Lattice parameter and T_c dependence of sintered MgB_2 superconductor on hydrostatic pressure

Jie Tang,[1] Lu-Chang Qin,[2] Akiyuki Matsushita,[1] Yoshihiko Takano,[1] Kazumasa Togano,[1] Hijiri Kito,[3] and Hideo Ihara[3]
[1]*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan*
[2]*JST-ICORP Nanotubulite Project, c/o NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan*
[3]*National Institute of Advanced Industrial Science and Technology, 1-1-4 Umezono, Tsukuba 305-8568, Japan*
(Received 2 April 2001; published 13 September 2001)

Hydrostatic pressure up to 10 GPa has been applied to determine the lattice compressibility and the dependence of transition temperature T_c of an MgB_2 superconducting material that shows a very narrow transition range when prepared by high-pressure sintering. The transition temperature T_c decreases with increasing pressure at a rate of 1.03 K/GPa. The material has a bulk modulus 172 GPa and the unit cell of the MgB_2 crystals shows an anisotropic compressibility with its c axis appearing more compressible than the a/b axis. The experimental results are discussed within the framework of the BCS theory, which gives rise to estimates in good agreement with the experimental results.

DOI: 10.1103/PhysRevB.64.132509 PACS number(s): 74.62.Fj, 62.50.+p, 74.25.Fy, 74.70.Ad

The discovery of superconductivity in MgB_2 crystals at 39 K by Nagamatsu *et al.*[1] has excited intensive interest in and research on this material. It represents the highest T_c so far discovered in a binary system, much higher than the Nb_3Ge alloy ($T_c = 23.2$ K). The simple MgB_2 crystal structure with the space group of P6/mmm ($a = 3.086$ Å and $c = 3.524$ Å) consists of a layered stacking with alternating Mg and B layers on top of each other. A few theoretical analyses have been presented to discuss the fundamental mechanism responsible for the superconductivity in this material. The conduction bands of the sp^2-bonded boron sheets have been suggested to contribute to the superconductivity, which result from the strong electron-phonon interaction and the high phonon frequency associated with the honeycomblike boron structure.[2]

Following the announcement of the discovery, several reports have been released reporting measurements of the pressure effects on MgB_2 materials prepared under various conditions. Vogt *et al.*[3] characterized the bulk modulus of the commercially available high-purity MgB_2 powders using high pressure and obtained $B_0 \approx 151$ GPa using the first-order Murnaghan equation of state

$$V = V_0\left(1 + P\frac{B_0'}{B_0}\right)^{-1/B_0'},$$

where V is the unit cell volume at pressure, P, $B_0' = 4$, and V_0 and B_0 are the unit cell volume and the bulk modulus at ambient condition, respectively. This measurement gives rise to a value for the volume compressibility, defined as $\kappa = -(1/V_0)dV/dP$, of about 6.7×10^{-3} GPa^{-1} to a good approximation. Pressides *et al.*[4] measured the compressibility of the material of Nagamatsu *et al.*[1] and obtained a volume compressibility of 8.3×10^{-3} GPa^{-1}. Lorenz, Meng, and Chu[5] prepared the MgB_2 material by a solid-state reaction method and measured the T_c dependence on hydrostatic pressure up to 1.84 GPa and obtained $dT_c/dP \approx -1.6$ GPa^{-1}. Loa and Syassen showed a theoretical analysis and suggested a reducing rate of 1.6 K/Ga in response to pressure.[6] Jorgensen, Hinks, and Short[7] reported their results on the crystal-lattice properties of MgB_2 versus both temperature ($11\sim297$ K) and pressure ($0\sim0.62$ GPa) using neutron diffraction.

In this paper, we report results on experimental measurement of the electrical resistivity and lattice compressibility, under hydrostatic pressure up to 10 GPa, of the MgB_2 superconducting material. The MgB_2 material employed in the present investigation was prepared using a higher pressure (3.5 GPa comparing with the pressure of 0.2 GPa used by Nagamatsu *et al.*[1]) and higher sintering temperature (1000 °C). This material shows substantial improvements in its superconducting performance.[8] For example, the transition range, defined by the width in temperature between points with 10% and 90% drop of resistivity during the transition from the normal to the superconducting state, is measured to be $\Delta T_c \approx 0.5$ K at the ambient pressure. Since the material was high-pressure sintered, no porosity was observed and it has a high mass density of 2.66 g/cm^3, close to the theoretical value of MgB_2 of 2.63 g/cm^3.

We utilized an anvil cell fitted into a clamp machine to obtain hydrostatic pressure for measuring the electrical resistivity using the standard four-probe method. For *in-situ* measurement of the lattice parameters under pressure, a diamond anvil cell was employed and synchrotron x-ray diffractograms were collected on imaging plates, using the photon factory beam line 18C at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan.

The electrical resistance of the MgB_2 superconducting material was measured as a function of temperature at each fixed pressure with the dc four-probe method using a cubic anvil apparatus operated up to 10 GPa. The cubic anvil device is compressed evenly from six directions with six anvil tops thereby producing a hydrostatic pressure on the sample material sealed in the gasket. The gasket material is a mixture of amorphous boron and epoxy resin in 4:1 weight ratio. Fluorinert liquid is used as the pressure medium to maintain hydrostatic pressure. Low temperature down to 7 K is attained with a continuous flow of liquid nitrogen and helium successively.

