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Mode softening in cubic $BaTiO_3$ and the problem of its adequate description

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We compare recent infrared and hyper-Raman-scattering measurements on $BaTiO_3$ in its cubic paraelectric phase. By reinterpreting the experimental data of Inoue and Akimoto, we show that the low-frequency part of all hyper-Raman-scattering spectra so far reported can be adequately accounted for by a single highly overdamped classical oscillator which softens continuously when the Curie temperature is approached from above. We discuss the adequacy of more complicated models and estimate the degree of compatibility between the hyper-Raman-scattering data and the infrared results of Luspin *et al.*

I. INTRODUCTION

Recently, the interest in the far-infrared dispersion of cubic $BaTiO_3$ has been renewed by three papers:

(a) Luspin *et al.*[1] fitted the parameters of a factorized dielectric function to their reflectivity data. They concluded that the low-frequency Cochran mode does not soften continuously in approaching the Curie temperature T_C from above, but stops softening at a temperature of about 100° above T_C, when its frequency is about 60 cm^{-1}.

(b) Applying the technique of hyper-Raman-scattering (HRS), Vogt *et al.*[2] directly measured the imaginary part of the dielectric function in the frequency range between 3 and 150 cm^{-1}. They found that their spectra can be adequately accounted for by a single overdamped classical oscillator. In contrast to (a), a monotonic decrease of the oscillator frequency down to at least 11 cm^{-1} was observed in approaching T_C from above.

(c) Inoue and Akimoto[3] also used HRS spectroscopy. They claimed, however, that their results cannot be described adequately by a classical dispersion formula with reasonable values of the parameters. Therefore they introduced a model in which the phonon is coupled to a system of pseudospins, the latter being identified with off-center positions of the Ti ions.

The present Brief Report intends to clarify these apparent discrepancies by analyzing the degree of compatibility of the experimental data. Results (a) and (b) have already been compared in Ref. 2. Here we add some further remarks.

II. COMPARISON OF HYPER-RAMAN-SCATTERING RESULTS

Both HRS works can be brought into considerable agreement if the spectra are interpreted in terms of a classical dispersion formula and the Bose-Einstein population factor $[n(\Omega)+1]$ for the Stokes side is properly taken into account. In contrast to Inoue and Akimoto,[3] we find that their HRS spectra closely follow the response function of a single oscillator, i.e.,

$$S(2\omega_L-\Omega)=A\,[n(\Omega)+1]\frac{4\pi\rho\,\Omega_0^2\gamma\,\Omega}{(\Omega_0^2-\Omega^2)^2+\gamma^2\Omega^2}\ , \qquad (1)$$

where S is the HRS efficiency, ω_L the laser frequency, Ω the HRS shift, Ω_0 the oscillator frequency, γ the damping constant, $4\pi\rho$ the oscillator strength, and A a coefficient which is independent of Ω. The adequacy of Eq. (1) is shown in Fig. 1, where the dots represent the experimental values of Ref. 3 and the full lines our classical oscillator fits. We applied the same method of nonlinear least squares as in Ref. 2. Starting from different input values of the three parameters Ω_0, γ, and $4\pi\rho A$, the fitting procedure always converged to the same result. Hence the fitting parameters are well defined by the experimental data. We could not analyze in a similar way the spectrum of Ref. 3 at 400 °C because the number of available data points is too small.

Figure 2 shows the temperature dependence of Ω_0 and γ as obtained by HRS spectrsocopy. The results of Ref. 2 are

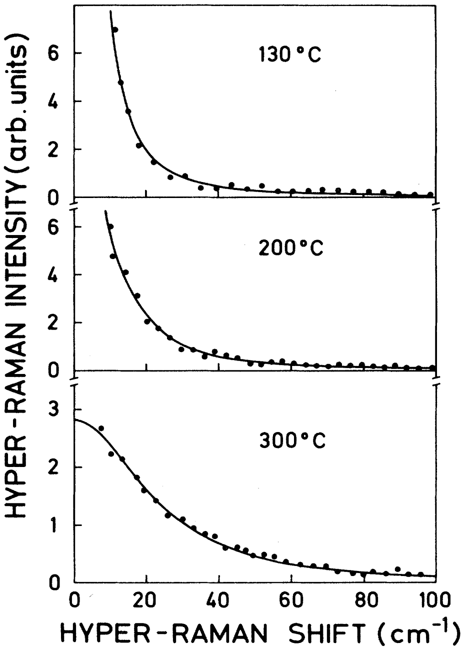

FIG. 1. Reinterpretation of the hyper-Raman-scattering spectra measured by Inoue and Akimoto (Ref. 3). Full circles: experimental points; full lines: classical dispersion oscillator fit according to Eq. (1).

