Phase Transitions

A phase transition is associated with a change of symmetry. For example at the ferromagnetic transition of Ni the symmetry changes from cubic to tetragonal at the onset of the ferromagnetism.

I hope to explain how neutron scattering has provided a large amount of information about phase transitions. I shall mostly describe the structural transition in $SrTiO_3$ but also use other transitions to illustrate some of the points I wish to make. The presentation will be a personal and historical view of the development of the field and of what we do and do not understand.

1. Landau Theory (1937)

$$F-F_0 = A P^2 + B P^4 + ...$$

$$T > T_C ,\ P = 0 ,\ A > 0,\ B > 0.$$

$$T < T_C ,\ P \neq 0 ,\ A < 0,\ B > 0.$$

$$F - F_0 = a (T - T_C) P^2 + B P^4 + ...$$

Where a and B are positive constants

$$P_S = [a (T_C - T) / 2 B]^{1/2} ,\ T_C > T .$$

$$X = 1/a (T - T_C)^{-1},\ T > T_C ,$$

$$X = 1/2a (T_C - T)^{-1} ,\ T < T_C .$$

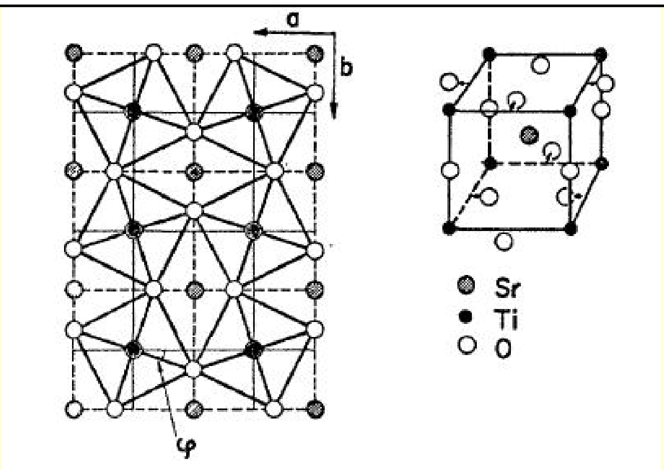
Soft Modes and Phase Transitions

In 1958 Cochran showed that, for structural phase transitions, the susceptibility was inversely proportional to the square of a normal mode frequency and this led to the prediction that:

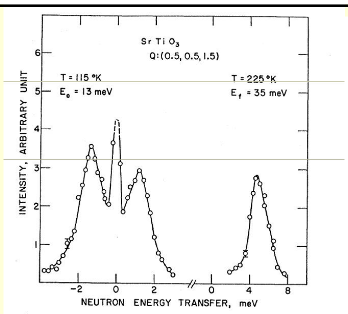
$\omega(qj)^2 = d\,(T - T_C)$ above T_C and

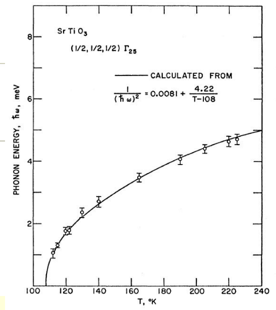
$\omega(qj)^2 = 2d(T_C - T)$ below T_C.

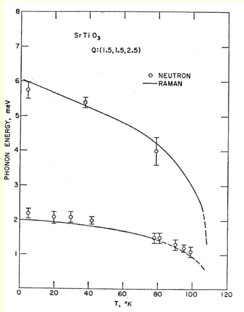
Structural phase transitions are dynamical instabilities of the normal modes. The frequencies decrease until at the transition they have zero frequency and below the crystal distorts to a new phase which stabilises the normal modes.



