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DISAPPEARANCE OF THE INFRARED SOFT MODE IN THE WEAK FERROELECTRIC $Li_2Ge_7O_{15}$

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The behaviour of the soft mode in $Li_2Ge_7O_{15}$ was studied in a wide temperature range in the transmission spectra. The fit results have been found in agreement with the phenomenological theory of weak ferroelectricity predicting vanishing infrared strength of the soft mode about 50 K below T_c.

Keywords: A. ferroelectrics, D. phonons, D. phase transitions, D. anharmonicity, E. light absorption and reflection

1. Introduction

Lithium germanate $Li_2Ge_7O_{15}$ (LGO) has attracted the attention due to its weak ferroelectric properties. It crystallizes in the orthorhombic space group $Pbcn$ (D_{2h}^{14}) with four formula units in the unit cell (Z=4)[1]. At $T_c = 283.5$ K it undergoes a second order pseudoproper ferroelectric phase transition into a polar group $Pbc2_1$ (C_{2v}^5) (Z=4). Permittivity ε_c displays a weak anomaly which, in a narrow temperature range of $T_c\pm6$ K, can be described by a Curie–Weiss law with an extremely small Curie constant ($C = 4.6$ K^2 or 3.2 K^3). Spontaneous polarization is very small and exhibits a non-monotonous temperature dependence changing its sign[4] at $T_p \approx 135$ K. The phase transition is of the displacive type as evidenced by observation of an underdamped Raman soft mode[5,6] active below T_c and infrared (IR) soft mode investigated above T_c by a backward-wave-oscillator (BWO) spectroscopy[6]. The IR spectra were measured in both phases[7] above $\approx$ 200 K. In a narrow range around T_c a Raman central mode was also observed and explained by weak-anharmonic two-phonon difference processes involving the soft branch[8]. An even more narrow central peak was observed by microwave spectroscopy[9].

Tagantsev[10–12] conceived a phenomenological theory which correlates the temperature dependence of P_s with that of the effective charge of the soft mode. The theory predicts a change of sign of this effective charge at certain temperature T_v between T_c and T_p, i.e. vanishing of the IR soft mode strength at T_v. This short communication is devoted to the experimental verification of this effect.

2. Theoretical predictions

To explain the soft mode behaviour of weak ferroelectrics, Tagantsev[10–12] developed a phenomenological theory. This theory assumes a one-dimensional order parameter η_1 bilinearly coupled with polarization P (uniaxial ferroelectrics) and nonlinearly interacting with another coordinate η_2 (the bilinear coupling is removed by choosing η_1, η_2 to be normal coordinates). The relevant part of the free energy expansion in the paraelectric phase reads

$$F = \frac{\alpha_1}{2}\eta_1^2 + \frac{\alpha_2}{2}\eta_2^2 + \frac{\beta}{4}\eta_1^4 + \delta\eta_1^3\eta_2 - PE\,, \qquad (1)$$

where $\alpha_1 = A(T - T_c)$. The total polarization is assumed to be a sum

$$P = e_1\eta_1 + e_2\eta_2\,, \qquad (2)$$

where the η_2 coordinate means an effective hard-mode coordinate of the same symmetry as η_1 (B_{1u}). $e_{1,2}$ are the corresponding paraelectric effective charges which are not explicitly temperature dependent.

Below T_c, η_1 and η_2 start to interact bilinearly and the new normal coordinates A_1 are to the first approximation ($T_c - T \ll T$) given by

$$\tilde{\eta}_1 = \eta_1 + \varphi\eta_2\,, \qquad \tilde{\eta}_2 = \eta_2 - \varphi\eta_1 \qquad (3)$$

with $\varphi(T) = -3\delta\eta_{1s}^2(T)/\alpha_2 \ll 1$, and the new effective charges become now temperature dependent like the new normal coordinates:

$$\tilde{e}_1 = e_1 + \varphi e_2 , \qquad \tilde{e}_2 = e_2 - \varphi e_1 . \qquad (4)$$

For $\delta > 0$ or e_1 and e_2 having opposite signs and sufficiently small $|e_1|$, $\tilde{e}_1$ may change its sign at temperature

$$T_v = T_c - \frac{e_1 \beta \alpha_2}{3 e_2 \delta A} . \qquad (5)$$

The soft oscillator strength S is proportional to $\tilde{e}_1^2$ so that it vanishes for $T = T_v$. T_v can be estimated from the fact that also the spontaneous polarization

$$P_s = \eta_{1s}(e_1 + \frac{\varphi}{3} e_2) \qquad (6)$$

changes its sign at a finite temperature

$$T_p = T_c - 3(T_c - T_v) . \qquad (7)$$

Using $T_p \approx 135$ K[4] gives $T_v \approx 234$ K. The predicted temperature dependence of the measurable soft oscillator strength below T_c is

$$S_{\mathrm{soft}}(T) = S_{\mathrm{soft}}(T_c) - \frac{2l}{e_1} S_{\mathrm{soft}}(T_c)(T_c - T) + \frac{l^2}{e_1^2} S_{\mathrm{soft}}(T_c)(T_c - T)^2 , \qquad (8)$$

where l is a temperature independent constant.

