# Elastic stiffness and ultrasonic attenuation of superconductor $MgB_2$ at low temperatures

T. Ichitsubo,[1] H. Ogi,[1] S. Nishimura,[1] T. Seto,[1] M. Hirao,[1] and H. Inui[2]
[1]*Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[2]*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*
(Received 4 April 2002; revised manuscript received 12 July 2002; published 29 August 2002)

Temperature dependencies of elastic constants and ultrasonic attenuation of a polycrystalline $MgB_2$ showing high-$T_c$ superconductivity are reported. An electromagnetic acoustic resonance method detected the specimen's resonance frequencies, from which we derived the elastic constants for nonporous $MgB_2$ using micromechanics calculation. The bulk and shear moduli extrapolated to 0 K are determined to be 96.6 GPa and 74.2 GPa, respectively, which gives the Debye temperature $\Theta_D = 819$ K and the coupling constant $\lambda \approx 0.76$–0.89 with McMillan formula. In the temperature behavior of ultrasonic attenuation, two anomalous peaks are observed near 30 K.

DOI: 10.1103/PhysRevB.66.052514 PACS number(s): 74.25.Ld, 74.25.Kc, 74.25.Nf

The remarkable discovery of intermetallic superconductor $MgB_2$ with a high $T_c$ of 39 K (Ref. 1) has triggered related extensive studies to elucidate the mechanism of its superconductivity. A significant boron isotope effect[2] implies that $MgB_2$ is a phonon-mediated superconductor. The *ab initio* calculations,[3,4] tunneling-spectroscopy studies,[5] nuclear spin-lattice relaxation,[6] and photoemission measurements[7] have concluded that $MgB_2$ is a conventional *s*-wave superconductor of "strong" or "intermediate" electron-phonon coupling, although an essential uncertainty still remains in whether $MgB_2$ is a *multiple-gap*[8–11] or *anisotropic-gap*[12,13] superconductor.

The elastic constants are important parameters for knowing the Debye temperature and the electron-phonon coupling constant in a phonon-mediated superconductor. Several related studies appeared: first-principles calculations predicted the single-crystal elastic constants;[14,15] x-ray measurements under high pressure gave the *isothermal* bulk modulus;[16] the flexural resonant method gave Young's modulus;[17] and other results were given in sound-velocity measurements.[18] However, these are inconsistent with each other. Also the temperature dependence has not been systematically measured yet.

Here we have examined the elastic and anelastic properties of $MgB_2$ through the ultrasonic characteristics. This paper presents the temperature dependence of elastic constants of nonporous $MgB_2$ deduced using a micromechanics model, the temperature behavior of ultrasonic attenuation, and observation of two anomalous attenuation peaks below 30 K.

A sample was prepared from commercially available powder by pseudo-HIP sintering at 1273 K for 12 h (referring to the method described in Ref. 1), and we checked that $T_c$ of the sample was about 39 K by an eddy-current method. The x-ray-diffraction spectrum indicated that the sample included a very small amount of MgO. The sample was machined into a rectangular parallelepiped, measuring $5.125(x_1) \times 3.940(x_2) \times 2.349(x_3)$ mm$^3$, where $x_i$ denotes the coordinate axis of the specimen. The mass density is 2301 kg/m$^3$, 87.7% of the theoretical value.

The resonance frequencies for all vibration modes (dilatation, torsion, shear, and flexure modes) were measured by the resonant ultrasound spectroscopy (RUS) method[19] at room temperature. Subsequently, each resonance frequency was identified with the electromagnetic acoustic resonance (EMAR) method, which can excite the specific vibration group through the Lorentz-force mechanism. This noncontact technique[20] is quite sensitive to the ultrasonic attenuation and can measure accurately the internal (intrinsic) friction. Figure 1 shows the resonance spectrum, the resonance peak of the $B_{2g}$-2 vibration mode (-2 denotes the order of the resonance), and the free-decay amplitude.

At low temperatures, we used only the EMAR measurement and focused on the two vibration groups: $B_{2g}$ (shear modes around the $x_2$ axis) and $A_g$ (dilatation modes). The ultrasonic attenuation was measured by the free-decay method, and the attenuation coefficient $\alpha$ was determined by fitting $\exp(-\alpha t)$ to the measured ring-down with time. The normalized attenuation coefficient (internal friction) is obtained by $Q^{-1} = \alpha / \pi f$.