Strontium Titanate above 100K is cubic with the atoms at Sr (0,0,0), Ti (1/2,1/2,1/2) and O at (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2). Below 100K the structure distorts by a rotation of the oxygen octahedra to give a tetragonal structure. There are 3 order parameters P_x, P_y,and P_z and the wavevector q = (1/2,1/2,1/2)





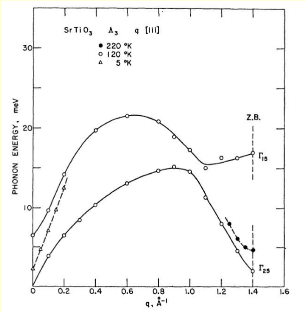


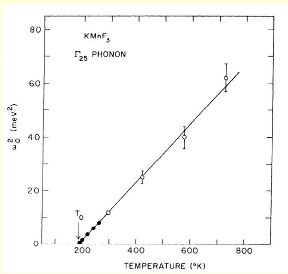
Neutron Scattering Results from $SrTiO_3$

The Intensity of scattering.

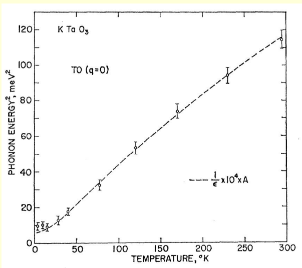
The temperature dependence of the frequency above and below the transition.

The phonon dispersion curves

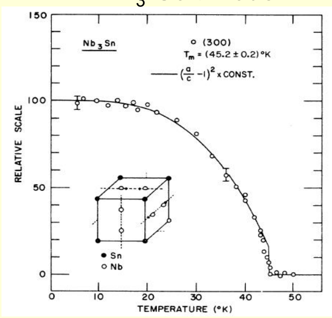




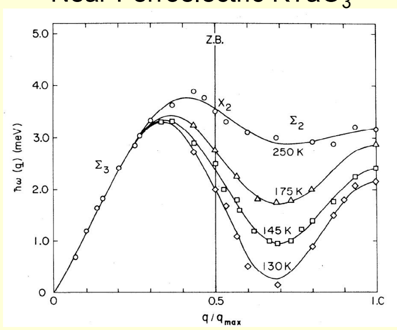
KMnF$_3$ Soft Mode



Near Ferroelectric $KTaO_3$



Acoustic Instability in $SnNb_3$



Incommensurate K_2SeO_4

2. Critical Phenomena

$T > T_C$

$\chi(T) = C_+ t^{-\gamma}$

$\zeta(T) = \kappa_+ t^{\upsilon}$

$T < T_C$

$\chi(T) = C_- |t|^{-\gamma}$

$\zeta(T) = \kappa_- |t|^{\upsilon}$

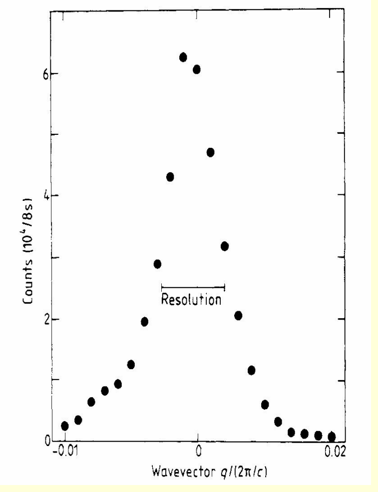
$P_s = P_0 |t|^{\beta}$

Where $t =(T-T_C)/T_C$'

