Stokes-to-anti-Stokes intensity ratio in the low-frequency light scattering of a paraelectric KH$_2$PO$_4$ crystal near the ferroelectric-phase-transition temperature

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We have investigated the Stokes-to-anti-Stokes intensity ratio for the low-frequency light scattering spectrum of a paraelectric potassium dihydrogen phosphate crystal. As the temperature approaches the ferroelectric-phase-transition temperature T_c, a central peak related to the soft mode increases prominently and the Stokes-to-anti-Stokes intensity ratio clearly deviates from the Boltzmann factor, approaching unity in the region below 30 cm^{-1}. It is suggested that a manifestation of Markovian nature in the soft mode is essential to understand the symmetric spectrum.

Light scattering is widely known as a method to probe dynamical properties such as molecular and lattice vibrations, individual and cooperative fluctuations, thermally activated sound waves, density fluctuations, and so on, in a wide variety of materials. In addition, since light scattering is a simple second-order optical process, it has often been employed as a tool to confirm the fundamental properties predicted by quantum and statistical mechanics. One such example is an experiment to confirm the validity of the quantum-mechanical fluctuation-dissipation theorem (QM FDT) in light scattering processes, which will be accomplished by a comparison of frequency response functions obtained from a temporal response and from a spectral measurement. A recent careful experiment has revealed that quite a good agreement is obtained between these functions measured with completely different methodologies.[1]

Another and very frequently employed relation based on the QM FDT is the Stokes-to-anti-Stokes intensity ratio. The intensities for Stokes and anti-Stokes spontaneous light scattering for a canonical system under nonresonant excitation are connected with each other through the time-reversal symmetry[2] and are given using QM FDT as[3]

$$I_S(\omega) = (\hbar/\pi)[n(\omega) + 1]\mathrm{Im}\,\chi(\omega) \qquad (1)$$

and

$$I_{AS}(\omega) = (\hbar/\pi)n(\omega)\mathrm{Im}\,\chi(\omega), \qquad (2)$$

respectively, where $\chi(\omega)$ is a linear response function expressed as $\chi(\omega) = (i/\hbar)\int_0^\infty dt\langle \alpha(t)\alpha(0) - \alpha(0)\alpha(t)\rangle\exp(i\omega t)$ with the angular frequency ω, the polarizability α, and the Bose-Einstein thermal factor $n(\omega)$. Consequently, Eqs. (1) and (2) lead to the relation

$$I_S(\omega)/I_{AS}(\omega) = [n(\omega) + 1]/n(\omega) = e^{\hbar\omega/k_B T}. \qquad (3)$$

Thus, the Stokes-to-anti-Stokes intensity ratio is given by the Boltzmann factor. This relation has been extensively investigated through many experiments and is now well established as one of the fundamental properties of light scattering. In fact, by using this relation, the local temperature has been successfully determined.

However, very recently, two suggestive experiments[4,5] have independently been reported concerning the deviation of the intensity ratio from the Boltzmann factor. The first one is that reported by the present authors,[4] in which the intensity ratio for cooperative orientational fluctuation in liquid CS$_2$ deviates from the Boltzmann factor and becomes unity in a frequency region less than several wave numbers. The second is related to the quasielastic light scattering in amorphous solids and supercooled liquids such as As$_2$O$_3$ and ZnCl$_2$ at room temperature or higher, and a symmetric quasielastic component is reported to be present at the spectral origin.[5] These characteristics are extremely important to understand the origin of these modes, because the symmetric spectrum with $I_S/I_{AS}=1$ implies that the fluctuation apparently loses its quantum character and behaves like a classical fluctuation, although it is not in the high-temperature or the low-frequency limit.