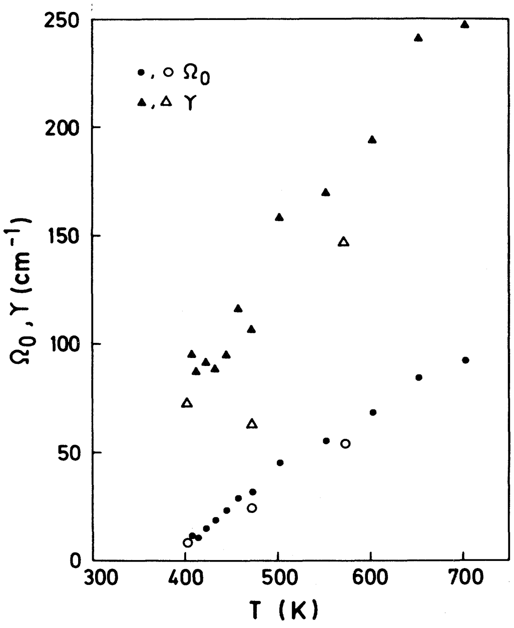

FIG. 2. Frequency Ω_0 and damping constant γ of the soft mode in cubic $BaTiO_3$ as obtained by hyper-Raman-scattering spectroscopy. Full symbols: Ref. 2; open symbols: derived from Ref. 3.

confirmed by our reinterpretation of the data from Ref. 3. In particular, there is no saturation of the mode frequency Ω_0, but a monotonic decrease.

III. ONE-MODE VERSUS TWO-MODE DESCRIPTION

Although Eq. (1) provides a satisfying description of the HRS spectra, we cannot exclude the possibility that the experimental data can be also interpreted in terms of more complicated models. If the Ti ions move in local multiwell potentials, it is suggestive to introduce hopping motions as additional degrees of freedom.[4] This has been done explicitly in Ref. 3, where a six-parameter formula has been derived for the HRS efficiency. In Refs. 1 and 4, on the other hand, a low-frequency dispersion step due to hopping motions has been postulated in order to reconcile the infrared results with the Curie-Weiss law of the static dielectric constant.

We should also point out that the unusually high damping of the soft mode introduces some arbitrariness even into the classical dispersion formula. When $\gamma > 2\Omega_0$, the single-oscillator dielectric function can be rewritten in a two-oscillator form, i.e., as the sum of two dielectric functions with parameters $(\Omega_1, \gamma_1, 4\pi\rho_1)$ and $(\Omega_2, \gamma_2, 4\pi\rho_2)$. An elementary calculation yields[2]

$$\begin{aligned} \Omega_{1,2} &= (\Omega_m \Omega_{-,+})^{1/2} , \\ \gamma_{1,2} &= \Omega_m + \Omega_{-,+} , \\ \rho_{1,2} &= \rho \frac{1-\Omega_{-,+}/\Omega_m}{1-\Omega_{-,+}/\Omega_{+,-}} , \end{aligned} \tag{2}$$

where either the left or the right indices have to be used. The frequencies Ω_+ and Ω_- are given by

$$\Omega_{+,-} = \tfrac{1}{2}[\gamma \pm (\gamma^2 - 4\Omega_0^2)^{1/2}] , \tag{3}$$

while Ω_m is an intermediate frequency confined by the condition $\Omega_- \leq \Omega_m \leq \Omega_+$.