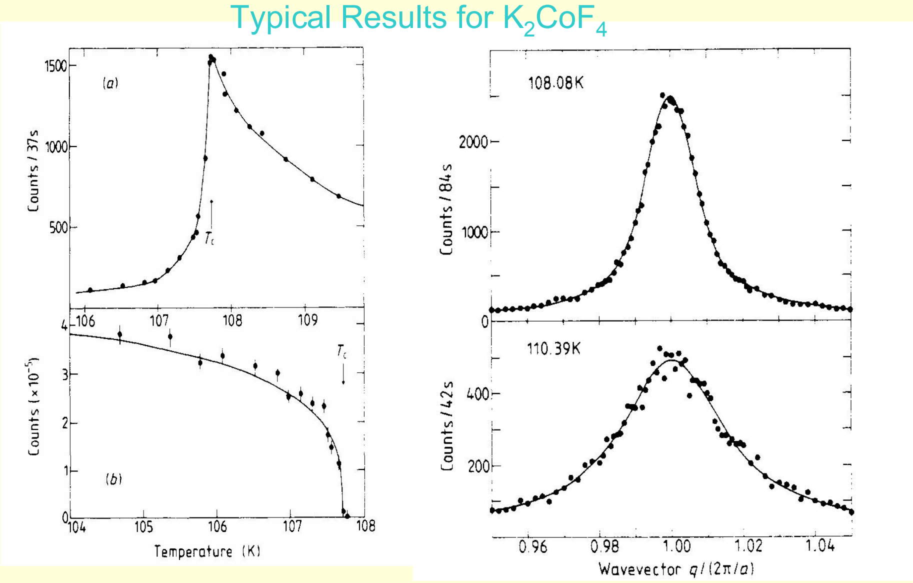
These results are universal because the exponents β, υ, and γ and the ratios C_+/C_- and κ_+/κ_- are the same for all materials with the same number of components and the same dimensionality. Note this is true for landau theory but for all phase transitions.

Experiments on d=2 n=1

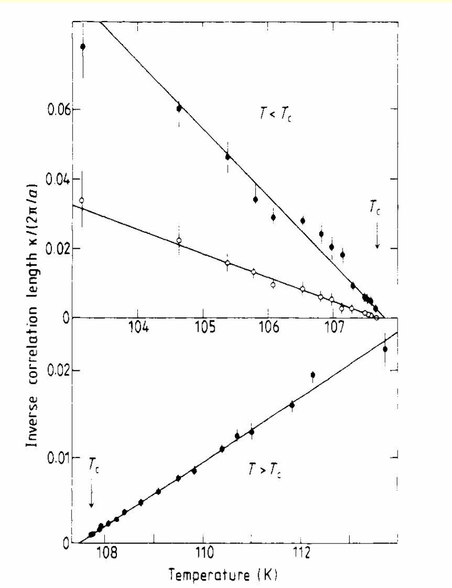
K_2CoF_4 is a close approximation to a 2d Ising model. The structure is tetragonal and the CoF_2 planes are separated by two KF planes. Consequently the exchange interactions between the planes are weak. The crystal field effects on the Co ions gives a ground state doublet and hence it produces an Ising model



Typical Results for K_2CoF_4



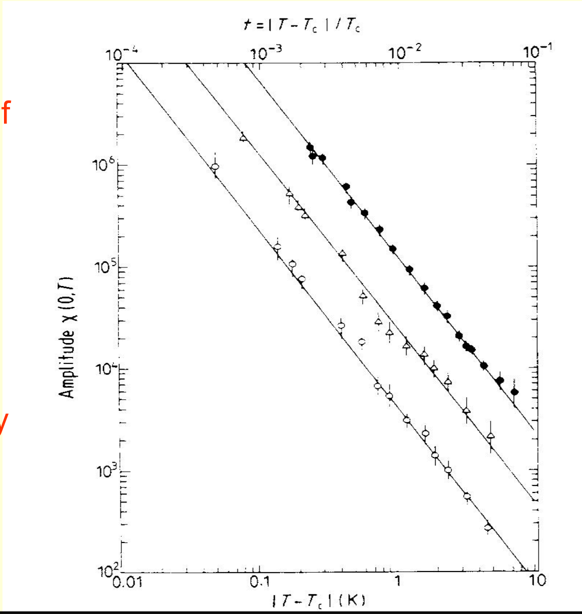
Correlation lengths



These results show that ν = 1.0, very different from 0.5 given by Landau Theory

Susceptibility

The intensity of the scattering gives the susceptibility. The results give γ = 1.75 again very different from Landau Theory



