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PLENARY SESSION.

Structural phase transitions : defects and dynamics

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Résumé. — L'application des techniques modernes de diffusion de la lumière à l'étude des transitions de phase structurales sera discutée, en insistant sur les déviations observées expérimentalement avec la théorie simple de type *mode mou*, pour un système sans défaut. Le phénomène du *pic central*, observé dans plusieurs spectres sera discuté, et sera appliqué, ou bien comme un effet de modes collectifs à basses fréquences, ou bien comme résultant de défauts. Des processus dynamiques comme les fluctuations d'entropie ou de densité de phonons contribuent, par couplage non linéaire, à un pic central *inélastique*. Par ailleurs, des processus statiques, associés aux défauts, sont responsables pour les pics centraux *élastiques*, qui se manifestent dans de nombreux cas. Les matériaux discutés seront entre autres, le KDP, le $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, le SrTiO_3 , et le $\text{K}(\text{H}_x\text{D}_{1-x})_3(\text{SeO}_3)_2$.

Abstract. — The application of modern light scattering techniques to the study of structural phase transitions is reviewed with emphasis upon observed departures from predictions of the simple soft mode theory for defect free systems. Particular attention is given to the so-called *central peak* phenomena evident in several light scattering spectra which arise from (a) very low frequency collective excitations and/or (b) defects. Such dynamic processes as entropy fluctuations and phonon density fluctuations are shown to contribute, via non linear coupling, to *inelastic* singular central peaks. In addition, static processes — associated with defects — are assigned responsibility for singular *elastic* central peaks accompanying several transitions. Materials to be discussed include KDP, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, SrTiO_3 , and $\text{K}(\text{H}_x\text{D}_{1-x})_3(\text{SeO}_3)_2$.

1. **Introduction.** — A discussion of structural phase transitions and critical phenomena may appear out of place at a conference devoted to defects in as much as departures from perfection are generally regarded to suppress or distort the strong singularities which constitute the essentials of critical behaviour. Indeed a major constraint in the experimental pursuit of transition phenomena has been the attainment of samples which are as *free of defects* as possible. Adherence to this constraint has produced over the past decade a remarkable advance in our understanding of critical phenomena, including their universal aspects, in a wide variety of systems (superfluids, magnets, ferro-electrics, etc.). Our present relatively complete understanding of phase transitions in ideal systems has set the stage for a more quantitative consideration of transitions in defected systems. Such considerations are still in a fairly primitive state theoretically, and very few systematic experimental investigations have thus far been carried out. The purpose of this paper is to put into perspective the status of structural phase transitions and critical phenomena in defected solids by (i) reviewing briefly the behaviour in *pure* systems, (ii) describing some theoretically predicted modifications of this behaviour induced by various types of defects, and (iii) outlining the (primarily spectroscopic) experimental evidence collected to date which may bear on these predictions. We are led to conclude that the subject of phase

transitions in defected systems is on the threshold of an active future.

2. **Structural phase transitions in « ideal » solids.** — We shall restrict our discussion to *continuous* or *second-order* structural phase transitions — those in which the order parameter goes to zero continuously at T_c . For the sake of simplicity we shall further restrict our attention to *displacive transitions* — those in which the microscopic order parameter $\psi(\mathbf{r}, t)$ is the eigenvector of a particular normal mode of the parent crystal structure. The dynamics of such systems are embodied in the *soft mode* and its interactions with other degrees of freedom.

All of the properties relevant to a phase transition can be expressed in terms of order parameter space-time correlation functions : $\langle [\psi(0, 0)]^n [\psi(\mathbf{r}, t)]^m \rangle$. The most common and useful of these correlation functions are [1]

$$\begin{aligned}\psi_0 &\equiv \langle \psi \rangle ; \langle \psi^2 \rangle \equiv \langle \psi(\mathbf{r}, t) \psi(\mathbf{r}, t) \rangle \\ G_1(\mathbf{r}, t) &\equiv \langle \psi(0, 0) \psi(\mathbf{r}, t) \rangle \\ G_2(\mathbf{r}, t) &= \langle \psi^2(0, 0) \psi^2(\mathbf{r}, t) \rangle\end{aligned}\quad (1)$$

where the brackets signify averages over the appropriate equilibrium ensemble. The space-time Fourier transforms of these functions are often rather directly measurable, as well as being amenable to theoretical calculation. ψ_0 is simply the macroscopic order

parameter $[\beta]$. $G_1(0, 0)$ is essentially the static susceptibility $[\gamma]$. $G_2(0, 0)$ is the specific heat $[\alpha]$. Each of these will be described near T_c by the appropriate critical exponent indicated in the square brackets above. A major and successful concern of modern theory has been to relate and to calculate the critical exponents for various universality classes taking fluctuations (which are neglected in mean field theory) properly into account. As far as static properties are concerned, this effort has been quite complete [2]. For dynamic properties, however, which require treatment of the *unequal time* correlation functions, theoretical predictions are less extensive [3].

