in the doped system $KMn_{0.99}Ca_{0.01}F_3$ which yield $\gamma=2.2\pm0.1$.[22] This is also a clear evidence that impurities do affect the temperature behavior of the CP.

B. X rays

The wave-vector dependence of the critical scattering above T_c was measured around the (0.5,0.5,2.5) R point. As previously reported, it was observed, as shown in Fig. 4, that the QBP width continuously decreases towards the instrumental resolution as T_c was approached from above. It is clear in that figure that only high-resolution measurements can provide a correct determination of the QBP linewidth and that the H9 neutron spectrometer and low-resolution x-ray spectrometers cannot measure this width in this temperature range. The very small values of the inverse correlation length, i.e., 0.0025 Å^{-1} at $T_c+0.5$ K, are characteristic of the QBP and make it differ from the soft mode which is associated to an inverse correlation length 10 times larger.[13–17] With the high flux available at the synchrotron and with a somewhat similar resolution as achieved with the high-resolution measurements performed with a rotating anode, it was possible to measure, in a reasonable time ($t<120$ s per point), some intensity for $T-T_c<5$ K, a temperature range considerably smaller than the neutron study. It must be noted that, owing to the very small reciprocal volume investigated with the high-resolution measurements, the contribution of soft phonons described by a Lorentzian term in Ref. 15 appears as part of the background. For a similar reason, it can be inferred that the measurement of the QBP intensity is not reliable when the QBP width becomes too broad which is the drawback of high-resolution measurements. That is why results were only analyzed in the range $T-T_c=0$–2.5 K. As evidenced in Fig. 3, the QBP peak intensity $H'(T)$ which defines the static susceptibility follows the power law

$$H'(T)=B(T-T_c)^{-\gamma'}$$

with $\gamma'=1.26\pm0.04$. This value is in very good agreement with the previous x-ray measurement $\gamma=1.24$ made by Nicholls and Cowley[17] in pure $KMnF_3$.

IV. DISCUSSION

The above results clearly show that, even with the use of powerful sources like the synchrotron, it is very

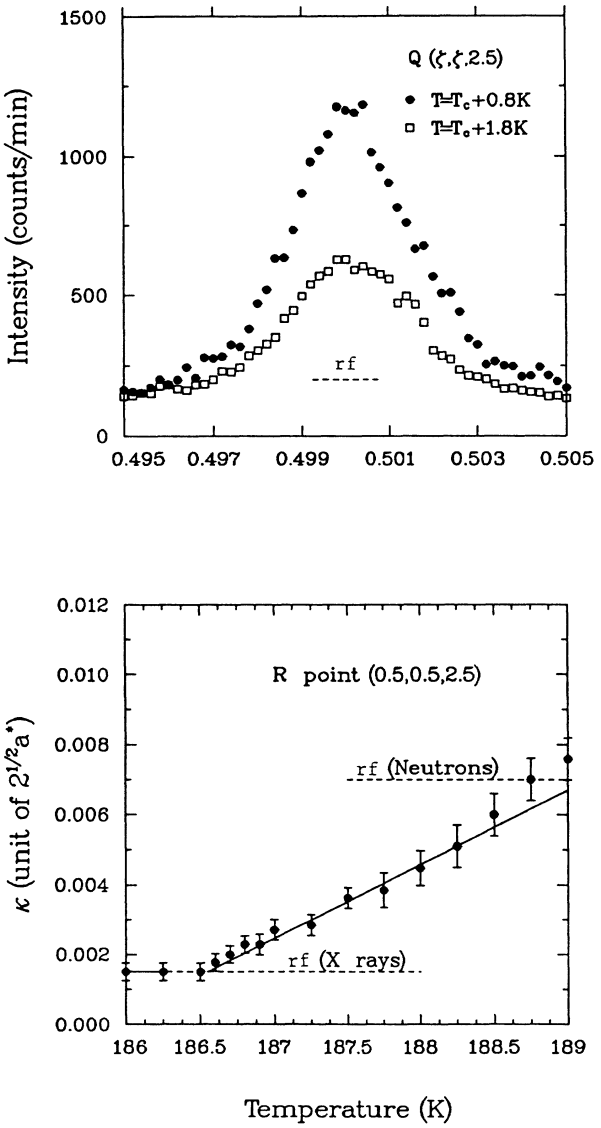

FIG. 4. X-ray scans about the (0.5,0.5,2.5) R point along the [110] direction of the cubic phase at $T_c+0.7$ K and $T_c+1.7$ K (top) together with the evolution of the inverse correlation length of the QBP in the [110] direction as a function of temperature (bottom) (note the difference between the resolution functions).