Despite its physical importance, these experimental evidences for the deviation are rather ambiguous at the present stage. In the case of the liquid sample, the maximum deviation is only 1% of the total intensity ratio and is found to be quite sensitive to the experimental determination of the spectral origin.[4,6] As for the amorphous solids and supercooled liquids,[5] the deviation is derived indirectly by subtracting the boson peak, which is assumed to satisfy Eq. (1), from the total spectrum, although the validity of expressing the spectrum as the sum of these two components has not been justified yet.[4]

In the present paper, we will show experimentally how the Stokes-to-anti-Stokes intensity ratio undoubtedly deviates from the Boltzmann factor in a particularly selected system. From an experimental viewpoint, the deviation is clearly discernible when the sample has a very strong Lorentzian-like central peak with sufficient spectral broadening even at low temperatures. We have come to the conclusion that crystals undergoing a ferroelectric phase transition are most suitable for this study. Thus, we have chosen a crystal of potassium dihydrogen phosphate KH$_2$PO$_4$ (KDP) as the sample, a well-known ferroelectric crystal showing a very strong central peak near the phase-transition temperature.

The KDP crystal undergoes a ferroelectric-ferroelastic phase transition at T_c=122.2 K and shows a Lorentzian-like central peak originating from the polarization fluctuation, which plays a significant role as a soft mode in the ferroelectric phase transition.[7–10] In fact, its intensity drastically in-

creases as the temperature approaches T_c, and the temperature dependence of T/I_0 with the integrated intensity I_0, which is proportional to the inverse of the static susceptibility under the low-frequency approximation, is characterized by the Curie-Weiss law.[10] Furthermore, a critical slowing down of the soft mode is clearly observed in the temperature dependence of the spectral width[11] and/or the decay time determined by impulsive stimulated Raman scattering.[12] Thus the KDP crystal is an ideal sample for this study. The present experiment establishes definitely the experimental evidence for the deviation from Eq. (3), which has not yet been accomplished in liquids and amorphous solids.

In order to accurately obtain the Stokes-to-anti-Stokes intensity ratio, the measurements and analyses were carried out with special care by using the following procedures. We employed a cw Ar ion laser (Spectra Physics 2016) as the excitation source. It was operated at 476.5 nm with a power of 190 mW, which was controlled within ±0.1 mW. Since the fundamental absorption band of the KDP crystal lies in the wavelength region below 200 nm,[13] the nonresonant excitation condition assumed in Eq. (3) is well satisfied under excitation at 476.5 nm. The scattering geometry was $x(y,x)y$, where x, y, and z are the crystallographic axes of the tetragonal phase. The scattered light was analyzed by a double monochromator (Jobin Yvon U-1000) with a spectral step of 0.2 cm^{-1} and a resolution of 1.0 cm^{-1}. The signal was detected by a photomultiplier (Hamamatsu R464). The smallest counts of the spectra in the present study were around 260 counts/s for the frequency shift of 50 cm^{-1} (anti-Stokes) at 136.5 K, while the dark counts of the photomultiplier were below 5 counts/s, which were then subtracted from the spectra. After correcting the measured spectra by the factor ω_s^3, where ω_s is the angular frequency of the scattering light, we carefully made a correction by using the wavelength-dependent sensitivity of the monochromator-detection system. To check the validity of the correction, we measured the quasielastic scattering spectrum of liquid nitrogen at 77.3 K under atmospheric pressure, for which Eq. (3) was reported to hold for $10-150 \text{ cm}^{-1}$ within ±5%.[14] The present result showed that the relation was valid within ±2% for $3-50 \text{ cm}^{-1}$, indicating that the wavelength-dependent sensitivity of the measurement system was well corrected.

A z-cut KDP crystal with a size of $9 \times 9 \times 9 \text{ mm}^3$ was maintained in index-matching liquid isopentane within a glass cell that was placed in atmosphere of He gas cooled by a closed-cycle He refrigerator. The temperature of the sample was measured by a thermocouple in isopentane and controlled within 0.1 K for the temperature region from 274.0 to 136.5 K.

