Measurement of the Elastic Constants of Polycrystals by the Resonance Method in a Cylindrical Specimen*

(Measurement at Liquid He Temperature)

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The resonance method of three-dimensional free vibrations with the cylindrical specimen, which has been developed by the authors, was applied to determine the elastic constants of polycrystals in a temperature range of 4–300 K. It was found that the temperature dependence of elastic constants of pure aluminum agreed well with published data measured by the ultrasonic pulse-echo technique over the temperature range of measurements. A sluggish change induced could also be detected in niobium. In addition, the temperature dependence of elastic constants for superconducting Al-Si and Al-Ge supersaturated solid solutions was examined, and the Debye temperature was determined by extrapolating the elastic constants to the values at 0 K.

Key Words: Material Testing, Elastic Constants, Resonance Method, Very Low Temperature, Aluminum Alloy, Solid Solution, Debye Temperature

1. Introduction

Elastic constants of solids are significant in the field of materials science. Specifically, superconducting phenomena of metals and alloys are closely related to elastic constants. As recent superconducting technology has shown remarkable improvements, greater accuracy of measurement of elastic constants at very low temperatures is expected.

In a previous paper⁽¹⁾, the resonance method of three-dimensional vibrations performed on a homogeneous and isotropic specimen was reported to be effective in the accurate determination of elastic constants at room temperature. Using a small cylindrical specimen ($\phi 6 \times 6$ mm), all independent elastic constants were determined with an accuracy within a few percent. In the next papers^{(2)–(3)}, the temperature

ranges were extended from a low temperature of -196°C (liquid nitrogen temperature) to a high temperature of 300°C , and the elastic anisotropy of axisymmetrical specimens and planar anisotropic sheets was measured.

In the present experiments the temperature ranges were extended further to a very low temperature of 4 K using a liquid He cryostat. As for the experimental procedure in this case, several problems had to be settled, such as the small-scale suspension of the specimen, the highly sensitive transducer used even at very low temperatures, and so on. First, to confirm the validity of the present experiments, the elastic constants of pure Al and pure Nb were measured across the entire temperature range, and compared to published data which used the ultrasonic pulse-echo method on single crystals. Next, the temperature dependence of elastic constants for superconducting Al-Si and Al-Ge supersaturated solid solutions was examined. These alloys have the potential to become superconducting materials, because it is reported^{(4),(5)} that the dependence of the solute content (density of valence electrons) for the superconducting transition temperature (T_c) has a very high slope. In

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addition, solute content dependence of the Debye temperature, which specified the thermal and elastic properties of materials and their relation to T_c , was investigated.

2. Experimental Apparatus and Methods

2.1 Measurement systems of resonance frequencies

The block diagram of the measurement system for resonance frequencies of the specimens is shown in Fig. 1. A frequency analyzer with synchronized sweep filter was used to detect the resonant spectra as in the previous paper⁽¹⁾. The resonant frequency was counted to the nearest 0.01 kHz on a five-digit frequency counter. The specimen temperature was measured by a thermocouple wire of 0.2-mm diameter of Au-0.07% Fe/Cr, which has good linearity of electromotive force at very low temperatures.

2.2 Experimental method at very low temperatures

The very-low-temperature apparatus is, as shown in Fig. 2, a continuous-flow cryostat (made by Oxford Co.), with a vessel size of 20 mm in diameter and 70 mm in length. The specimen in the vessel is cooled by vaporizing the liquid He, which is induced into the cryostat by a gas flow pump. The temperature

Fig. 1 Block diagram of the measurement system for elastic constants

Fig. 2 Block diagram of the very-low-temperature apparatus

is controlled in the PID system by flow control valves and a heater in the vessel. The temperature fluctuation is kept to ± 1 K.

The contrivance to suspend the specimen in the cryostat is shown in Fig. 3. Piezoplates of LiNbO_3 (size of $7 \times 7 \times 0.5$ mm and Y-cut) were used for the transducer of vibrations as actuator and sensor, because usual piezoplates of PZT ($\text{Pb}[\text{Zr-Ti}]\text{O}_3$) were not sensitive enough to detect resonance at very low temperatures. Both sides of the plates of LiNbO_3 were coated by silver-film electrodes in which thin electric wires were fixed. Sapphire needles to suspend the specimen were adhesively attached to the center of each plate with low temperature varnish (# 7031 made by General Electric Co.). A lead plate was inserted between the piezoplate and an aluminum support ($27 \times 10 \times 0.2$ mm) in order to avoid spurious spectra created by the resonance of the suspension parts. The load of the specimen was controlled by the size of the spacers. As the S/N ratio is much lower at very low temperatures, one must be skillful in the clipping of the specimen to generate a stable resonance.