This mathematical kind of mode splitting is demonstrated in Fig. 3. The values of Ω_0, γ, and hence $\Omega_{+,-}$ have been taken from Ref. 2, whereas Ω_m has been adjusted in such a way that Ω_2 (open circles) becomes identical with the mode frequency obtained by Luspin *et al.*[1] The additional parameter Ω_m being fixed, the values of Ω_1, γ_1, and γ_2 (full circles and triangles) follow from Eqs. (2). The upper half of Fig. 3 shows the relative oscillator strength of the Ω_1 component as a function of temperature. With increasing temperature oscillator strength is transferred from the Ω_1 to the Ω_2 mode.

The models of Refs. 1, 3, and 4 as well as the mathematical transformation just illustrated may be characterized as a two-mode description of the low-frequency dispersion. They all are justified barely by the available dielectric data. From the experimental and phenomenological point of view, there is no need to abandon the simple single-mode

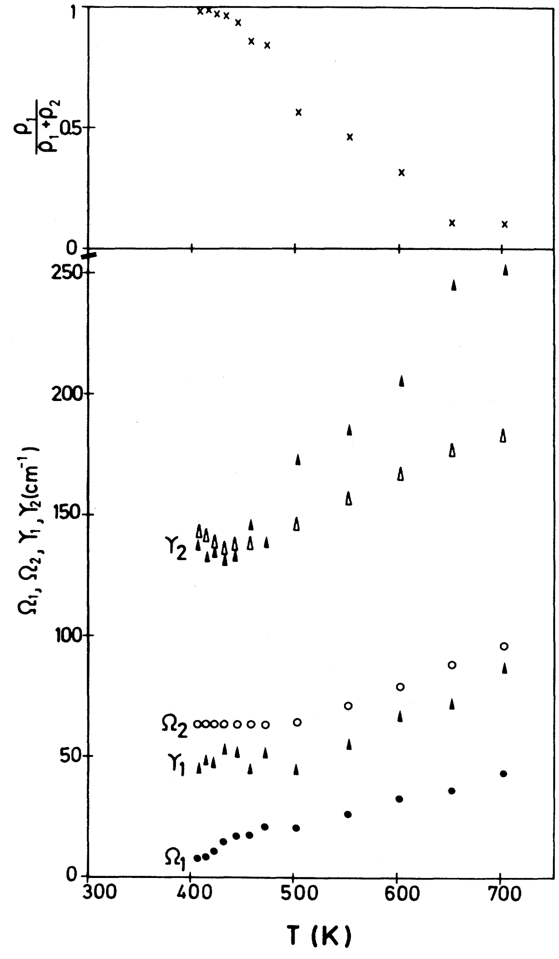

FIG. 3. Splitting of the soft mode into two components. See text for explanation.

description and to introduce a more complicated model with two different time scales.

IV. COMPARISON OF HYPER-RAMAN-SCATTERING AND INFRARED RESULTS

Although the mode splitting of Fig. 3 may have a questionable physical meaning, it may help in estimating the degree of compatibility between the HRS and the infrared results. One may identify the Ω_1 mode with the extra dispersion mechanism postulated in Ref. 1, and may argue that it is hardly accessible to infrared spectroscopy. Below 500 K the value of Ω_1 is too small, while above 500 K the dispersion is dominated by the Ω_2 mode. If this argument is accepted, only a discrepancy in the damping constant γ_2 is left. The values of γ_2 calculated from the HRS data according to Eqs. (2) (full triangles) turn out to be larger then the values of γ_2 directly taken from Ref. 1 (open triangles).

Finally, we should mention two problems which require further experimental investigations:

(i) Below 40 cm^{-1} the far-infrared reflectivity predicted from the HRS data is in better agreement with the older results of Ballantyne[5] than with the more recent ones of Luspin *et al.*[1] (see Fig. 5 in Ref. 2).

(ii) The influence of surface conditions on the far-infrared reflectivity of perovskites is still unclear. On the other hand, field-induced Raman scattering and HRS certainly yield bulk properties. However, as has been shown for $SrTiO_3$ (Refs. 6 and 7) and $KTaO_3$ (Refs. 6 and 8), the damping constants obtained by these techniques can differ quite considerably from those derived from infrared measurements.

Hence an accurate measurement of the reflectivity in the millimeter and submillimeter wave region under defined surface conditions is desirable.

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