3. Experimental details

Single crystal plates 8×12.5 mm^2 in area and of thickness 1 and 1.35 mm were used. The measurements were performed at temperatures 7–473 K using the Fourier interferometer Bruker IFS 113v, equipped with polarizers and a He-cooled Ge bolometer for the range below 100 cm^{-1}. The spectral resolution used was 2 cm^{-1}. Transmission measurements were carried out in the 15–100 cm^{-1} range, reflectivity measurements in the 100–2000 cm^{-1} range. Complex transmittance measurements (power transmission and phase of the transmitted light) in the 5-18 cm^{-1} range were performed with the home-made spectrometer Epsilon based on tunable BWO sources[13] using a 4 mm thick sample.

4. Results and evaluation

Fig.1 shows the temperature dependence of $E \parallel c$ polarized transmission spectra (in the range of 15–100 cm^{-1}; for frequencies higher than 100 cm^{-1} the specimen was opaque) between 7 K and 473 K. Due to the limited spectral resolution, no interference pattern on the plane-parallel sample was observed in the transmittance spectra.

The soft mode was observed within temperatures 7-175 K (A_1 symmetry) and 290-473 K (B_{1u} symmetry). In the range of 200 K-T_c, the soft mode is unobservable, although it has been seen in the Raman measurements[5,6]. Further, a hard mode of the

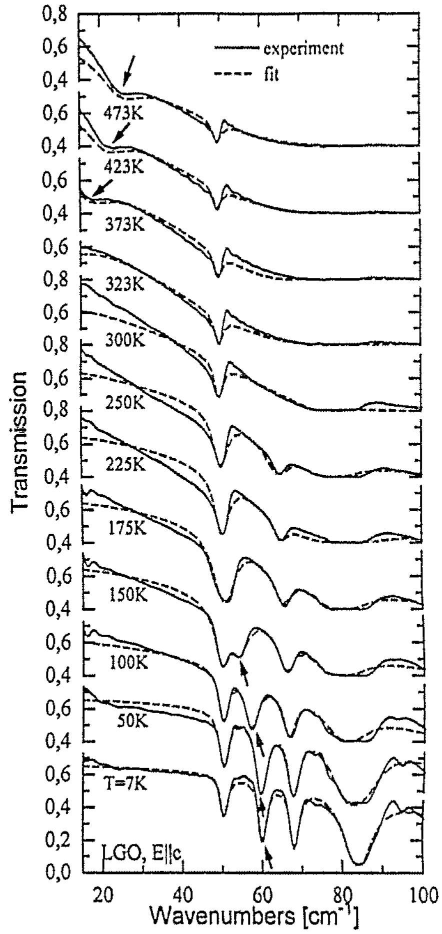

Fig.1 Far IR transmission spectra of LGO as a function of temperature; sample thickness is 1 and 1.35 mm for temperatures below and above T_c, respectively. The arrows mark the soft mode position where clearly observable.

same symmetry was observed, its frequency changing between 50 cm^{-1}and 60 cm^{-1}. Below T_c, an additional A_1 hard mode appears at about 68 cm^{-1}. This mode is IR-inactive above T_c (A_g symmetry) but it can be seen in the Raman spectra[7]. In the region of 100–2000 cm^{-1}, the $E \parallel c$ polarized reflectivity was measured at the same temperatures to make possible the common fitting of the spectra. The full results will be published elsewhere.

All the data were fitted using a lattice vibration model consisting of up to 34 damped harmonic oscillators. During the fitting process, $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ curves are computed using the formula

$$\varepsilon(\nu) = \varepsilon_\infty + \sum_{i=1}^{N} \frac{\Delta\varepsilon_i \nu_{0i}^2}{\nu_{0i}^2 - \nu^2 + i\nu\gamma_i} \qquad (9)$$

where ε_∞ denotes the high-frequency permittivity, $\Delta\varepsilon_i$ means the contribution of individual oscillators to the static permittivity $\varepsilon(0)$, γ_i their damping and ν_{0i} bare resonance frequencies. Then, model reflectivity and transmissivity spectra are determined and compared with the measured spectra. To compute the transmissivity, the formula which takes into account all multiple reflected beams as noncoherent was used. The obtained model for a particular temperature fits both the reflectivity and the transmission. The value of ε_∞ is taken as the value of the refractive index squared[14] and the resulting values of $\varepsilon(0)$ are in agreement with those obtained from the BWO experiment.