2.3 Specimen

Specimens of seven kinds of materials were prepared; i. e., two kinds of casts from pure aluminum (99.99 %) and pure niobium (99.96 %), and five kinds from the supersaturated solid solutions of Al-5, -10, -15 at%Si, and Al-5, -10 at%Ge, which were solution-treated under very high pressure. The processes for high-pressure treatments were as follows:

Fig. 3 Suspension of the specimen in the cryostat (a) External appearance (b) Details of transducers and suspended specimen

pure powders (made by Rare Metallic Co.) of Al (99.9%, 200 mesh), Si (99.9%, 150 mesh) and Ge (99.9%, 100 mesh) were mixed for each desired composition. The mixtures were preformed into cylindrical specimens ($\phi 6 \times 6$ mm) up to approximately 1 GPa by a handpress, since the specimens were then heat-treated under very high pressure at 5.4 GPa to make super-saturated solid solutions. The treatment temperature was chosen to be 600°C for the Al-Si system and 400°C for the Al-Ge system after the high-pressure phase diagrams⁽⁶⁾. Each specimen was kept at high pressure and temperature for 10 hours, and then quenched to room temperature by shutting off the heating current. The solution-treated specimens were examined by X-ray diffraction to confirm the absence of Si and Ge precipitate.

Then, all specimens were carefully lathed into a cylindrical shape to measure the elastic constants. The size of the specimen was measured to the nearest 0.01 mm on a micrometer, and density was deduced from buoyancy in water by an accurate balance (0.1–mg minimum scale).

2.4 Determination methods of the Debye temperature

The Debye temperature is a characteristic constant for lattice vibrations in solids, from which some information on thermal and elastic properties can be obtained. For example, since some types of superconducting phenomena are directly related to lattice vibrations, this is a very important parameter in McMillan's equation⁽⁷⁾ which must be used to estimate superconducting transition temperature. The Debye temperature could also be determined using measurements of specific heat at low temperature or X-ray-diffraction intensity, but these experiments are not as easily and accurately performed.

Debye theory assumes that a solid material is an isotropic-, homogeneous- and continuous- elastic medium. The Debye temperature is a characteristic value deduced from the energy of limited frequency ν_D which must be excited by a sufficiently high temperature⁽⁸⁾.

$$\theta_D = h\nu_D/k_B \quad (1)$$

Here, θ_D , h and k_B are the Debye temperature, Planck's constant and the Boltzmann constant, respectively. The Debye temperature is given by a longitudinal sound velocity v_L and a transverse one v_T , in solids, as follows:

$$\theta_D = (h/k_B) \cdot (9N/4\pi V)^{1/3} \cdot [1/v_L^3 + 2/v_T^3]^{-1/3} \quad (2)$$

Here, N is the amount of atoms included in the solid volume V . Two sound velocities of an isotropic solid are given by two elastic constants c_{11} and c_{12} and density ρ , as follows:

$$v_L = (c_{11}/\rho)^{1/2}$$

$$v_T = [(c_{11} - c_{12})/2\rho]^{1/2} \quad (3)$$

These two elastic constants are related to the shear modulus G and Poisson ratio ν .

$$c_{11} = 2G(1 - \nu)/(1 - 2\nu)$$

$$c_{11} - c_{12} = 2G \quad (4)$$

The elastic constants at 0 K are estimated from the measurements to a temperature of 4 K through the use of the Varshni's equation⁽⁹⁾

$$C = C_0 - s/[\exp(t/T) - 1] \quad (5)$$

where C is the elastic constant at T K, C_0 at 0 K, and s and t are fitting parameters. This correction due to the extrapolation is, however, less than 0.05 %.

3. Experimental Results and Discussion

3.1 Determination of the elastic constants

The procedure for the determination of the elastic constants was fully described in the previous paper⁽¹⁾. The vibration modes of the observed spectra were assigned to the trial calculations up to the 20th mode. The order of these modes was not changed across the entire temperature range from temperature to very low temperature, so that mode assignment was relatively easy. At low temperature, noises with some irregular peaks were gradually generated at a frequency range of 200 to 400 kHz, and the S/N ratio had obviously fallen. As the Q -values due to the inner friction of specimens were, however, as large as 5000 to 10000, the resonance peaks were remarkably distinct from such noise peaks. The sensitivity of LiNbO₃ decreased at frequencies above 500 kHz, so that several modes could not be measured below a temperature of 20 K. Examples of the observations of the resonance frequencies in pure Al at 299 K and 6 K are shown in Tables 1 and 2, respectively.

To determine the exact elastic constants, some changes in the size of the specimen at each temperature have to be made, but the error is usually less than 0.7 % as reported in the previous paper⁽²⁾. Hence, in the present experiments, the size and density of the specimen at 20°C were used for the entire temperature ranges.