Nevertheless it is well known that the fundamental dynamic information is contained in the space and time dependent susceptibility

$$\chi_\psi(\mathbf{r}, t) \equiv \langle \psi(\mathbf{r}, t) \psi(0, 0) \rangle.$$

Its Fourier transform is closely related to the so-called dynamic structure factor $S(\mathbf{q}, \omega)$

$$S(\mathbf{q}, \omega) = - (n(\omega) + 1) \text{Im} \chi_\psi(\mathbf{q}, \omega) \quad (2)$$

which may be rather directly probed by inelastic neutron, or light scattering experiments [1, 4]. Neutron scattering measures $G_1(\mathbf{r}, t)$. Depending on crystal symmetry, light scattering measures $G_1(\mathbf{r}, t)$ or $G_2(\mathbf{r}, t)$. In the simplest, quasi harmonic approximation, the corresponding dynamic susceptibility may be written [5] :

$$\chi_\psi(\mathbf{q}, \omega) = \bar{\chi}_0(\omega_q^2 - \omega^2 - 2i\Gamma_q \omega)^{-1}. \quad (3)$$

The divergence of the static ($\omega = 0$) susceptibility

$$\chi_\psi(\mathbf{q}, 0) = \frac{\bar{\chi}_0}{\omega_q^2} = \text{constant} |T - T_c|^{-1} \quad (4)$$

implies a vanishing of ω_q^2 as $T \rightarrow T_c$

$$\omega_q^2 = \text{constant} |T - T_c|. \quad (5)$$

This softening or critical slowing down is the essence of the soft mode description of structural phase transitions. Within the quasi harmonic approximation the critical dynamics will produce a collapsing pair of Lorentzian peaks (at $\pm \omega_q(T)$) in the scattered spectrum.

This simple behaviour is, however, almost never observed in real systems for at least two reasons. First, it does not take into account anharmonic effects such as the coupling between the soft mode and other dynamic degrees of freedom. Second, it ignores completely any effects which impurities or defects might have on either the static or dynamic critical phenomena. We shall end this section with a brief consideration of the first and shall discuss the second in the next section.

Many of these effects can be formally described by [6]

$$S(\mathbf{q}, \omega) = - (n(\omega) + 1) \text{Im} \chi_T(\mathbf{q}, \omega) \quad (6)$$

where

$$\chi_T(\mathbf{q}, \omega) = \sum_{i,j} F_i F_j \chi_{ij}(\mathbf{q}, \omega). \quad (7)$$

The χ_{ij} 's are elements of the matrix describing the full set of coupled modes. Defects can be accommodated here through χ_D as a delta function for frozen defects or as a Lorentzian for mobile defects, where the characteristic frequency measures the defect mobility. The F_i 's measure the coupling of the experimental probe (photon or neutron) to the i th mode. Full discussion of equation (7) is given elsewhere [5]. Let us consider only the simple situation of two coupled modes. Then

$$\chi_{ii} = \frac{\chi_i}{1 - A^2 \chi_1 \chi_2}; \quad \chi_{12} = \chi_{21} = \frac{A \chi_1 \chi_2}{1 - A^2 \chi_1 \chi_2} \quad (8)$$

where A is the coupling strength between modes 1 and 2.

In the familiar case where 1 = soft optic mode and 2 = acoustic mode, $S(\mathbf{q}, \omega)$ will consist of two pairs of Lorentzians. That is the result when both modes are underdamped, propagating excitations. The above description however holds as well when either or both of the modes is overdamped. For example, mode 2 is diffusive

$$\chi_2(\mathbf{q}, \omega) = \bar{\chi}_2(1 - i\omega\tau_q)^{-1}; \quad \tau_q^{-1} = Dq^2. \quad (9)$$

The coupled mode spectrum will then contain an additional central peak, where frequency width $\Gamma_q = Dq^2$ far from T_c , but which will critically narrow as the soft mode approaches zero frequency, through what is essentially a *level repulsion* between the interacting modes.