As for the parameters of the soft mode, the following approach was used:

The values of the soft mode damping near T_c were taken from Raman measurements[5]. They show a sharp increase in the damping just below T_c.

The soft mode eigenfrequency was fitted at those temperatures where this mode was observable. This was not the case in the region of 200 K–T_c because of the very small soft oscillator strength $S_i = \Delta\varepsilon_i\nu_i^2$ (there is no corresponding absorption peak in the spectrum). Here, the frequency was also fixed according to the results of Raman measurements[5,6].

The temperature dependences of the resulting loss spectra and soft mode parameters are shown in Figs. 2 and 3. As shown in Fig. 3c, in the range of approx. 100 K below T_c, the behaviour of the soft oscillator strength corresponds within the range of accuracy to the predicted dependence (8); the error bars around the symbols were estimated from maximum changes in $\Delta\varepsilon$ which do not result in substantial differences between the model and experimental curves. Thus, the maximum values allowed by the error bars for the temperatures 200–250 K correspond to the limit where the soft mode absorption peak in the model transmittance spectrum starts to appear.

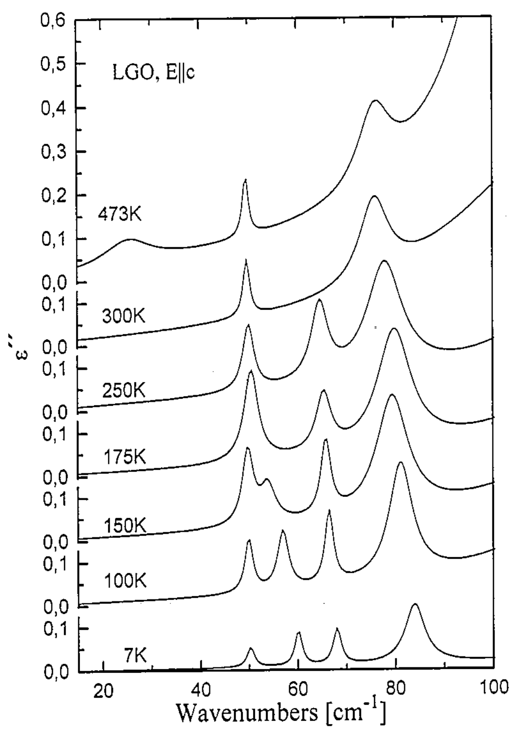

Fig.2 Imaginary part of the complex permittivity computed from the fit in Fig.1 as a function of temperature.

5. Discussion

The fit in Fig.1 is by no means perfect. This could be expected mainly because the overall absorption level is so low (of the order 1–10 cm^{-1}) that two-phonon absorption becomes comparable to one-phonon processes. Therefore the simple classical damped oscillator model (9) is no more expected to describe the spectra precisely. Another reason for taking the quantitative results of the fit with caution consists in approximations used for deriving the formula for the transmittance of the thick slab (interferences not resolved, in reality non-ideal plane wave). Nevertheless, all the important features of the spectra are taken into account by the fit.

On cooling above T_c, the oscillator strength of the hard mode S_{hard} increases and that of the soft mode S_{soft} decreases monotonously. Just below T_c, S_{hard} still increases; in the temperature range about $T_v = 234$ K $\pm$ 50 K, S_{soft} is small, in agreement with Eq. 8. Between 175 and 150 K, the anticrossing takes place as reported by Wada et al.[7]; the Eq. 8 is no more valid, presumably due to the presence of higher order terms in Eq. 1. S_{hard} is turned down and S_{soft} increases dramatically. Below 150 K, S_{soft} becomes even greater than S_{hard}. The latter effect was also observed in the Raman spectra[7].

It is interesting to note that S_{soft} (effective charge) increases with temperature above T_c which can be understood as an effect of the real coupling between the soft mode and higher-frequency stronger hard modes. Such a coupling may increase the IR strength if the soft-mode frequency hardens and approaches those of the hard modes.

The effect of the sharp increase in the soft mode damping when approaching T_c from below is connected with the appearance of the central mode in the Raman spectrum[8]. Our data support such an increase, smaller damping would make the mode observable near 250 K, which is not the case. However, no analogous increase seems to be observable above T_c which leads to somewhat unusual asymmetry in damping around T_c, but correlates with the BWO data[6] and with the microwave data on the central peak[9] showing its presence in a very narrow temperature range ($T_c \pm 2$ K) only.

