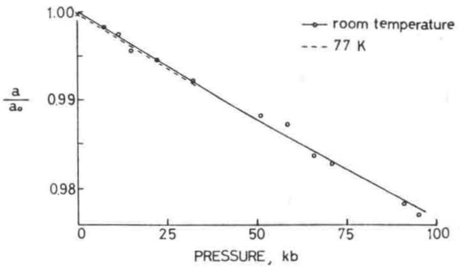

Fig. 2. a/a_0 vs. pressure for Si. The solid curve represents the experimental values at room temperature, and the broken curve the expected ones at 77K. The cross is from Ibach's measurement on thermal expansion of Si.

at room temperature[7] is about a quarter of that of NaCl,[8] whereas the amount of thermal contraction from room temperature to 77K in Si at atmospheric pressure[9] is extremely small compared to that in NaCl,[10,11] that is, one-thirtieth. The solid curve in Fig. 2 shows the lattice parameter-pressure relation of Si at room temperature obtained by using the present camera. The pressure values of the abscissa were determined from the lattice parameter of NaCl mixed with Si. The cross on the ordinate in Fig. 2 represents the lattice parameter of Si at 77K obtained from Ibach's measurement at atmospheric pressure on thermal expansion.[9] If a broken curve passing through the cross point and being parallel to the solid curve, represents the lattice parameter-pressure relation of Si at 77K, the overestimation of pressure at 77K caused by using the solid curve instead of the broken curve is about 1 kbar. Generally a thermal expansion becomes smaller with increasing pressure. Therefore, the overestimation of pressure at 77K will be fairly less than 1 kbar at about 100 kbar. Since the present accuracy in pressure determination by X-ray technique is ±2 kbar, the overestimation is rather small. Consequently the curve obtained at room temperature was used to determine the pressure at 77K. Thus, the compression measurement of NaCl at liquid nitrogen temperature was made using a mixture of NaCl and Si. Two reflections, 200 and 220 were used for determining the lattice parameter of NaCl. The reflections of Si that were used are 111 and 220.

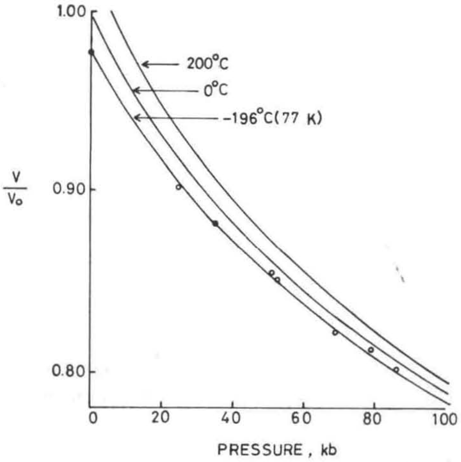

Fig. 3. Volume change as a function of pressure for NaCl. Solid lines are the calculated ones using Decker's equation, and circles are experimental results at 77K.

§3. Results and Discussion

In Fig. 3, the volume change of NaCl is plotted against pressure along three isotherms. The curves of 0 °C and 200 °C represent the results of calculation by Decker,[2] and that of −196 °C (77K) the result of a simply extended calculation. The circles represent the experimental values at liquid nitrogen temperature obtained in the present study. The circles agree with the isothermal curve at 77K within experimental error.

Decker's calculation used the Mie-Grüneisen equation of state, *i.e.*,

$$P=-(\mathrm{d}\Phi(V)/\mathrm{d}V)+(\gamma_E/V)E_v(V,T),$$

where P is the pressure, $\Phi(V)$ the lattice potential energy, V the volume, γ_E the Grüneisen parameter, $E_v(V,T)$ the vibrational contribution to the energy, and T the absolute temperature.[1] At high temperatures where the heat capacity at constant volume has attained its classical value, γ_E is a function of volume only and identical with the parameter γ defined by the Grüneisen relation:

$$\gamma=V\beta/C_VK$$

where β is the coefficient of (volume) thermal expansion, K the isothermal compressibility, and C_V the heat capacity at constant volume of the solid.[12,13] Thus, Decker assumed a volume dependence of γ_E of the form

$$\gamma_0(V/V_0)^A$$

where γ_0 is the Grüneisen parameter defined by the Grüneisen relation at atmospheric pressure and 25 °C, V_0 the volume under these

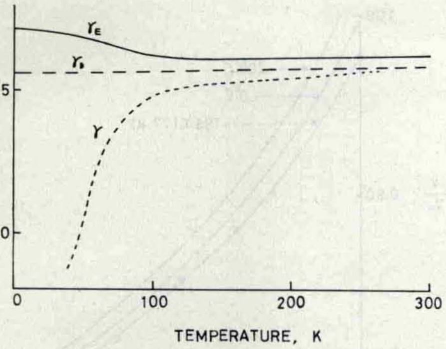

Fig. 4. Grüneisen parameters γ_E, γ_D and γ of NaCl as functions of temperature at atmospheric pressure.

conditions, and A constant.[2)] The value of γ_E obtained from Decker's assumption will be referred to as γ_D. At low temperatures, however, γ and γ_E are not identical and dependent on volume only, but are different functions of both volume and temperature.[12,13)] Therefore, Decker's assumption is not valid at low temperatures. Pautamo[13)] calculated γ_E at atmospheric pressure in the temperature range from 0K to 500K for NaCl.* The values of γ_E calculated by Pautamo are shown in Fig. 4. The values of γ_D used to extend Decker's calculation to low temperatures are also included in Fig. 4. In addition, the values of γ[10,11)] are shown for purpose of comparison.

The error in the pressure calculation caused by using γ_D instead of γ_E reflects on the second term on the right-hand-side of the Mie-Grüneisen equation, *i.e.*, $(\gamma_E/V)E_v(V,T)$. From the values of γ_E and γ_D in Fig. 4, the values of pressure obtained by an extension of Decker's calculation using γ_D are found to be about 0.2 kbar low at 77K and 0.35 kbar low at 0K at atmospheric pressure compared to those calculated by using γ_E. It is difficult to know the values of γ_E at high pressures by theoretical calculation. However, if the difference $\gamma_E-\gamma_D$ at 100 kbar is equal to that at atmospheric pressure at all temperatures, the pressure in the extended Decker's calculation using γ_D is also low by the amount of about 0.3 kbar at 77K and 0.6 kbar at 0K around 100 kbar.

The present experimental result indicates these assumed values of the difference $\gamma_E-\gamma_D$ at high pressure do not deviate appreciably from the true ones at least at 77K. Thus, the present compression curve determined by high pressure X-ray technique with the extended equation of state of NaCl is useful for determining the pressure at 77K.

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*Pautamo calculated γ_E from the following equation.

$$\gamma_E=\gamma+\frac{E_Z}{E}(\gamma_Z-\gamma_{T\to 0K})-\frac{1}{E}\int_{\gamma_{T\to 0K}}^{\gamma}E\mathrm{d}\gamma.$$

Here, E and E_Z are the total vibrational energy and the zero point energy of the crystal, respectively, $\gamma_{T\to 0K}$ the low temperature limit of γ, and γ_Z the low temperature limit of γ_E, γ_Z is evaluated by interpolation from $\gamma_{T\to 0K}$ and γ_∞, the high temperature limit of γ.