More generally, any degree of freedom with the appropriate symmetry will modify the critical dynamics even though it may not itself be singular near T_c . The complexity of this modification is directly related to the complexity of the uncoupled response function $\chi_2(\mathbf{q}, \omega)$ and to the mode coupling strength A^2 . The detailed spectral shape $S(\mathbf{q}, \omega)$ will further be influenced by the ratio F_1/F_2 . Complexities have frequently been observed near structural transitions in the form of an additional central peak [7] whose intensity diverges near T_c . This is usually accompanied by an arresting of the soft mode frequency decrease and by a transfer of scattering intensity from the soft mode doublet into the central peak.

However, the central peak phenomenon has continued to defy unambiguous or general explanation. Recent high resolution light scattering experiments [7] have shown that there are several different microscopic central peak mechanisms at work, which divide broadly into two classes : (a) *intrinsic* and (b) *extrinsic* or defect related. The intrinsic mechanisms thus far considered theoretically and observed experimentally are all dynamic in nature and hence

give rise to central peaks of finite frequency width. The value of this width and its dependence upon temperature, wave vector, and scattering geometry may be used to distinguish among the various intrinsic mechanisms. Extrinsic or defect related central peaks may be either static or dynamic depending on factors discussed below.

3. Theoretical considerations of transitions in defected systems. — The types of effect which defects may have on structural transitions fall into three classes : (i) The transition temperature may be shifted or smeared. (ii) The static critical exponents may be altered — i.e. crossover to a different universality class may occur. (iii) The dynamic response function may change through soft mode coupling with defects, through defect induced coupling of the soft mode to other formerly orthogonal degrees of freedom, or through the formation of local modes [8, 9].

Halperin and Varma [10] have categorized defects according to symmetry and mobility. Both static and dynamic consequences are indicated in table I. *Symmetry breaking defects* will either increase or decrease T_c depending on whether they are relaxing or frozen. A *relaxing* symmetry breaking defect will tend to induce a local nonzero value to ψ above T_c^0 in response to the diverging susceptibility. The ability of the defects to relax permits alignment of the locally induced ψ 's and hence leads to long-range order at $T_c > T_c^0$. *Frozen* symmetry breaking defects on the other hand will result in local nonzero ψ 's which are randomly directed. The result is in effect a spatial *fluctuation* in $\psi(\mathbf{r})$ which *opposes* the attainment of long range order and hence lowers T_c below T_c^0 .

The weakly perturbed *non-symmetry breaking defect* will couple to ψ only in higher order — through energy terms like ψ^2 and will have a relatively weak effect on T_c .

The effects on universality class have not yet been thoroughly explored. Obviously within MFT there can be no change since MFT admits of only one universality class. In so far as static phenomena are concerned, alteration of the universality class beyond MFT depends again on defect symmetry and mobility. For completely mobile defects (symmetry breaking or not) Halperin and Varma [10] expect *no change in asymptotic critical behaviour provided that $(T - T_c)$ is corrected to refer to measurements at constant chemical potential rather than at constant defect concentration*. For frozen symmetry breaking defects Imry and Ma [11] predict deviations from pure system asymptotic behaviour for any system with spatial dimensionality d less than 6, but explicit calculations for $d < 3$ systems have not been carried out. For quenched defects (trapped in a given unit cell, but able to relax locally with it) modified static critical behaviour is expected, and *crossover* to a different universality class can occur.

The dynamic situation is even more complicated. In pure systems one expects that the renormalization group theory refinements of MFT will change the detailed shape of the dynamic response and may alter the dynamic critical exponents, but should not result in additional *characteristic frequencies* — i.e. those unrelated to the mean field soft mode. The dynamics of the quenched non-symmetry breaking defect system have been studied by Grinstein *et al.* [12] who find a small departure of the dynamic critical exponent, X , from its pure system value. Halperin and Varma argue that the same applies to the quenched symmetry breaking defect case. For mobile defects the ultimate dynamic critical behaviour should be that of the appropriate pure system. More detailed considerations beyond MFT on the one hand and beyond the quasi harmonic phonon approximation on the other await future theoretical effort.

4. Experiments in defected solids. — Until quite recently experiments on structural transitions in defected solids were performed by accident rather than intent. Although it was not long after its discovery [13] that the central peak phenomenon was speculatively attributed to defects [14], definitive investigation of this speculation has only just begun to be pursued. Indeed it has only recently become clear that the early view of the central peak as a single (and universal) phenomenon is incorrect. The contradictory requirements of increasing resolution and contrast for a long time prevented distinguishing static from dynamic central peaks in both neutron and light scattering experiments. However, quite recent high resolution light scattering experiments have verified and measured the *dynamic* character of singular central peaks in several structural transitions. In no case to date, has any of these dynamic central peaks been successfully associated with mobile defects, but rather they have been accounted for by anharmonic interactions among intrinsic excitations (e.g. phonon density fluctuations, phasons, entropy fluctuations). In addition, of the other central peaks which clearly originate from defects some have been examined only under sufficient spectral resolution to set an *upper limit* on possible defect mobility. Static defect related central peaks have been verified in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ [6] in KDP [15] and in $(\alpha\text{-}\beta)\text{SiO}_2$ [16].