6. Conclusions

The IR ferroelectric soft mode was observed vanishing in a limited temperature range below T_c. This is caused by its extremely weak IR strength in which case even a weak temperature dependence of the soft-mode

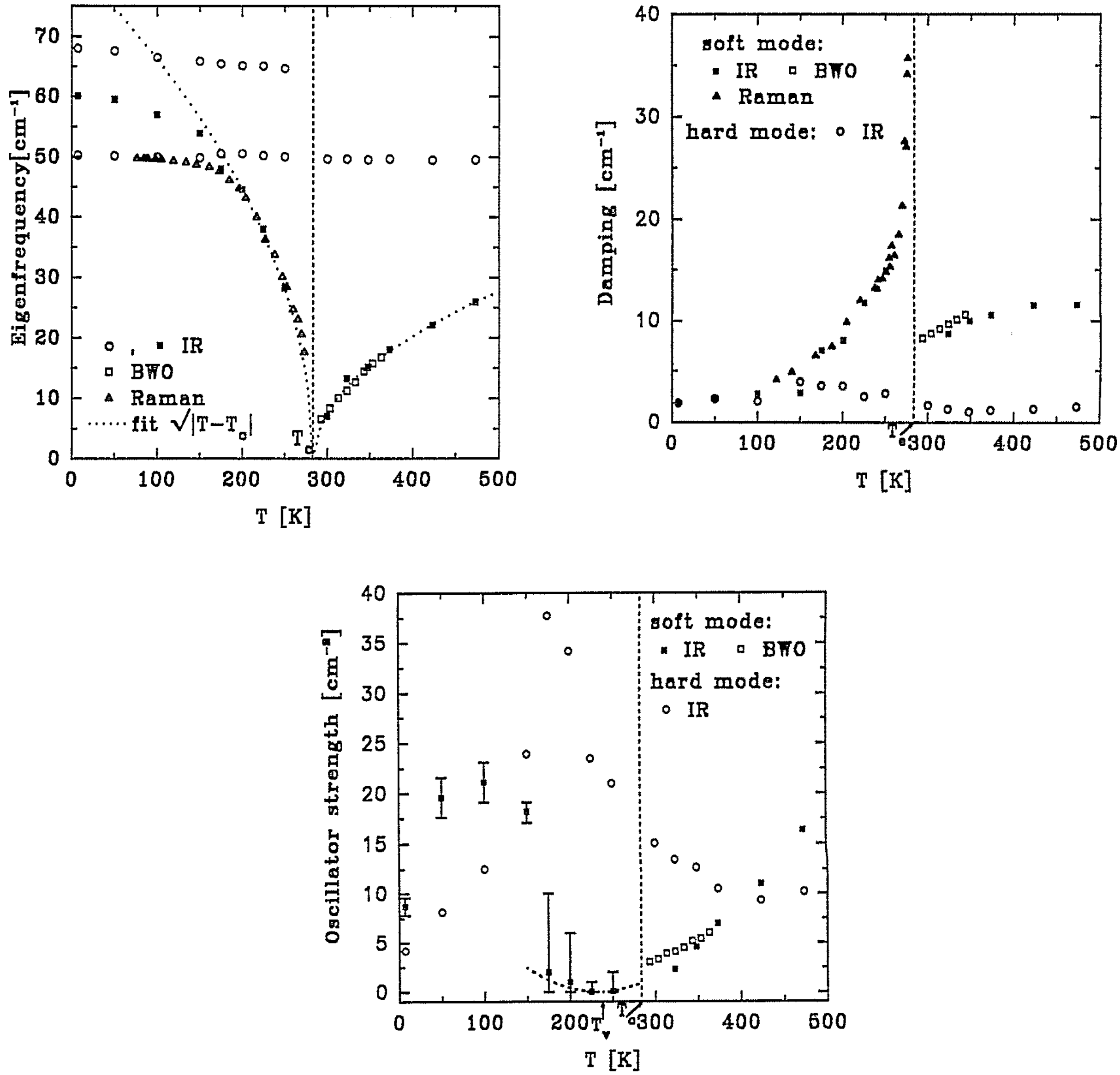

Fig.3 Parameters of the soft mode and low-frequency hard modes in LGO compared with the Raman[5] and BWO[6] data : (a) Eigenfrequency; the dotted line shows the fit to Landau theory, (b) Damping, (c) Oscillator strength; the dotted line corresponds to Eq.8. In case of (b) and (c) only the lower-frequency hard-mode parameters are given.

effective charge can result in changing its sign. The temperature of the soft mode vanishing T_v agrees with predictions of the phenomenological theory of weak ferroelectricity correlating it with the temperature T_p where the spontaneous polarization P_s changes its sign.

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