of the $90°$-rotation.

There are two sorts of rotations, namely clockwise and counterclockwise. It is considered that uniformity of the rotations is favorable, because the dipole interaction in the direction of the c-axis will become stronger by the uniform rotation. Moreover taking account of the fact that the refractive index is maximum in the direction of the c-axis, mechanism of the anomalous rapid sidewise propagation of the polarization reversal in $NaNO_2$ will be explained, where the strong internal field is induced in the direction of the c-axis accompanied by the NO_2-rotation round the a-axis.

Soft Zone-Boundary Phonon Modes in CsPbCl$_3^*$

Y. Fujii[†] and G. Shirane

Brookhaven National Laboratory Upton, New York 11973

It was previously reported that three successive phase transitions of the perovskite crystal $CsPbCl_3$ (T_C = 47, 42 and $37°C$) are caused by the condensation of the zone-boundary phonon modes M_3 and R_{25} at the $M(\frac{1}{2}\frac{1}{2}0)$ and the $(R\frac{1}{2}\frac{1}{2}\frac{1}{2})$ points respectively [Y. Fujii, S. Hoshino, Y. Yamada and G. Shirane, Phys. Rev. B9, 4549 (1974)]. Inelastic neutron scattering experiments have been carried out in its cubic phase ($T>47°C$) in order to investigate properties of these two phonons, both of which correspond to the rotational vibration of the $PbCl_6$ octahedra around the $<100>$ axis.

The temperature dependence of the energy-profile of the M_3 as well as the R_{25} phonons was precisely measured up to the temperature of about $300°$ above the transition point. Both phonons were found to remain overdamped throughout this temperature range. With a least-squares method, the observed phonon profiles were fitted by a damped-harmonic-oscillator formula convoluted with the resolution function. This analysis gave the value of ω_0^2/Γ (ω_0: harmonic frequency, Γ: damping constant) as a function of

temperature. In the present case, however, ω_0 and Γ could not be obtained separately because the observed phonon never becomes underdamped in the temperature range investigated. The value of ω_0^2/Γ (meV) for the M_3 phonon varies from 0.12 at $56°C$ through 0.89 at $331°C$ while that for the R_{25} one from 0.20 ($51°C$) through 0.59 ($249°C$). Here, $\sqrt{2}$ can be looked upon as a boundary between the overdamping and the underdamping. This heavy damping in $CsPbCl_3$ is really anomalous in comparison with other perovskites such as $SrTiO_3$ (R_{25}), $KMnF_3$ (R_{25}, M_3) and $LaAlO_3$ (R_{25}) in which even the most-heavily-damped-phonon responsible for the transition (R_{25} in $LaAlO_3$) becomes underdamped at $70°$ above the transition point. The recent NMR study by van Driel and Armstrong has also shown the anomalously heavy damping in this crystal [Phys. Rev. B12, 839 (1975)].

These experimental results suggest that the potential for the rotation of the $PbCl_6$ octahedra is strongly anharmonic. This anharmonicity probably results from the interaction between the Cl and the Cs ions as Pytte and Feder took it into account as a main anharmonic term in their theory of a structural phase transition in perovskites [Phys. Rev. 189, 1077 (1969)]. The empirical rule for an occurrence of the transition recently found by Rousseau et al. seems to support it [Phys. Rev. B12, 1579 (1975)]. The order-disorder model of the Cl ion originally proposed by Møller is also discussed as one more possible explanation for these experimental results.

An attempt to observe the "central peak" at both the M and the R points was made at the high energy resolution (0.1 meV FWHM). But its existence could not be confirmed because the heavily damped phonon (M_3, R_{25}) gives a sharp peak at the $\omega = 0$ position in a wide temperature range.