In Fig. 1, we show the light scattering spectra of the KDP crystal measured at several temperatures in the paraelectric phase. The intensity of the Lorentzian-like spectrum of the soft mode centered at $\omega=0$ drastically increases as the temperature approaches T_c. Here, we notice that a tail of a strong elastic scattering peak remains within ±3 cm^{-1}. The inset shows the peak frequency ω_{max} of Im $\chi(\omega)$ obtained from the Stokes component as a function of temperature, indicating a critical slowing down of the soft mode. The straight line is the least-squares fitting to $\omega_{max} \propto (T-T_0)$ for $T < 180$ K, where T_0 is obtained as 118 K, which is consistent with previous results.[7,11,12]
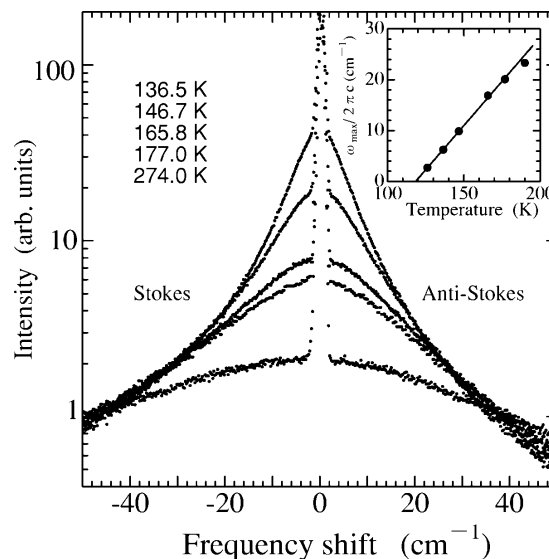

FIG. 1. Light scattering spectra of KDP at temperatures of 136.5 (top), 146.7, 165.8, 177.0, and 274.0 K (bottom). The inset shows the peak frequency ω_{max} of Im $\chi(\omega)$ obtained from the Stokes component. The straight line is the result of a least-squares fit to $\omega_{max} \propto (T-T_0)$ for $T < 180$ K.

To obtain the Stokes-to-anti-Stokes intensity ratio, it is necessary that the spectral origin is determined as accurately as possible, because the ratio is extremely sensitive to the position of the spectral origin. However, it is eventually difficult to determine the origin from the spectrum obtained, because strong elastic scattering overlaps the spectrum around the origin. To overcome this problem, we have assumed in the following analysis that Eq. (3) is generally satisfied in the high-frequency region of $40-50 \text{ cm}^{-1}$, where the temperature variation of the spectrum is small enough, as shown in Fig. 1. This assumption is consistent with the result of Lagakos and Cummins,[9] in which the response functions obtained from the Stokes $(I_S/[n(\omega)+1])$ and anti-Stokes $(I_{AS}/n(\omega))$ spectra at 206 K coincided with each other in the range of $10-240 \text{ cm}^{-1}$. Thus, we have calculated $R \equiv (I_S/I_{AS})\exp(-\hbar\omega/k_BT)$ at each ω and have obtained its mean value $\langle R \rangle$ averaged over the region of $40-50 \text{ cm}^{-1}$. As we change the relative position of the origin by 0.2 cm^{-1}, the mean value $\langle R \rangle$ almost linearly changes by about 0.01 and 0.02 at 274.0 and 136.5 K, respectively. Thus the spectral origin for each spectrum can be determined with an accuracy of ~0.02 cm^{-1} under the condition that $\langle R \rangle = 1$ holds within 0.001–0.002 in the high-energy region. Then, we investigate the temperature variation of R in the spectral region below 40 cm^{-1}. Further, by comparing the spectra obtained with the resolutions of 0.6 and 1.0 cm^{-1}, and by numerical simulation, we have confirmed that the effect of the finite spectral resolution of 1.0 cm^{-1} on the intensity ratio is estimated to be less than 10^{-3} in the present frequency and temperature regions.