Clear evidence exists in several cases for both intrinsic and extrinsic (defect related) central peaks. Let us briefly describe these ($\text{Pb}_5\text{Ge}_3\text{O}_{11}$, SrTiO_3 and KH_2PO_4) before considering the purely extrinsic examples comprising the $\text{K}(\text{H}_x\text{D}_{1-x})_3(\text{SeO}_3)_2$ family.

$\text{Pb}_5\text{Ge}_3\text{O}_{11}$ experiences a second order non piezoelectric (C_{3h}^1) to ferroelectric (C_{3h}^1) transition at $T_c = 451\text{ K}$. Following neutron scattering studies of soft mode behaviour which observed but failed to resolve singular central peak behaviour, a coordinated series of high resolution Raman and Brillouin scattering experiments were carried out. Full details appear

elsewhere [6]. For our purposes the new findings can be summarized as follows. The soft $A_{1g}(q=0)$ mode is underdamped well below T_c ; for

$$(T_c - T) > 55 \text{ K}$$

it softens as predicted by MFT; for

$$10 \text{ K} < (T_c - T) < 55 \text{ K}$$

it is overdamped with a singular width of

$$\omega_s^2/\Gamma_s = b'(T_c - T),$$

where $b' = 12 \text{ GHz/K}$; for $(T_c - T) < 10 \text{ K}$ the overdamped soft mode wing ceases to change and a new dynamic but narrow central component grows up. This component narrows from $\sim 15 \text{ GHz}$ to $\sim 4 \text{ GHz}$ as $T \rightarrow T_c$ and acquires a complex low frequency lineshape due to its interaction with the LA phonon. The integrated intensity of this dynamic C.P. diverges weakly below T_c (consistent with RGT predictions for a uniaxial dipolar system) and persists slightly above T_c . Its behaviour is consistent with that expected for phonon density fluctuations, coupled to the soft A_{1g} phonon.

In addition, a more strongly singular *elastic* central peak of the same A_{1g} symmetry appears. This feature has been determined by a combination of experiments to be narrower than $\sim 10 \text{ Hz}$. Its behaviour is consistent with that expected from *frozen symmetry breaking defects*. However, no correlation was found between the local value of $T_c(r)$ (observed to vary by $\pm 3 \text{ K}$ in different regions of the crystal) and the elastic central peak intensity. Thus those defects responsible for the elastic central peak are apparently not dominant in shifting T_c . The complicated temperature dependent spectral lines shapes observed in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ have been quantitatively reproduced using the coupled mode approach of equation (7) involving the soft optic mode, its relaxing self energy, and the LA phonon. The static central peak occurs as a non interacting addition to the dynamic response, implying that the defects are sufficiently dilute that the condition $N\xi^3 < 1$ is satisfied for $|T - T_c|/T_c$ as small as 5×10^{-4} . Figure 1 illustrates the complete singular spectrum at T_c . Figure 2 compares the intensity divergences for the static and dynamic C.P.'s in lead germanate.

The unit cell doubling cubic (O_h^1) to tetragonal (D_{4h}^{18}) transition in SrTiO_3 has been studied by several probes (light, neutron, X-ray and γ -ray scattering, ultrasonics, EPR) which have provided conflicting values for the width of the central peak. At present, the evidence suggests that it contains both an intrinsic and an extrinsic component. Depolarized light scattering spectroscopy [17] measured a dynamic C.P. linewidth of 15 GHz , which when coupled to the TA phonon reproduced the observed spectra. However, the inferred behaviour of the soft mode frequency very close to T_c suggested the presence of a much

Fig. 1. — Composite mode spectrum of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ at $T = T_c$ showing the overdamped soft mode wing, w, the L-A-Brillouin peaks B, the dynamic central peak, D, and the static central peak, S.