In the RUS procedure, the elastic constants are determined by comparing the measured and calculated resonance

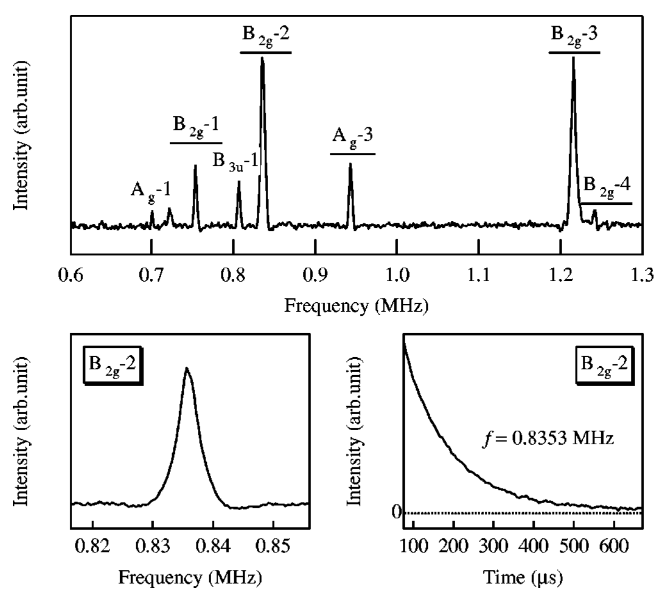


FIG. 1. EMAR resonance spectrum at room temperature (upper), the resonance peak of the $B_{2g}$-2 mode (lower left), and the free decay at this resonance frequency (lower right). Underlined modes were used for determination of the elastic constants.

 

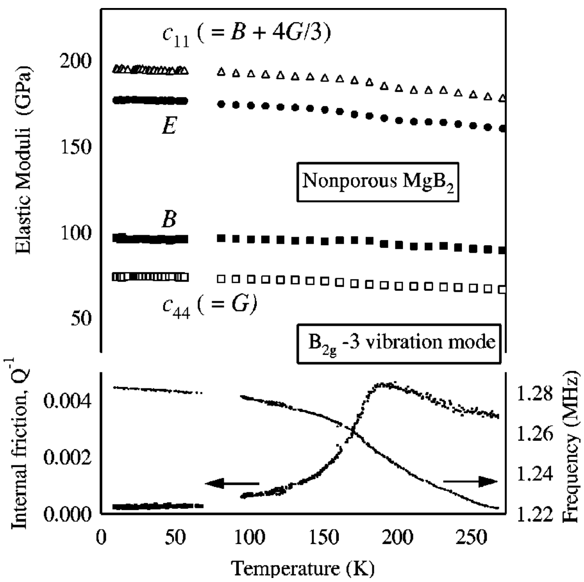


FIG. 2. Temperature dependence of elastic constants (upper) of the nonporous $MgB_2$, internal friction, and resonance frequency (lower).

spectra.[19] The resonance frequencies are first calculated by the Rayleigh-Ritz method, assuming the elastic constants and using the dimensions and mass density of the specimen. Then, attaining good agreement between the measured and calculated spectra after iterations, the assumed elastic constants can be regarded as the true values.

No texture was found from the three-directional longitudinal-wave velocities by pulse-echo measurements. We then supposed a polycrystalline $MgB_2$ to be elastically isotropic. The elastic constants of *porous* $MgB_2$ are determined to be $c_{11}^{(p)}=136$ and $c_{44}^{(p)}=51.7$ GPa (at room temperature). We confirmed the validity with two more specimens of different sizes and virtually the same porosity.