3.2 Temperature dependence of elastic constants of pure aluminum

In Figs. 4 and 5 the temperature dependence of the shear modulus G and Young's modulus E are shown. The latter is reduced from G and the Poisson ratio ν . The temperature dependence of an elastic constant has a negative constant coefficient from room temperature to 100 K, reflecting the lack of harmonic potential between the atoms. Below temperatures of 100 K this coefficient is gradually decreased, and then approaches zero at 0 K. Such a tendency agrees with the thermodynamic approach⁽¹⁰⁾ to the temperature dependence of elastic constants.

The elastic constants obtained in the present experiments are compared to the data of single crystals by an ultrasonic pulse-echo method⁽¹¹⁾. These data in the same figures are reduced to polycrystals under the Voigt or the Reuss condition. The Voigt's values are the average of the elastic stiffness assuming homogeneous strain in whole polycrystals, and the Reuss's are the average of the elastic compliance assuming homogeneous stress in polycrystals. So, the Voigt's value and the Reuss's value are the upper and the lower limits of the polycrystal elastic constants, respectively. As mentioned in the previous paper⁽²⁾, the values of the poisson ratio ν were scattered a little, because the contribution of ν to the frequency was less than G as shown in Tables 1 and 2. Consequently

Table 1 Comparison among experimental and calculated values of the resonance frequencies in pure Al at 299 K

$\phi 5.985 \times 6.174$ mm, $\rho = 2.706$ g/cm³
 $G = 26.0$ GPa, $\nu = 0.350$, $E = 70.3$ GPa

No.	Mode	Exp. (kHz)	Calc. (kHz)	$\frac{df/f(\%)}{d\nu/\nu}$	$df/f(\%)$
1	0E-2	251.79	252.24	0.0	-0.178
2	10-2	322.59	321.55	7.1	0.321
3	2E-1	328.95	329.84	0.3	-0.269
4	1E-2	352.94	351.89	1.5	0.299
5	00-2	375.87	376.86	1.3	-0.263
6	20-1	386.49	386.95	0.1	-0.120
7	20-2	409.76	408.58	4.6	0.288
8	10-3	469.28	469.06	11.0	0.048
9	0E-3	491.18	491.04	20.0	0.029
10	00-3	502.77	504.48	0.0	-0.338
11	1E-3	509.87	509.30	4.9	0.112
12	00-4	519.34	521.48	25.7	-0.411
13	2E-2	525.46	525.44	3.4	0.004
14	3E-1	528.76	530.26	0.3	-0.284
15	30-1	550.46	551.42	1.4	-0.175
16	10-4	559.62	559.48	6.7	0.024
17	0E-4	585.13	581.72	5.4	0.586
18	30-2	603.54	603.63	2.5	-0.014
19	1E-4	651.26	650.10	10.3	0.178
20	2E-3	661.99	660.89	2.5	0.167

Fig. 4 Temperature dependence of the shear moduli G in pure Al

the reduced values of E were scattered slightly more than for G . The results in the present experiments were between the upper and the lower limits for the entire temperature range: thus, the present methods were considered to be reasonable ones. The accuracy of the elastic constants obtained was $\pm 1\%$, which was estimated by the standard deviations of the results in each vibration mode.

3.2 Temperature dependence of elastic constants of pure niobium.

The temperature dependence of the Young's modulus E is shown in Fig. 6. The Young's moduli of pure Nb at each temperature were also between the Voigt's and Reuss's values, and the qualitative changes almost agreed with the reduced values of the single-crystal data. Being different from the case of Al, the temperature dependence of the Young's

Table 2 Comparison among experimental and calculated values of the resonance frequency in pure Al at 6 K

$\phi 5.985 \times 6.174$ mm, $\rho = 2.706$ g/cm³
 $G = 29.2$ GPa, $\nu = 0.339$, $E = 78.3$ GPa

No.	Mode	Exp. (kHz)	Calc. (kHz)	$\frac{df/f(\%)}{d\nu/\nu}$	$df/f(\%)$
1	0E-2	-265.77	266.18	0.0	-0.153
2	10-2	340.04	338.84	7.1	0.353
3	2E-1	347.38	348.27	0.3	-0.256
4	1E-2	372.70	371.34	1.5	0.366
5	00-2	397.32	397.64	1.3	-0.080
6	20-1	—	408.54	0.1	—
7	20-2	431.92	430.92	4.6	0.232
8	10-3	493.85	494.19	11.0	-0.070
9	0E-3	515.51	516.55	20.0	-0.202
10	00-3	531.27	532.36	0.0	-0.204
11	1E-3	—	537.16	4.9	—
12	00-4	—	547.90	25.7	—
13	2E-2	—	554.31	3.4	—
14	3E-1	—	559.86	0.3	—
15	30-1	580.92	582.01	1.4	-0.187
16	10-4	—	589.82	6.7	—
17	0E-4	614.63	613.40	5.4	0.201

