QUASIELASTIC LIGHT SCATTERING NEAR
STRUCTURAL PHASE TRANSITIONS

K. B. Lyons and P. A. Fleury
Bell Telephone Laboratories
Murray Hill, N. J. 07974

The focus of the this binational symposium lies in the consideration of the interaction of light with matter. One manifestation of this interaction is found in the phenomenon of light scattering. In many situations, in order to understand the light scattering spectrum, it is sufficient to consider first order (ie: one-phonon) scattering processes only. However, the study of higher order processes is also of interest. One kind of system where higher order (multiphonon) scattering may be important is a crystal undergoing a structural phase transition. In the present paper we shall discuss the way in which recent light scattering studies of such systems demonstrate the importance of higher order processes. We will discuss these effects with emphasis on the role of second order or two-phonon scattering.

Our understanding of structural phase transitions has evolved in the last decade through several stages from the simple soft mode and mean field theories (MFT) to the modern coupled-mode, renormalization group and dynamic scaling ideas. Crucial to this evolution has been an increasingly detailed interpretation of the experimental data, particularly those resulting from scattering experiments.

In the simplest theory, the order parameter fluctuations are characterized by a soft mode whose frequency goes to zero at the transition temperature $T_c$ as

$$\omega_s^2 \propto |T_c - T|^{2\zeta}; \quad 2\zeta = 1.0$$

The initial thrust of phase transition scattering studies was to extract soft mode frequencies and compare these to predictions of MFT.

The dynamic susceptibility associated with the order parameter was assumed to be quasi-harmonic, of the form

$$\chi \propto \left[(\omega^2 - \omega_0^2) + i2\Gamma,\omega\right]^{-1}$$

Using this approximation it was possible to extract values for $\omega_0$ and $\Gamma$, from neutron and light scattering spectra. It was soon found, however, that the values obtained did not always behave as expected. The value of $\omega_0^2$ did not extrapolate to zero at the transition. Moreover, in the same temperature region where this deviation was evident, a new spec-
tral component was observed, centered at zero energy, with a very narrow width. This feature has since been called the "Central Peak". In the early observations of this phenomenon, via neutron scattering, the peak width was instrumentally limited. Nevertheless it was possible to parametrize the spectra by adding a term to $\Gamma_s$ of the form

$$\Sigma(\omega) = \frac{\delta^2 \tau}{1 - i\omega \tau}$$

representing the coupling of the soft mode to a relaxation process, of unknown origin, characterized by a relaxation time $\tau$ and a coupling strength $\delta$. This has the effect, in Eq. (2), of replacing $\omega_{io}$ by the quantity $\omega_2 = \omega_{io}^2 - \delta^2 / (1 + \omega^2 \tau^2)$, and $\Gamma_s$ by $\Gamma_s' = \Gamma_s + \delta^2 \tau / (1 + \omega^2 \tau^2)$, where $\omega_{io}^2 = \omega_{io}^2 + \delta^2$. Since the central peak was instrumentally narrow, no information was available on $\tau$, but $\delta$ was measurable by extrapolation of the observed value of $\omega_2 (- \omega_{io}^2)$ to the transition temperature, where $\omega_{io} = 0$ by definition. This treatment also yielded a quantitative description of the central peak intensity.

The obvious question then arose as to the nature of the relaxation process responsible for the self energy in Eq. (3). A number of mechanisms were proposed, all of which yielded self energy forms similar to Eq. (3). However, in the absence of experimental information on the value of $\tau$ and its dependence on temperature, wavevector, and other experimental parameters, it was not possible to differentiate among these mechanisms.

A natural approach to this problem was to utilize the greater energy resolution capability of light scattering to study the same phenomenon. However, for a number of years, quantitative study of any central component was prevented by the very strong elastic scattering from sample defects. Recently, a technique, developed by the present authors and reported elsewhere, has been used to circumvent this problem. It is based upon use of a molecular iodine reabsorption filter in conjunction with appropriate computer data analysis. By this technique, it has been possible to observe in detail the spectral profile at energies as low as 0.002 meV (0.5 GHz), and thus investigate central peaks near structural phase transitions in various materials.

Before considering the results of these investigations, it is important to understand the differences between the light scattering and neutron scattering experiments. These differences lie in the scattering wavevector, the selection rules, and in the properties of the iodine filter. The wavevector $q$ involved in light scattering is typically in the range $1-4 \times 10^3$ cm$^{-1}$, at least an order of magnitude less than the resolution of a typical neutron scattering experiment. The effect of this difference is to introduce the acoustic modes into the low frequency light scattering spectrum. These modes, in light scattering, lie in the range 0.01-0.25 meV, and thus may interact with the soft mode near $T_c$. The observed spectrum is that of the coupled modes, which, although considerably different in appearance, contains information similar to that in the neutron spectrum. For a soft optic mode, the soft mode frequency is virtually $q$-independent, while the acoustic mode frequency increases as $q$. Hence, at large $q$, for the neutron scattering spectrum, the modes are effectively uncoupled. In the light scattering spectrum, on the other hand, this coupling may be significant. The light scattering spectrum of such a coupled mode system may be written

$$S(\omega) = \sum_i \omega_i \omega_j F_i F_j \chi_{ij},$$

where $F_i$ represent the scattering strengths of the uncoupled modes. In the simple case of two coupled modes $\chi_{ij}$ are expressed in terms of $\chi_i$, the uncoupled susceptibilities, as