From the determined elastic constants of the porous $MgB_2$, we deduced those for the nonporous material through a micromechanics model.[21] We assume that (i) the matrix is elastically isotropic, and (ii) the pores (inclusions) are spherical. The elastic constants $\mathbf{C}_{mat}$ of the nonporous $MgB_2$ are obtained by solving Eqs. (1)–(3) self-consistently:

$$\mathbf{C}_{mat}=[\mathbf{I}-c_1\mathbf{A}]^{-1}(\mathbf{C}_{com}-c_1\mathbf{C}_{inc}\mathbf{A}), \tag{1}$$

$$\mathbf{A}=[c_0\mathbf{I}+c_1\mathbf{B}]^{-1}\mathbf{B}, \tag{2}$$

$$\mathbf{B}=[\mathbf{I}+\mathbf{S}\mathbf{C}_{mat}^{-1}(\mathbf{C}_{inc}-\mathbf{C}_{mat})]^{-1}. \tag{3}$$

Here, $\mathbf{C}_{com}$ are the measured elastic constants of the porous $MgB_2$, $\mathbf{C}_{inc}$ are those of the inclusion (now $\mathbf{C}_{inc}=\mathbf{0}$), $\mathbf{I}$ is the unit matrix, $c_0$ and $c_1$ are the volume fractions of the matrix and the pores, respectively, and $\mathbf{S}$ is the Eshelby tensor[22] for the spherical inclusion, which depends on $\mathbf{C}_{mat}$ and the pore shape.

Figure 2 shows the temperature dependence of the elastic constants, $c_{11}(=B+4G/3)$, $c_{44}(=G)$, Young's modulus $E$, and the bulk modulus $B$, of *nonporous* $MgB_2$ (upper part) and the normalized attenuation coefficient $Q^{-1}$ of the $B_{2g}$-3 mode (lower part). In the behavior of the elastic constants, we found no anomaly such as lattice instability as seen in the $A15$ superconductors.[23] The polycrystalline elastic constants extrapolated to 0 K are $c_{11}=196$, $c_{44}=74.2$, $E=177$, and $B=96.6$ GPa. Our Young's modulus is close to 167 GPa (uncorrected for porosity, impurities, and temperature) acoustically measured by Cordero *et al.*,[17] and the longitudinal and transverse sound velocities at 77 K (Ref. 18) are very consistent with our measurements. However, the bulk modulus appears to be very different from the *isothermal* bulk modulus by x-ray measurements[16] and the *ab initio* calculations;[14,15] $B$ ranges from 120 to 160 GPa in the literature.

TABLE I. Lattice properties and bulk moduli of $AlB_2$-type compounds at room temperature. $\sqrt{B/\rho}$ is a quantity with a dimension of the sound velocity.

| | $c/a$ | $\rho$ (kg/m$^3$) | $B$ (GPa) | $\sqrt{B/\rho}$ (m/s) | Reference |
|---|---|---|---|---|---|
| $TiB_2$ | 1.067 | 4491 | 243 | 7364 | 24 |
| $CrB_2$ | 1.305 | 5225 | 233 | 6777 | 25 |
| $ZrB_2$ | 1.112 | 6139 | 239 | 6239 | 25 |
| $MgB_2$ [a] | 1.142 | 2625 | 120-160 | 6761-7807 | 14–16 |
| $MgB_2$ | 1.142 | 2625 | 86.1 | 5728 | present work |

[a]At low temperature (or 0 K).

According to the calculation,[15] the bulk and Young's moduli are 158 and 299 GPa for the isotropic $MgB_2$, respectively. Probably, the *ab initio* calculations are based on the elastic property of $TiB_2$, which has the $AlB_2$ crystallographic structure as $MgB_2$. Table I shows the lattice properties and the bulk moduli of $TiB_2$,[24] $CrB_2$, $ZrB_2$[25], and $MgB_2$.[14–16] The compound $TiB_2$ has the ideal axial ratio $c/a=1.067$ for the $AlB_2$ structure, i.e., a close-packed structure; therefore, the bond strength is predicted to be stronger than those of the other compounds. The present study indicates that the elastic property of $MgB_2$ is similar to that of $ZrB_2$ (rather than $TiB_2$) in terms of both axial ratio $c/a$ and sound velocity $\sqrt{B/\rho}$. The elastic stiffness of $MgB_2$ is not particularly large among these compounds, as naturally predicted from its low condensation. From the above viewpoints, the present elastic constants are more reliable and reasonable.