In Fig. 2, R thus obtained is shown for temperatures ranging from 274.0 to 136.5 K. At 274.0 and 177.0 K, $R=1$ holds in the entire frequency region within the experimental error. These results well agree with those for 206 K reported
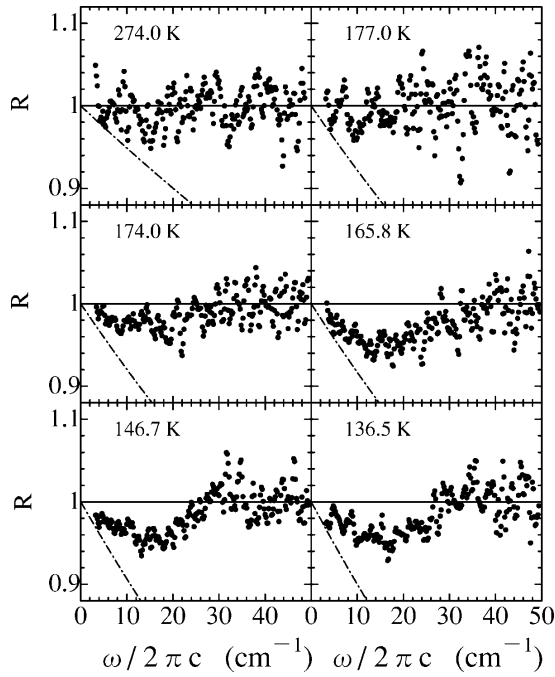
FIG. 2. The ratio $R \equiv (I_S/I_{AS})\exp(-\hbar\omega/k_B T)$ obtained for several temperatures. The dash-dotted lines indicate $R = \exp(-\hbar\omega/k_B T)$ corresponding to $I_S/I_{AS}=1$ for a classical fluctuation.
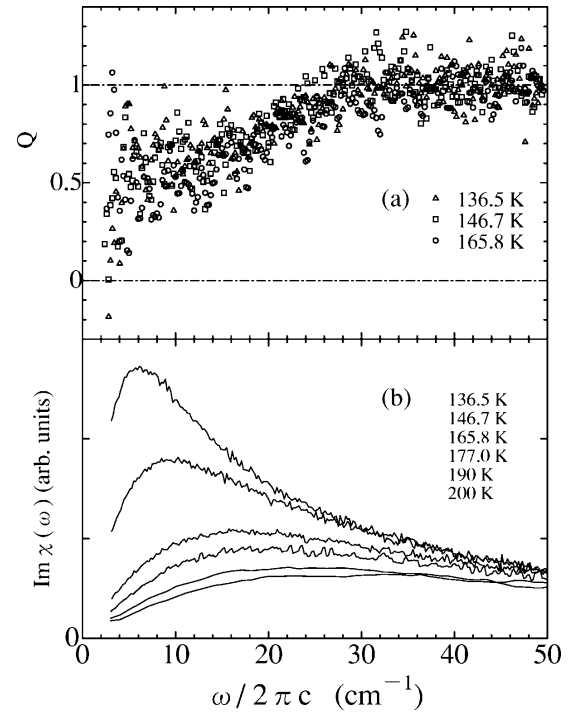

FIG. 3. (a) Temperature variation of Q defined as $Q \equiv (I_S/I_{AS}-1)/[\exp(\hbar\omega/k_B T)-1]$. (b) The frequency response functions Im $\chi(\omega)$ for temperatures of 200–136.5 K obtained via Im $\chi(\omega) \propto I_S/[n(\omega)+1]$ from the Stokes component.

by Lagakos and Cummins.[9] However, below ~ 170 K, we have found that R deviates considerably from unity in the region below 30 cm^{-1}. At 165.8 K, R reaches the maximum deviation of ~ 0.95 at 15 cm^{-1}. The dash-dotted lines in the figure indicate $I_S/I_{AS}=1$, which is expected for a classical fluctuation. These results imply that Eqs. (1) and (2) are not applicable to the spectral analysis of the soft mode below ~ 170 K. If they held, the response functions Im $\chi(\omega)$ evaluated using three different methods, i.e., $I_S/[n(\omega)+1]$, $I_{AS}/n(\omega)$, and I_S-I_{AS}, should agree with each other. However, the present result means that they do not agree with each other in the region below 30 cm^{-1}.