TABLE II. Comparative values of the experimental parameters for x rays and neutrons for the different measurements of the CP and QBP showing the correlation between the sensitivity of the probe (given by the product of the incident flux by the resolution volume and by the volume of the sample) and the extent δT of the temperature range over which the CP and the QBP have been observed.

Instr.	Flux. (particle/s mm^2)	$\Delta^3 q$ (Å^{-3})	Volume (m^3)	Product	δT (K)
Rot An. H.R.	10^7	10^{-7}[a]	10^{-11}	10^{-11}	1
Synchrotron	10^{10}	10^{-7}	10^{-11}	10^{-8}	5
Rot. An. L. R.	10^9	10^{-5}[a]	10^{-11}	10^{-7}	10
Neutron	10^4	10^{-5}	10^{-5}	10^{-6}	40

[a]Reference 19.

difficult to observe, over the same range of temperatures, the CP and the QBP. One reason is that with neutron scattering, the overdamped phonons impede any correct interpretation for $(T-T_c)<3$ K and with x-rays the broadening of the QBP is a major problem in the reliable measurement of its intensity above $T_c+2.5$ K. However, if we restrict ourselves in the temperature range where both the CP and the QBP have been measured, they do display a similar temperature behavior. Furthermore, the fact that the CP and the QBP are not observed over the same range of temperatures is not, in our point of view, a sufficient reason to assume that the CP and the QBP are of different origins. Indeed, the following major differences arise from the two types of measurements.

(1) X rays only probe a tiny volume of the sample, approximately 1 mm$\times$1 mm$\times 10\mu$m, whereas neutron probe in our case a 8 cm^3 volume which makes a difference of 5 orders of magnitude in favor of neutron sensitivity.

(2) X ray resolution functions are typically $10^{-3}\times10^{-3}\times10^{-1}$ Å^{-3} in the case of high resolution whereas a typical neutron spectrometer has a $10^{-2}\times10^{-2}\times10^{-1}$ Å^{-3} which once again makes a difference of two orders of magnitude in favor of neutrons.

(3) X-ray sources have intensities which can vary a lot according to the resolution of the instrument and to the nature of the source but generally they are more powerful than neutron sources which is, in this case, in favor of x rays.

In order to make a meaningful comparison, it is necessary to take into account all these factors which are summarized in Table II. In our opinion, the relevant parameter is the product of the reciprocal resolution volume, the volume of the sample, and the particle flux available in the incident beam. As shown in Table II, it is clear that this factor which measures the sensitivity of the probe to the measurement is much larger in the neutron case then for x rays. Furthermore, it can be seen that in case of x-ray measurements, the larger this factor, the wider the temperature over which the QBP is observed.

It is also clear that as T increases, the cluster size gets smaller and the x-ray measurements have some difficulty in distinguishing between the CP and the thermal diffuse scattering coming from the soft mode since the x-rays do not discriminate in energy. On the contrary, neutron measurements, as we have seen, have difficulty separating the CP and the soft mode as T approaches T_c because the phonon contribution becomes more and more part of the CP.

These results, together with the above considerations, show that the QBP and the CP are the same feature. A similar conclusion was recently drawn by Andrews[23] who attributes both the CP and the QBP to the existence of tetragonal distorted regions. In these regions, the magnitude of the tetragonal distortion is temperature independent as evidenced in $RbCaF_3$ (Refs. 13 and 14) and the clusters simply increase in extent as T_v is approached. Further progress in the understanding of the CP can be expected from measurements of the q width of the CP with both neutrons at zero-energy transfer and with the use of x-ray synchrotron sources. Let us finally point out that the large difference in γ observed in the doped and in the nominally pure material seems to indicate that the defects responsible for the CP in the nominally pure material are not of the substitutional type. It is clear that the influence of impurities on the CP still deserves more experimental work and these experiments are now in progress.

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