Fig. 5 Temperature dependence of the Young's moduli E in pure Al

Table 3 Debye temperature and parametrs of Varshini's equation

Sample	Shear modulus G			Young's modulus E			Debye temp.(K)
	C_0 (GPa)	s (GPa)	t (K)	C_0 (GPa)	s (GPa)	t (K)	
pure-Al	29.22	3.392	218.06	78.27	7.434	195.5	430
Al- 5at%Si	28.37	3.100	190.36	76.20	8.656	200.2	421
Al-10at%Si	26.80	3.060	181.84	72.20	7.887	183.6	411
Al-15at%Si	25.72	2.543	149.72	69.53	6.447	147.6	402
Al- 5at%Ge	26.98	2.903	185.87	72.46	7.680	191.9	398
Al-10at%Ge	24.56	2.283	152.31	66.51	5.867	153.0	366

Fig. 6 Temperature dependence of the shear moduli G in pure Nb

modulus of Nb became sluggish at a temperature range of 100 K to 200 K. This phenomenon has been known to exist in metals which have 4d-or 5d-orbit electrons such as Nb, Mo, Ta, W, etc. The elastic constant of Nb, the superconducting element, was supposed to be thermodynamically discontinuous at the superconducting transition temperature (8 K on the present specimen)⁽¹²⁾. The discontinuity was, however, very small, i.e., less than the experimental error; thus, it could not be detected in our experiments. This discontinuity in the superconducting element, Si, was observed to be a small amount of 10^{-6} by single-mode resonance⁽¹³⁾.

3.4 Temperature dependence of elastic constants of Al-Si and Al-Ge supersaturated solid solutions

The variations of shear moduli G of the Al-Si and Al-Ge supersaturated solid solutions, which were heat-treated under very high pressures, are shown in Figs. 7 and 8. The moduli of both alloys were monotonously increased according to the decrease in temperature as in the case of pure Al, and the discontinuity due to superconducting transition at 4 K to 6 K⁽⁴⁾⁽⁵⁾ was not observed in these specimens as in that of pure Nb. It is speculated that no structural transformation or magnetic transition inducing remarkable changes in the elastic constants ever occurred.

On the other hand, these elastic constants were decreased with increasing solute atom contents (mean

Fig. 7 Temperature dependence of the shear moduli G in Al-Si supersaturated solid solutions Fig. 8 Temperature dependence of the shear moduli G in Al-Ge supersaturated solid solutions

density of the valence electrons) across entire temperature ranges. The reason for this was hypothesized in the case of simple metal alloys as follows: The interatomic forces became weak due to changes in the state of the valence electrons which resulted in an increase in the number of electrons per atom.

3.5 Determination of Debye temperatures

The obtained Debye temperatures of pure Al and supersaturated solid solutions of Al-Si and Al-Ge are shown in Table 3. Those values were calculated from the shear moduli G and Young's moduli E at 0 K, which were estimated by the regression equation of Varshini. When Eq. (3) was calculated, the density ρ of solid solutions of Al-Si and Al-Ge was assumed to

be equal to that of pure Al. The error in these determinations was ± 1 K. The value of pure Al in the present experiment agreed fairly well with the Debye temperature of 425 K obtained by a pulse method⁽¹⁴⁾. The Debye temperatures of supersaturated solid solutions of Al-Si and Al-Ge showed linear decreases with increasing solute contents. According to the McMillan's equation the superconducting transition temperature is increased with decreasing Debye temperature. Such a tendency agrees qualitatively with experimental results of the superconductors of Al-Si and Al-Ge solid solutions.

4. Conclusions

By the use of the resonance method with a cylindrical specimen, elastic constants under very low temperatures, down to the liquid-He temperature, were determined. The experiments were performed on pure Al, Nb, and supersaturated solid solutions of Al-Si and Al-Ge, and then the temperature coefficients were measured. The conclusions are as follows:

(1) Improvements were made on the resonance apparatus using piezoplates of LiNbO_3 as transducers of vibrations; hence, the resonance spectra could be detected enough to determine the elastic constants under very low temperature, down to 4 K, when the Q -values of the specimens were determined to be several thousands. The measurement accuracy was $\pm 1\%$ across the entire temperature range.

(2) The elastic constants of pure Al almost agreed with the reduced values from those of single crystals, and then the present experiments were confirmed to be adequate methods. In pure Nb anomalous variations with temperature were observed, but the discontinuity of elastic constants caused by the superconducting transition was not detectable.

(3) The Debye temperatures of supersaturated solid solutions of Al-Si and Al-Ge could be determined from the temperature coefficients of elastic constants, and it was deduced that the superconducting transition temperatures of these alloys had been dependent on the solute contents.

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