To compare the degree of deviation from Eq. (3), we introduce the parameter Q defined as

$$Q \equiv (I_S/I_{AS}-1)/(e^{\hbar\omega/k_B T}-1), \qquad (4)$$

which is usually unity for a quantum fluctuation, while it is expected to be zero for a classical fluctuation. As shown in Fig. 3(a), Q is unity above 30 cm^{-1} and decreases as ω approaches zero at 165.8, 146.7, and 136.5 K. It is noteworthy that these behaviors are rather independent of temperature, although the peak frequency ω_{max} of Im $\chi(\omega)$ considerably changes from 16.9 cm^{-1} at 165.8 K to 6.2 cm^{-1} at 136.5 K. Thus the deviation from the Boltzmann factor has a kind of universal character depending only on the frequency.

We plot in Fig. 3(b) the response functions Im $\chi(\omega)$ for various temperatures from 200 to 136.5 K obtained through the relation Im $\chi(\omega) \propto I_S/[n(\omega)+1]$. It is found that the response function increases rapidly below ~ 30 cm^{-1} as the temperature approaches T_c, which just corresponds to the frequency region where Q deviates from unity. Since the

sudden temperature variation in Im $\chi(\omega)$ implies the presence of strong anharmonicity in the modes within this frequency range,[15] the deviation from Eq. (3) is deeply connected with the anharmonicity in the coupling among microscopic polarizations.

Before closing, we will briefly comment on the origin of the deviation of the Stokes-to-anti-Stokes intensity ratio from the Boltzmann factor. It is generally believed that the deviation under nonresonant excitation originates from the breakdown of the time-reversal symmetry, which mostly comes from the dissipative nature of the level. To our knowledge, however, theoretical study on the breakdown of Eq. (3) has not been reported even for simple spectral broadening due to dissipation. One may think that some kind of dissipation may also affect the present result. However, in the present case of the soft mode, the central mode should not be expressed in terms of a simple dumped-oscillator model because of its cooperative nature. In the KDP crystal, it is known that the soft mode arises from the collective motion of the polarization fluctuation related to PO_4 tetrahedrons.[16,17] From a statistical-mechanical viewpoint, such a collective motion should be expressed by macroscopic variables that are created after elimination of numerous degrees of microscopic freedom. Further, such macroscopic behaviors should be expressed by a suitable macroscopic equation of motion,[18] and a Lorentzian-like spectrum and/or exponential response should be considered as a manifestation of its Markovian nature.[19]

This situation is analogous to the behavior of a Brownian particle in a liquid. When the particle size is comparable to that of the liquid molecules, the particle motion is strongly

affected by the microscopic motion of the liquid molecules. However, when the particle size becomes much larger, the particle motion loses microscopic memory and becomes dissipative, i.e., the dynamics becomes Markovian. In a similar manner, as the temperature approaches T_c, the correlation length for the polarizations of individual PO_4 tetrahedrons increases, and the amplitude of polarization fluctuation grows considerably. Then, the macroscopic polarization fluctuation loses microscopic memory and becomes dissipative. Under Markovian dynamics, the frequency distribution of the fluctuation is not expressed by an ensemble of discrete energy levels connected with the microscopic dynamics, and, as a result, the Boltzmann factor should not be applied to the spectra of such fluctuations. To promote further discussion and to understand truly the whole energy region of the light scattering spectrum, it is necessary to develop a new model that will explain both microscopic and macroscopic dynamics from a common standpoint.

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