X-Ray Measurement on the Compression of NaCl to 80 kbar at Liquid Nitrogen Temperature

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An X-ray camera for use at high pressure and low temperature was designed to measure the lattice parameter of NaCl as a function of pressure up to 80 kbar at liquid nitrogen temperature. The change in pressure on cooling the clamp vessel was corrected by using the lattice parameter-pressure relation of Si at room temperature. The result on the pressure-volume relation of NaCl is in agreement within the experimental error with simply extended Decker's calculation of the equation of state of NaCl.

§1. Introduction

Recently Decker[1,2] calculated an equation of state of NaCl up to hundreds kilobars at elevated temperatures by using the vibrational Mie-Grüneisen equation in order to establish the calibration of pressure in high-pressure high-temperature apparatus. Since his calculation agreed with the results of both the dynamic compression and the static compression, it has been used as a reliable scale of pressure.

On the other hand, a strong requirement began to arise to calibrate high pressure precisely at lower temperatures as the high pressure technique has been employed in the solid state physics. Similarly to high temperature experiments, a pressure calibration established at room temperature can not be used directly for low temperature experiments because of the changes in thermal and elastic properties of a pressure transmitter. The pressure dependence of superconducting transition temperature T_c of metals such as tin and lead is often used as a low temperature manometer.[3] However this method is not established, since the pressure calibration itself involves a problem as to measuring the pressure effect on T_c, though there is an exception of the careful measurement by Jennings and Swenson[4] who used solid parahydrogen as a transmitter to produce quasi hydrostatic pressure up to 10 kbar.

It seems that Decker's method of pressure calibration by using the equation of state of NaCl can still be used at lower temperatures, although he did not calculate the equation at the temperature below 0 °C. In order to extend Decker's calculation to the lower temperature range, one needs to check his assumption that the Grüneisen parameter is a function of volume only and to see if it is applicable in the range of high pressure and low temperature of interest. The purpose of this paper is to develop a high-pressure low-temperature X-ray camera and to examine the validity of the extended Decker's calculation by measuring lattice parameter of NaCl under pressure at liquid nitrogen temperature.

§2. Experimental

2.1 *High-pressure and low-temperature X-ray camera*

A camera was designed to obtain Debye-Scherrer patterns of substances under conditions of high pressures and low temperatures. As shown in Fig. 1, the camera consists of a pressure clamp vessel, a frame with a film cassette, and a dewar. The clamp vessel has almost the same structure as a room temperature camera previously reported.[5] The whole part of the clamp vessel except Bridgman anvils was made of copper-beryllium alloy because of its ductility at low temperatures. A collimator consisting of two circular apertures with diameter 0.3 mm separated by a distance 20 mm is contained in the body of the clamp vessel. A boron-epoxy cell of 3.0 mm in diameter and 0.5 mm in thickness with a powdered sample at its center is placed between Bridgman anvils made of tungsten carbide. After pressure is clamped with the same method as described in a previous paper,[5] the clamp vessel is suspended by a stainless steel bar from the center of the ceiling of the frame so as to

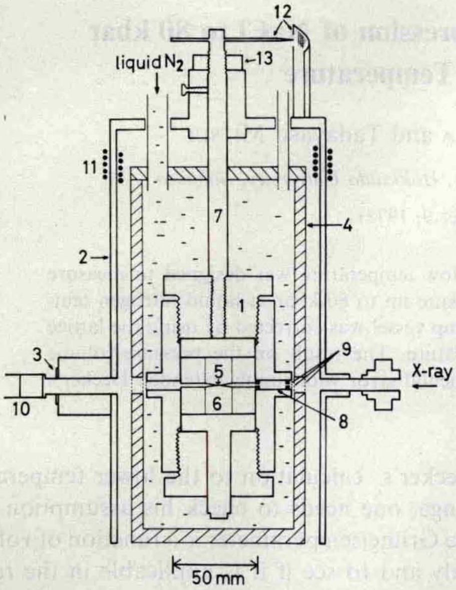

Fig. 1. Cross section of high-pressure and low-temperature X-ray camera.
1) pressure clamp vessel 2) frame 3) film 4) dewar 5) sample in boron-epoxy cell 6) Bridgman anvil 7) stainless steel bar 8) pinhole collimator 9) mylar sheet 10) beamtrap with fluorescent screen 11) heating coil 12) helm with indicator, and scale 13) nut.

construct a 172 mm diameter Debye-Scherrer camera.

