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Brillouin Scattering Study on the Relaxation Time of Polarization Fluctuation in Mixed Crystals $\mathrm{KDP}_{1-x}\mathrm{DKDP}_x$

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On the assumption that polarization fluctuation is of Debye type, a relaxation time of an individual dipole in mixed crystals $\mathrm{KDP}_{1-x}\mathrm{DKDP}_x$ is obtained from Brillouin scattering spectrum in the geometry $x(y, x)y$. The relaxation time increases from 0.19×10^{-12} sec at $x=0.04$ to 1.03×10^{-12} sec at $x=0.72$. It is found that Debye type susceptibility is a good approximation even for the crystal with $x=0.04$.

§1. Introduction

Brillouin scattering study is a useful tool for the investigation of a dynamical property of a phase transition mechanism. Assuming that the complex susceptibility of KD_2PO_4 (DKDP) is of the Debye type, Reese et al.[1)] obtained the relaxation time of the polarization fluctuation in DKDP by analyzing spectra observed in the geometry $x(y, x)y$. In contrast to DKDP, the polarization fluctuation in KH_2PO_4 (KDP) seems to be described by the over-damped soft optical phonon model.[2)] However, dielectric dispersion in KDP in the frequency range of 5–12 cm^{-1} is well explained by the Debye model as well as by the over-damped soft optical phonon model.[3)]

In order to see which model is preferable for describing the polarization fluctuation in KDP, a Brillouin scattering study of $\mathrm{KDP}_{1-x}\,\mathrm{DKDP}_x$ is performed in the geometry $x(y, x)\,y$ and the relaxation time of the polarization fluctuation is evaluated by fitting experimental data to the theoretical formula[4,5)] which is derived with the Debye model. The theory takes account of a piezoelectric coupling between polarization and acoustic phonon systems. It is especially important to include the piezoelectric coupling for analyzing a spectrum in the low x region, where the intensity of the broad central component becomes smaller than that of the phonon peak.

§2. Experimental Procedure

Powdered KDP was dissolved in water mixed with appropriate amount of heavy water. In order to obtain a large single crystal, pH of aqueous solutions was adjusted to be about 5 by dissolving K_2CO_3. Aqueous solutions were filtered with a micron filter of 0.1 μm pore size. Single crystals were grown by lowering temperature. The concentration x was obtained by an equation,[6)]

$$T_c(^\circ\mathrm{C}) = 107x - 152.1, \qquad (1)$$

where -152.1°C is the phase transition temperature of pure KDP grown by us. Crystals were correctly oriented by observing the angular dependence of acoustic phonon frequencies associated with $(C_{11}+C_{12}+2C_{66})/2$, where C_{ij} is an elastic stiffness constant. The error in angle was within ± 1 degree. A sample is placed in a small cavity which is filled with iso-pentan, which provides a partial refractive index matching. Temperature fluctuation was kept within $\pm 0.1^\circ$C by controlling the current to heater with Ohkura EC-61. The temperature gradient in the sample cell was about 0.1°C/cm along the vertical direction. The light source was the Ar^+ laser of a longitudinal single mode at 4880 A. Incident power was usually kept to be 150 mW. Acquired data were punched on a paper tape to process the data with FACOM 270–25/35.

§3. Results and Discussion

In the geometry $x(y, x)y$ a spectrum consists of an acoustic phonon peak and a broad central component the intensity of which increases as temperature approaches T_c. The elastic stiffness constant associated with this phonon frequency ω_a is $C_a = (C_{11}+C_{12}+2C_{66})/2$. Figure 1 shows the typical example of the concentration dependence of spectra. Since the Brillouin shift is about 18 GHz and the free spectral range of Fabry-Perot interferometer is 29.8 GHz, the phonon peak at the right is concerned in the Rayleigh peak at the left in Fig. 1. The width of

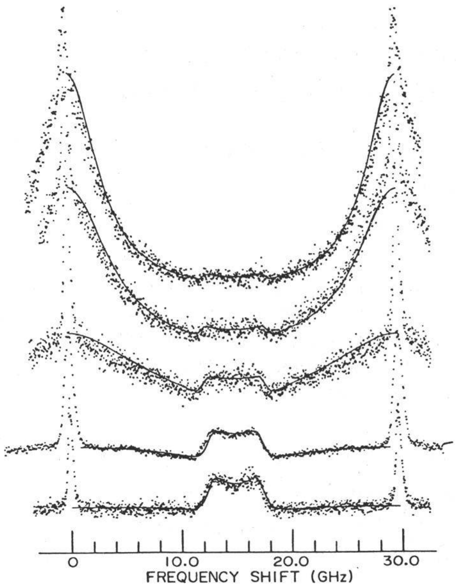

Fig. 1. The x dependence of Brillouin spectra in the geometry $x(y, x)y$ at $T-T_c=0.2$°C. x(from top to bottom): 0.72, 0.46, 0.23, 0.08 and 0.04.

the broad central component decreases as the concentration x increases. For $x=0.0$ (not shown in Fig.) and 0.04, the broad central component does not appear even near T_c but the base line of the spectrum rises slightly (Fig. 2). This fact indicates that the central component of crystals with $x=0.0$ and 0.04 are too broad to be osberved as a peak by the Fabry-Perot interferometer with the relatively narrow free spectral range.