Summary for n=1, d=2

	Theory	K_2CoF_4
Order parameter β	0.125	0.155±0.02
Correlation length ν	1.0	1.04±0.05
Susceptibility γ	1.75	1.82±0.07
K_+/K_-	0.5	0.54±0.06
C_+/C_-	37.33	32.6±3.7

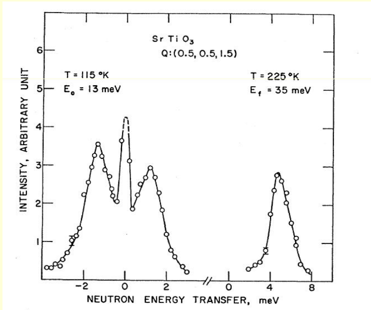
Other Systems

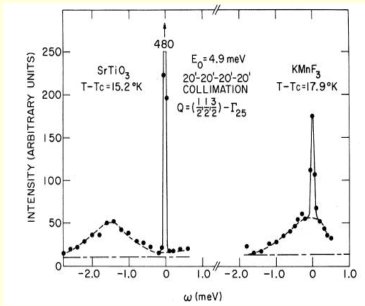
	Theory			Exp.t		
	β	ν	γ	β	ν	γ
n=1d=3	0.326	0.631	1.240	0.325	0.64	1.25
n=2 d=3	0.345	0.669	1.316	0.35	0.683	1.26
n=3 d=3	0.376	0.707	1.388	0.32	0.701	1.366
n=1 d=2	0.125	1.0	1.75	0.155	1.02	1.82
n=1d=3 random	0.325	0.70	1.39		0.73	1.44

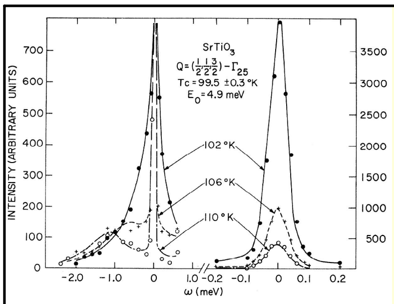
3. Two-Time Scales or the Central Peak

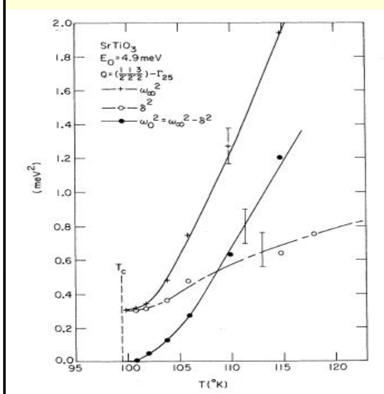
We have seen that scaling theory has a single distance scale, the correlation length, and that this is a very successful theory for magnetic phase transitions. Since there is only one distance scale it follows that there is only one time scale. In 1972 this was shown to be incorrect for $SrTiO_3$

This figure shows the scattering from $SrTiO_3$. Note the elastic scattering that we assumed came from order contamination. Riste used a time-of-flight instrument that does not have order contamination and showed this scattering was real and came from the critical fluctuations as shown on the second figure









The results were analysed by replacing the normal mode frequency with:

$\omega^2(qj) + \delta^2/(1+i\omega\tau)$.

The plots show this formula gives a good account of the results showing that there is a coupling to a new relaxation process.

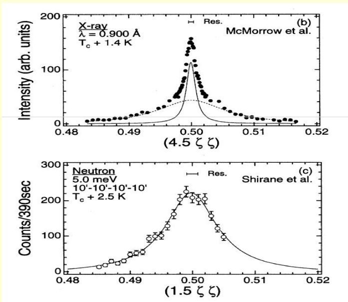
What is the process?

1. Intrinsic interactions between the normal modes. It has not proved possible to get the right order of magnitude for the relaxation time.