A dewar is inserted between the clamp vessel and the frame. A sample can easily be held at 77K by putting the clamp vessel into liquid nitrogen. Intermediate temperatures, when necessary, can be obtained by using ethyl alcohol, isopentane, and other suitable fluid cooled by liquid nitrogen instead of liquid nitrogen itself. The temperature was measured with a copper-constantan thermocouple attached to an anvil near a boron-epoxy cell. In order to prevent the film cassette and a film from shrinking due to conduction cooling, the temperature of the frame was kept at room temperature by winding heating coils around the frame. The dewar has an opening for admitting an incident X-ray and a slot for extracting X-rays diffracted in the angle range $-50° < 2\theta < +50°$. These opening and slot are covered on both sides with mylar film transparent to X-rays. In order to protect a coolant from filling the gap between the anvils and absorbing the X-rays, the collimator and the slot of the clamp vessel are also covered with mylar film. In addition, a clearance between the inside of the dewar and the outside of the clamp vessel was designed to be as small as possible to minimize the absorption and the scattering of the X-rays by a coolant.

At each run, the frame was placed at the definite position in front of the X-ray tube. Then the height and the direction of the clamp vessel were adjusted relative to the frame with the aid of a nut and a helm respectively, so that the collimated beam was observed at the center of the fluorescent screen. The readjustment of the height was necessary, because the clamp vessel and the stainless steel bar shrinked on cooling.

Filtered Mo Kα radiation from a Rigaku Denki RU-3H rotating anode X-ray generator was used. It took 1.5 hours to obtain diffraction pattern of NaCl or Si at high pressure and low temperature at an output of 50 kV and 80 mA. The diffraction pattern obtained at liquid nitrogen temperature was as clear as that obtained at room temperature. The precision of lattice parameter determination by using the present camera is approximately $\pm 0.1\%$.

2.2 *Pressure determination*

The value of the pressure clamped at room temperature was easily determined from the measurement of the lattice parameter of NaCl on the basis of Decker's calculation[2)] of equation of state of NaCl at 25°C. Preliminary measurements showed clearly that this pressure gets intensified when the clamp vessel is cooled. This is mainly due to a difference in thermal contraction of load-bearing members (copper-beryllium clamp vessel, tungsten carbide anvil, and boron-epoxy cell). A large amount of pressure intensification was also reported by Christoe and Drickamer[6)] who developed a clamp cell for high pressure X-ray and Mössbauer resonance studies.

In the present study the following method was employed to determine directly the pressure at a sample at low temperature. If thermal expansion is negligibly small compared to compressibility, a lattice parameter-pressure relation at room temperature can be employed for the pressure calibration at low temperatures. For this purpose Si was adopted in this experiment. Namely, the compressibility of Si

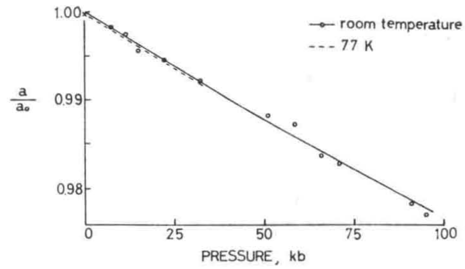

Fig. 2. a/a_0 vs. pressure for Si. The solid curve represents the experimental values at room temperature, and the broken curve the expected ones at 77K. The cross is from Ibach's measurement on thermal expansion of Si.

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.

§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.

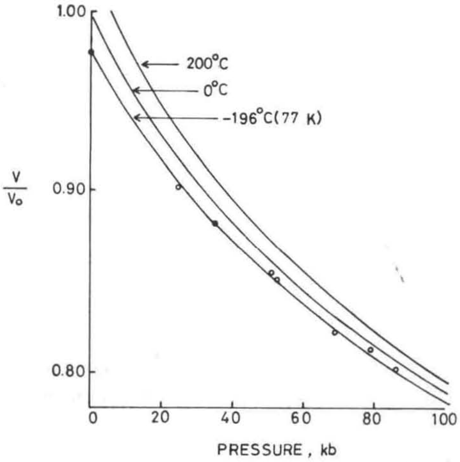

Fig. 3. Volume change as a function of pressure for NaCl. Solid lines are the calculated ones using Decker's equation, and circles are experimental results at 77K.

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:

$$\gamma = V\beta/C_V K$$

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

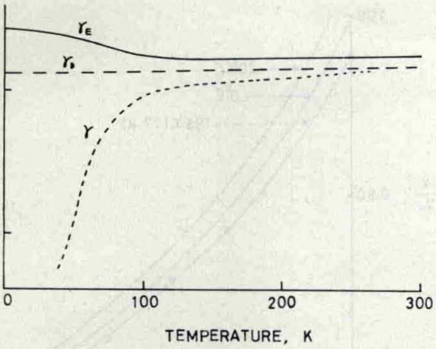

Fig. 4. Grüneisen parameters γ_E, γ_D and γ of NaCl as functions of temperature at atmospheric pressure.

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.