The spectrum is expressed[4,5] as eq. (2) in terms of the reduced angular frequency $\Omega=\omega/\omega_a$, where ω is the deviation of the angular frequency from that of the incident light.

$$I(\Omega)\propto\frac{(1-\Omega^2-R)^2}{\Omega^6+\alpha\Omega^4+\beta\Omega^2+\delta}, \tag{2}$$

where $\alpha=z^2-2$, $\beta=1-2z(z-z_0)$, $\delta=(z-z_0)^2$ and $R=p_{66}a_{36}/f_{63}C_a$.

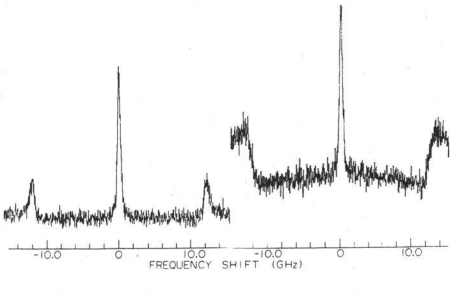

Fig. 2. Spectra of mixed crystal with $x=0.04$ at $T-T_c=7.3$°C (left) and 0.1°C (right).

The parameters z_0 and z are given by

$$z_0=\left.\frac{a_{36}^2\chi_0}{C_a\omega_a\tau_0}\right|_{T=T_c}=\frac{\varepsilon_c}{\omega_a\tau_0} \tag{3}$$

and

$$z=\frac{\varepsilon}{\omega_a\tau_0}\text{with } \varepsilon=(T-T_0)/T. \tag{4}$$

In the above equations, a_{36}, p_{66} and f_{63} are piezoelectric, elasto-optic and electro-optic coefficients, respectively. The other notation χ_0 is the susceptibility of an isolated-dipole system and τ_0 is the relaxation time of an isolated dipole. The transition temperature T_c is given as

$$T_c=T_0+\frac{a_{36}^2}{C_{66}}\mathrm{C}, \tag{5}$$

where C is a Cuire constant. The parameter T_0 can be estimated as follows. We assume that T_c-T_0 is proportional to C with the proportional coefficeint independent of x, because C_{66}[7] and a_{36}[1,8] depend weakly on x. The x dependence of Curie constant was reported by Samara[9] and T_c-T_0 for $x=1.0$ is 4.5°C.[1] From these values we can obtain T_c-T_0 for each x (Table I). The parameter ω_a and R are determined simultaneously with τ_0 by fitting the calculated $I_c(\Omega)$ to the experimental one at a certain temperature, for example 1°C above T_c, where $I_c(\Omega)$ is the spectrum convoluted with the instrumental resolution function with half width at half maximum of 300 MHz. Using T_0, ω_a and R thus obtained, we determine τ_0 at other temperatures.

Values of the parameters are listed in Table I, where τ_0 is the averaged value. In this paper the temperature dependence of τ_0 is neglected because the temperature range studied is narrow. In Fig. 1 calculated spectra are shown by solid lines. The calculated line shapes agree well with experimental ones. This implies that the assumption of the Debye type susceptibility is reasonable even for crystals with low concentration of DKDP. The ratio of τ_0 of KDP to τ_0 of mixed crystals are shown in Fig. 3, where τ_0 of KDP is 1.1×10^{-13} sec.[3] It is found from Fig. 3 that the x dependence of τ_0 is qualitatively similar to that reported by Volkov et al.;[10] in the low x region, the inverse of τ_0 decreases rapidly with increasing x up to ~0.20 and it decreases slowly in the high x region.

Table I Parameters used for calculation of the intensity of scattered light.

x	T_c(°C)	T_c-T_0(°C)	ω_a(GHz)	$-R$	$\tau_0\times10^{12}$(sec)
0.72	−75.5	4.2	17.8	0.024	1.03 ± 0.05
0.46	−102.9	3.8	18.0	0.032	0.76 ± 0.05
0.23	−126.9	3.7	18.0	0.032	0.50 ± 0.03
0.08	−143.0	3.3	18.0	0.035	0.25 ± 0.02
0.04	−147.6	3.3	18.2	0.040	0.19 ± 0.02

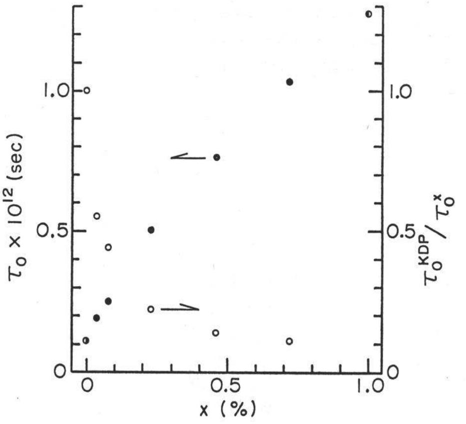

Fig. 3. The x de pendence of relaxation times τ_0 (solid circles) and the ratio of $\tau_0^{\mathrm{KDP}}/\tau_0^x$ (open circles), where τ_0 is 1.1×10^{-13} sec. The relaxation time τ_0 for $x=0$ is that reported by Volkov *et al.* and τ_0 for $x=1.0$ is calculated one from the data by Reese *et al.*

Takagi and Shigenari found in Raman scattering study[11] that the gradient of the inverse of the relaxation time $\tau(T)$ versus temperature curve tends to zero in the neighborhood of $x\sim0.21$, when they used the Debye type formula for the complex susceptibility. They suggested that there is a qualitative difference in the phase transition mechanism in the neighborhood of $x\sim0.21$. However, in the present study, the x dependence of τ_0 is smooth and monotonic and we cannot find the aspect which seems to show the change in the phase transition mechanism. As far as Brillouin scattering study is concerned, spectra in mixed crystals can be described by assuming the Debye type susceptibility.

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