Fig. 2. — Integrated intensities of the static (solid curve) and dynamic (dashed curve) central peaks in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ near T_c . The dashed curve intensity has been amplified fivefold for comparative display purposes.

lower frequency process ($< 300 \text{ MHz}$) which could not be directly observed in the light scattering experiments. Recent neutron scattering experiments [18] have confirmed that the central peak intensity in SrTiO_3 increases (sublinearly) with oxygen vacancy concentration, confirming the existence of an extrinsic component in SrTiO_3 . The observed decrease in T_c with increasing vacancy concentration would suggest that the defects are symmetry breaking and mobile. The lack of directly observed linewidth and the sublinear dependence of C.P. intensity on concentration call for further work before theory is confirmed. The presence of two singular central peaks in SrTiO_3 (the directly observed $\tau_1^{-1} = 15 \text{ GHz}$ intrinsic, and the inferred $\tau_2^{-1} < 0.3 \text{ GHz}$ presumably extrinsic) would account for all the apparently conflicting observations to date on this transition. Nevertheless a systematic study with defects of known identity, symmetry and concentration is yet to be done.

The piezoelectric-ferroelectric transition at 121 K in KDP is very slightly first order, but is one of the

most thoroughly studied of all structural transitions. A diverging but unresolved central peak has first noted near T_c in early Brillouin scattering experiments [19]. Recently using very high resolution, Lakagos and Cummins [19] found that, above T_c , the complete Raman-Brillouin spectra could be quantitatively fit by the familiar mode coupling formalism described above and that the static central component appeared as a mere non interacting additive to the spectrum. Using photographic techniques, Durvalsula and Gammon [15] have confirmed that this central component is predominated elastic. Immediately below T_c , a narrow but clearly dynamic component to the central peak has been measured by Mermelstein and Cummins [20]. Seen only within ~ 1 K of T_c , the component has a linewidth of ~ 50 MHz, in close agreement with that predicted for entropy fluctuations (62 MHz) for right angle scattering in KDP. Such a component is expected below T_c because of the generally allowed linear coupling between the order parameter and temperature fluctuations and the singular behaviour of $(d\psi_0/dT)$.

Progress has been made recently in understanding the elastic C.P. in KDP. Courtens' suggestion [21] that it might arise from frozen and deuterium impurities (present as a naturally occurring isotope of hydrogen) has not been supported by his own subsequent experiments [22]. He has succeeded in *annealing* away the static central peak. (Annealing for 18 hrs at 140 °C reduced the singular elastic C.P. intensity by nearly a factor of 50.) The combined time-space behaviour of the elastic peak intensity suggests that it arises not from impurities but from dislocations or growth strains.

The related $K(H_xD_{1-x})_3(SeO_3)_2$ system has shown evidence of both annealable and persistent defects in their Brillouin spectra [23-25]. For $x = 1$, $T_c = 212.8$ K. For $x = 0$, $T_c = 302$ K. Yagi and his coworkers [23-25] have studied this system for $x = 0, 0.05, 0.95$ and 1, and have observed two kinds of apparently elastic central peaks (an upper limit of ~ 200 MHz has been placed on the C.P. linewidth). For $x = 1$, as shown in figure 3, temperature cycling and annealing near T_c can reduce the C.P. intensity by nearly an order of magnitude. The annealable C.P. however, is polarized (VV) orthogonally to the scattering from the soft acoustic mode (VH). It has attributed to strains rather than impurities. For the mixed samples ($x = \sim 0.95$ and ~ 0.05) a depolarized (VH) and non annealable singular C.P. is seen in addition. This has been attributed to scattering from the appropriate (D or H) minority impurity. While measurements to date have not definitely established the degree of mobility (if any), the identity of the defects is clear. Their concentrations, however, are too large to expect the available theories to apply very close to T_c . This system seems

Fig. 3. — Brillouin spectra (VV + VH) of $KH_3(SeO_3)_2$: (a) as grown sample, (b) sample after annealing at -30 °C for 24 h. $T_c = -61.4$ °C. After ref. [23].

a good candidate for future experimental and theoretical effort.

5. Summary and conclusions. — The progress in understanding structural phase transitions in pure systems and the detailed knowledge of defect behaviour in some model, non-transforming crystal hosts have set the stage for a more systematic and detailed investigation of phase transitions and critical phenomena in defected systems. Theoretical considerations have identified several categories of defect according to symmetry and mobility and have suggested some of the static and dynamic consequences of each for critical behaviour. Experiments on structural transitions, however, have not been concerned in a positive way with defects, but rather have sought either to eliminate them or to *subtract out* their effects so as to learn more about the pure system. The recent spectroscopic studies of some transitions (e.g. $SrTiO_3$ and $K(H_xD_{1-x})_3(SeO_3)_2$) clearly point to the neces-

sity for elevating the investigation of transitions in defected systems to a subject in its own right. Careful investigations of transitions in crystals deliberately doped with impurities of known identity,

position, and symmetry may provide not only tests of the theory, but new insight into defect mobility and interactions with collective modes difficult or impossible to acquire in non-transforming hosts.

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