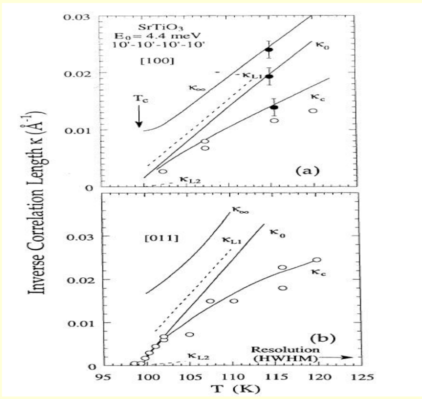
2. Extrinsic defects in the sample. Unknown defects can explain anything. Why does the effect occur in many different crystals. Why does introducing many defects give only a small increase in the magnitude of the effect.

3. The final conclusion is that the origin is not so far understood although the observations basically contradict one of the main assumptions of critical phenomena

4. Two-length Scales

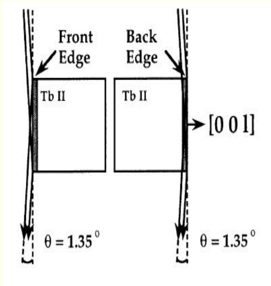


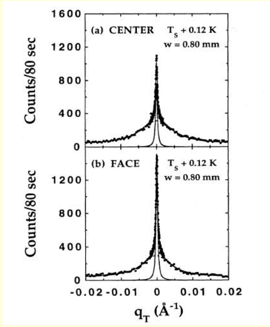
This figure shows that the result of the x-ray scattering is much narrower than that of the neutron scattering

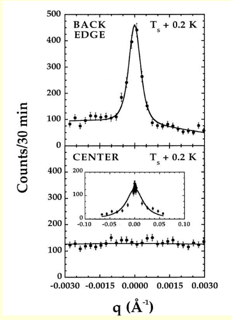


The x-ray scattering has two parts. One is the same as the neutron one and the other is much longer

Surfaces and Neutron Scattering

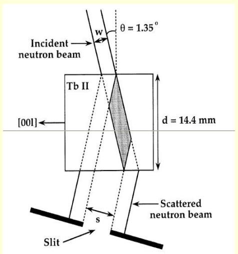


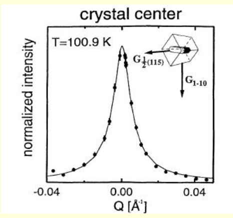


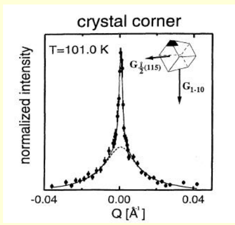


Scattering coming from a surface is narrower than that from the bulk. The long length scale is associated with the surface

High Energy X-ray Scattering







The x-ray scattering shows more and narrower scattering from $SrTiO_3$ from a corner than from the bulk.

Where does the second length scale come from?

- 1. It is associated with the surface
- 2. Conventional critical phenomena says this should not matter there is a single scale length
- 3. Defects at the surface could be the origin
- 4. Why do strontium titanate, Tb and uranium dioxide all have the same behaviour
- 5. Is it intrinsic and due to relaxation of the surface by static surface waves.

Summary and Conclusions

- 1. Landau theory is a good description so long as we do not look too carefully and explains many features of phase transitions.
- 2. Critical Fluctuation theory is also successful especially for describing the statics and for many magnetic systems and is generally accepted
- 3. many systems show central peaks and two time scales. The only theory of this is that it is due to defects but this seems unlikely as it occurs in very different materials.
- 4. Two length scales are observed and are associated with surfaces. It is not yet known whether these observations are due to defects or intrinsic in origin.
- 5. There is still much to do to understand phase transitions.

References

1. Stanley: Introduction to Phase transitions and Critical Phenomena
2. Collins: Magnetic critical Scattering
3. Bruce and Cowley: Structural Phase Transitions
4. Cowley and Shapiro: J. Phys. Soc. Japan, 75, 111001 (2006)