The Debye temperature $\Theta_D$ is an important quantity to estimate the electron-phonon coupling constant $\lambda$, which is proportional to the mean sound velocity $v_m$,

$$\Theta_D=\left(\frac{h}{k_B}\sqrt[3]{\frac{3}{4\pi\Omega}}\right)v_m, \quad \frac{3}{v_m^3}=\frac{1}{v_l^3}+\frac{2}{v_s^3}, \tag{4}$$

where $h/k_B$ has the usual meaning in quantum mechanics, $\Omega$ is the mean atomic volume, and $v_l$ and $v_s$ are the isotropic sound velocities given by $[(B+4G/3)/\rho]^{1/2}$ and $(G/\rho)^{1/2}$, respectively. The present elastic constants at 0 K yield $\Theta_D=819$ K. According to the McMillan formula,[26] the critical temperature $T_c$ is expressed using $\Theta_D$, $\lambda$, and the Coulomb pseudopotential $\mu^*$ as

$$T_c = \frac{\Theta_D}{1.45} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right]. \tag{5}$$

$T_c = 39$ K requires $\lambda \approx 0.76$–0.89 with the conventional values of $\mu^* \approx 0.05$–0.1; $MgB_2$ is thus within the intermediate-coupling regime. Nevertheless, the high Debye temperature (owing to the light component elements) contributes to its high $T_c$.

As seen in Fig. 2, a clear internal-friction peak appears at about 180 K, where the curvature of the resonance frequency changes and a slight modulus variation appears. A similar peak was first reported by Cordero *et al.*;[17] their peak temperature was located within 70–120 K, being different from our measurement, which is probably attributed to the difference in the frequency ranges used in both measurements (we used ~1 MHz, while they used 5–73 kHz). Thus, this large peak at about 180 K, showing a frequency dependence, can be a relaxation type like a Bordoni peak and not related to the superconductivity. In our measurement, since the large peak was located at relatively high temperature (180 K), the ultrasonic attenuation at the low-temperature region near $T_c$ was possible to be studied, without being obscured by the large peak.

Figure 3 (upper part) shows the square of the resonance frequency and the internal friction of mode $B_{2g}$-2 near $T_c$. The square of frequency corresponds to the elastic constant representative for the resonance vibration. Obviously, the slope of the $f^2$ curve decreases below $T_c$, which indicates that the elastic softening occurs with the superconducting transition. However, the degree of softening is much less than in monoatomic superconductors[27] and the $A15$ superconductors.[23] Less softening means that the lattice still remains stiff below $T_c$, which results in the high Debye frequency.

It is noticeable that two very sharp attenuation peaks appear both in mode $B_{2g}$-2 and in mode $B_{2g}$-3 below 30 K, see Fig. 3. However, peak 2 is clearly shifted in temperature between $B_{2g}$-2 and $B_{2g}$-3. A third peak marked $T_c$ appears in mode $B_{2g}$-2, but is absent in $B_{2g}$-3. These findings make it difficult to interpret our results at this stage. Currently we are investigating the possibility that the peaks are linked to the superconducting state. At the same time we have to exclude effects due to sample porosity.

In conclusion, we have examined the elastic property and ultrasonic attenuation behavior of the high-$T_c$ intermetallic superconductor $MgB_2$. The salient results are summarized as follows:

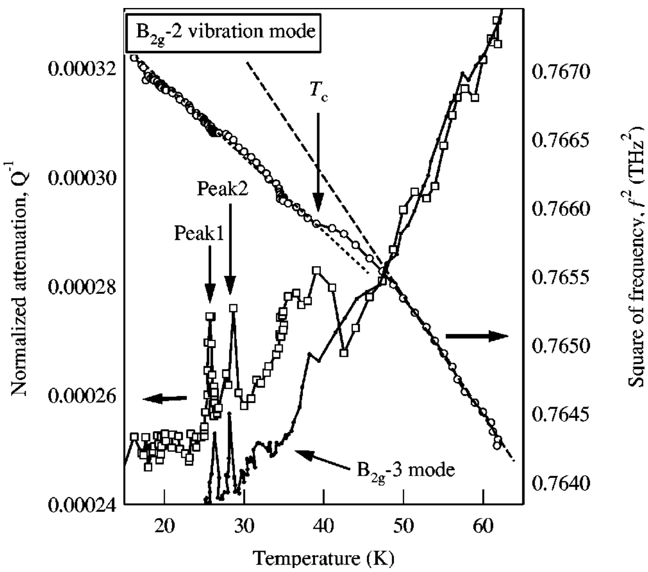


FIG. 3. Temperature behaviors of the square of resonance frequency and the internal friction of the $B_{2g}$-2 mode near $T_c$ showing two peaks at 26 and 29 K. The dotted line shows $Q^{-1}$ of the $B_{2g}$-3 mode, being shifted downward to avoid the overlap of the two curves. The background attenuation is $\sim 2.5\times 10^{-4}$ $\mu$s/MHz. The magnetic field of ~0.2 T was applied for the EMAR excitation.

