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OBSERVATION OF PRETRANSITIONAL EFFECTS ON THE SHAPE OF THE E$_2$
(17 cm$^{-1}$) OPTICAL MODE IN $\beta$-AgI BY RAMAN SPECTROSCOPY

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Abstract.- Resonance interference between the E$_2$(17 cm$^{-1}$) optical mode and the continuum of one-phonon density of state has been observed in $\beta$-AgI. From a fitting of the E$_2$ optical node shape with a "Fano" formula we have obtained the temperature behaviour of the coupling parameter $\eta$ and the true half-width which show substantial change near the $\beta$-$\alpha$ transition temperature.

The lattice dynamics of AgI has been extensively studied in recent years$^{(1)}$. Of particular interest is to understand the vibrational dynamics near the superionic transition. Since the ionic conductivity jump at $T_0 = 147^\circ$C is coupled with a change in the crystal structure$^{(1)}$ it is reasonable to assume that phonons play an important role in driving the transition. However no detectable pre-transitional effects have been observed in Raman spectra upon approaching $T_0$.

The nature of the Raman spectra in AgI and its change with temperature is clearly anomalous and has been the subject of some controversy. Recently we have shown that the anomalous features in the Raman spectra and their temperature dependence were connected with a first order phonon partial density of states, activated in the $\beta$-phase by a local low temperature desordering of the Ag$^+$ ions$^{(2-3)}$. In Fig. 1 we show the temperature dependence of Raman spectra in $\beta$-AgI. It is clear from the figure that the perfectly normal spectrum due to zone center optical modes changes continuously into a continuum of vibrational states, as temperature is increased, with the sole exception of the E$_2$(17 cm$^{-1}$) optical mode. Thus such optical mode is barely affected by the local disordering of Ag$^+$ ions: this is probably due to the extreme flatness of dispersion curve$^{(4)}$. Bührer and Bruesch$^{(4)}$ argue that the sharp E$_2$ optical mode induce the phase transition by favouring of Frenkel pairs in the Ag sublattice. In fact the E$_2$ mode has the appropriate eigenmode structure and disappears discontinuously at 147$^\circ$C. However the "coupling" of such mode to jumping cations does not appear to produce important effects on the mode dynamic structure factor as the phase transition is approached. One reason for apparent insensitivity of E$_2$ mode may be that overall vibrational response of AgI is similar in two $\beta$ and $\alpha$-phase$^{(3,5)}$. However, a finer experimental analysis of

Fig. 1: Experimental Raman spectra at various Temperature from 5 to 150 cm$^{-1}$.
E$_2$ mode spectral region does show some pretransitional effects as $T_0$ is approached (fig. 2). From these experimental data we see that:
1 - the E$_2$ mode damping increases considerably;
2 - the shape of E$_2$ line is visibly asymmetric;
3 - there is a slight shift towards low frequencies;
4 - the total Raman Intensity divided by the Bose-Einstein factor remains constant.

In order to interpret these data we hypothesize a Fano interference\(^6\) between the 17 cm$^{-1}$ peak and the underlying continuum of vibrational states. From inelastic neutron scattering we can assume that such continuum is due to the phonon density of states associated with an acoustical branch: such branch has, at zone edge, the same symmetry and nearly the same energy as the almost flat branch of the E$_2$ optical mode. For a given temperature the Fano spectral shape can be written as\(^7\)

$$\sigma(e) = \frac{(q + e)^2}{1 + e^2} + \sigma'$$

where $\sigma'$ is the cross section for the underlying continuum which does not interact with the discrete state, and

$$\begin{align*}
q &= \frac{\langle 1 | a_1 | 0 \rangle}{\pi \langle 1 | \omega | 2 \rangle \langle 2 | a_2 | 0 \rangle} \\
\varepsilon &= \frac{E - E_1}{\pi |\langle 2 | a_2 | 0 \rangle|^2} , \quad E_1 = E_q + F
\end{align*}$$

where $E_q$ is the eigenvalue of the uncoupled one-phon state (i.e. the energy of the E$_2$ mode) and $F$ is the slight shift from $E_q$ due to admixture of states. A simple scheme of Fano interference is to view the like shape of a discrete mode interacting with a continuum as due to interference between two coherent scattering channels into the same heavily damped final state: the first is a direct channel $\langle 2 | a_2 | 0 \rangle$ coupling the ground state $|0\rangle$ to the continuum $|2\rangle$; the second is an indirect one, coupling states $|0\rangle$ and $|2\rangle$ via the discrete state $|1\rangle$ and is given by

$$\Gamma = 2\pi |\langle 2 | \omega | 1 \rangle|^2$$

In the figure 3 we show a typical fit of the spectra for $T = 403$°K together with the calculated true experimental band shape.

If the reasonable assumption that $\langle 1 | a_1 | 0 \rangle$ and $\langle 2 | a_2 | 0 \rangle$ are independent or weakly dependent on temperature is also made, then we have that

$$\begin{align*}
q &= \frac{1}{\pi |\langle 2 | \omega | 1 \rangle|^2} \quad \text{and thus the main contribution to the temperature dependence in the Fano fitting of the E$_2$ mode lineshape will be connected with the behaviour of the true linewidth. We have verified the assumptions leading to (3) by fitting the E$_2$ lineshape using (1) with both}
\end{align*}$$
q and r as free parameters. We have found that the product $q \Gamma^{-1}$ was independent temperature within our 10% estimated error.

In fig. 4 we show separately the behaviour of the coupling parameter $q$ and the halfwidth $\Gamma$ vs temperature.

From inelastic neutron scattering data (4) we found that the $E_2$ optical mode and the density of states associated with the acoustical branch change little with temperature. Thus the change in the $<1|\omega|2>$ matrix elements as $T_0$ is approached cannot be due to changes in the vibrational dynamics. Rather the increase in the coupling must be connected with a "static" property of the system, such as an order parameter.

In the framework of our interpretation of the anomalous features in the Raman spectrum of $\beta$ and $\alpha$-AgI, we are led to associate the behaviour of $q$ (or $\Gamma$) to the jump motion of the Ag$^+$ ions and to the associated degree of disorder. Thus the appropriate order parameter could be the concentration of Frenkel pairs, itself connected with macroscopic ionic conductivity.

Fig. 4: Behaviour of the $q$ and $\Gamma$ parameters versus temperature.

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