(i) The elastic constants are determined to be $B = 96.6$ and $G = 74.2$ GPa at 0 K through the micromechanics calculation. The bulk modulus $B$ is smaller than the previous reports. However, the presented value is more reliable and reasonable in terms of both the axial ratio of the $AlB_2$ structure and its low condensation.

(ii) The elastic constants determined in this work yield the Debye temperature $\Theta_D = 819$ K and the intermediate coupling constant $\lambda \approx 0.76$–0.89 with the isotropic McMillan formula.

(iii) In the temperature behavior of ultrasonic attenuation, two anomalous peaks were observed.

One of the authors, T.I., thanks Dr. S. Miyata (Kyoto University) for the valuable discussions and comments.


[1] J. Nagamatsu *et al.*, Nature (London) **410**, 63 (2001).
[2] S. L. Bud'ko *et al.*, Phys. Rev. Lett. **86**, 1877 (2001).
[3] T. Yildirim *et al.*, Phys. Rev. Lett. **87**, 037001 (2001).
[4] Y. Kong *et al.*, Phys. Rev. B **64**, 020501 (2001).
[5] H. Schmidt *et al.*, Phys. Rev. B **63**, 220504 (2001); A. Sharoni, I. Felner, and O. Millo, *ibid.* **63**, 220508 (2001); G. Rubio-Bollinger, H. Suderow, and S. Vieira, Phys. Rev. Lett. **86**, 5582 (2001); A. Kohen and G. Deutscher, Phys. Rev. B **64**, 060506 (2001).
[6] H. Kotegawa *et al.*, Phys. Rev. Lett. **87**, 127001 (2001).
[7] T. Takahashi *et al.*, Phys. Rev. Lett. **86**, 4915 (2001).
[8] A. Y. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. **87**, 087005 (2001).
[9] F. Bouquet *et al.*, Phys. Rev. Lett. **87**, 047001 (2001).
[10] Y. Wang, T. Plackowski, and A. Junod, Physica C **355**, 179 (2001).
[11] P. Szabó *et al.*, Phys. Rev. Lett. **87**, 137005 (2001); F. Giubileo *et al.*, *ibid.* **87**, 177008 (2001).
[12] S. Haas and K. Maki, Phys. Rev. B **65**, 020502 (2001).
[13] M. Angst *et al.*, Phys. Rev. Lett. **88**, 167004 (2002).
[14] I. Loa and K. Syassen, Solid State Commun. **118**, 279 (2001).
[15] A. K. M. A. Islam and F. N. Islam, Physica C **363**, 189 (2001).

[16] T. Vogt *et al.*, Phys. Rev. B **63**, 220505 (2001); J. D. Jorgensen, D. G. Hinks, and S. Short, *ibid.* **63**, 224522 (2001); K. Prassides *et al.*, *ibid.* **64**, 012509 (2001).
[17] F. Cordero *et al.*, Phys. Rev. B **64**, 132503 (2001).
[18] T. V. Ignatova *et al.*, J. Low Temp. Phys. **28**, 190 (2002).
[19] H. H. Demarest, Jr., J. Acoust. Soc. Am. **49**, 768 (1971); I. Ohno, J. Phys. Earth **24**, 355 (1976).
[20] H. Ogi, H. Ledbetter, S. Kim, and M. Hirao, J. Acoust. Soc. Am. **106**, 660 (1999).
[21] Y. Benveniste, Mech. Mater. **6**, 147 (1987).
[22] J. D. Eshelby, Proc. R. Soc. London, Ser. A **241**, 376 (1957).
[23] L. R. Testardi, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. X, p. 193.
[24] P. S. Spoor *et al.*, Appl. Phys. Lett. **70**, 1959 (1997).
[25] H. Inui, K. Tanaka, and S. Otani (private communication).
[26] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[27] M. Levy, in *Handbook of Elastic Properties of Solids, Liquids, and Gases*, edited by M. Levy *et al.* (Academic Press, New York, 2001), Vol. II, p. 185.