We measured the dependence of the superconductivity transition temperature T_c on pressure up to 10 GPa. The sharp drop of resistivity observed at ambient conditions is maintained even when pressure was applied, as is shown in Fig. 1. A remarkable linear behavior is observed up to the

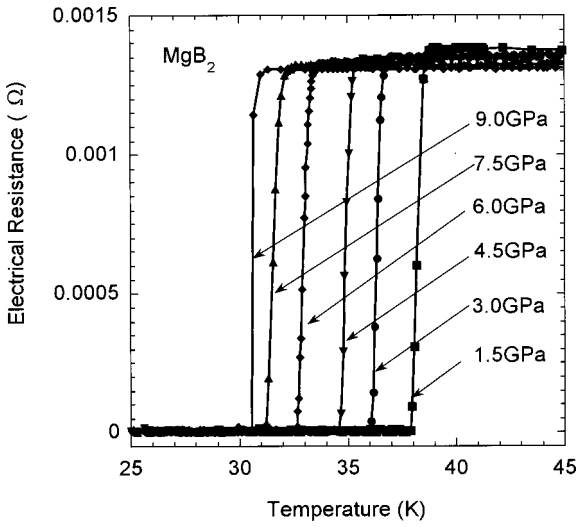

FIG. 1. Electrical resistance versus temperature when the sample is subject to various pressures up to 10 GPa. The transition from the normal sate to superconducting state takes place within a very narrow temperature range of about 0.5 K.

full range of 10 GPa and Fig. 2 shows the experimental data with a fitted linear curve that is expressed by

$$T_c = 39.6 - 1.03P.$$

The decreasing rate of T_c, 1.03 K/GPa, is much lower than the value of 1.6 K/GPa obtained by Lorenz, Meng, and Chu, and the negative slope of the $T_c \sim P$ relationship is against the theoretical predictions by Hirsch.[9] On the other hand, the experimental observation suggests that T_c could be increased further if a chemical substitution could increase the lattice parameter while maintaining the same electronic structures in equivalence to producing a negative pressure.

The transition range is about 0.5 K between the normal state and superconducting state, demonstrating the superb

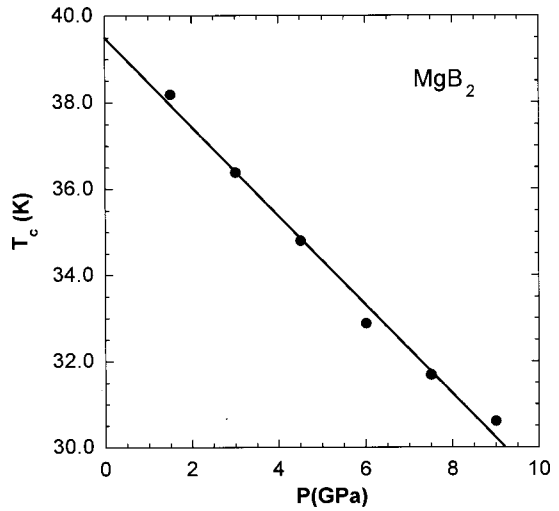

FIG. 2. Plot of transition temperature T_c versus pressure P. A linear behavior is observed and T_c decreases with increasing pressure at a rate of about 1.03 K/GPa.

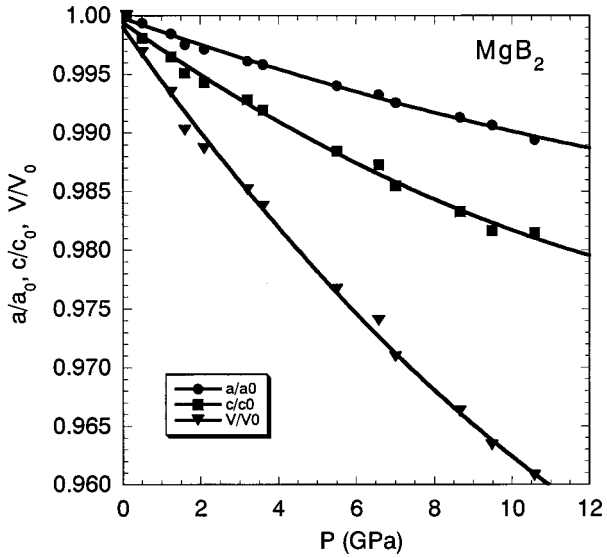

FIG. 3. Dependence of lattice parameters a and c and the unit cell volume V on the applied pressure up to 10 GPa. The plots are given in ratios with the corresponding values at ambient condition. The deduced bulk modulus of the MgB_2 material is $B_0 = 172$ GPa.

quality of the MgB_2 material. Even when the material is subject to high pressure, the transition width changed only slightly. For example, at pressure 7.5 GPa, the transition width is measured to be 0.6 K, giving rise to the increase of the transition width at a rate less than 0.015 K/GPa. In addition, before the transition to superconducting occurred, the material showed a metallic behavior upon cooling with a ratio of electrical resistivity $\rho(300K)/\rho(40K) = 1.93$ at 1.5 GPa pressure and it increased linearly with pressure reaching 2.05 at 9.0 GPa pressure.

Figure 3 shows the dependence of lattice parameters a and c, and the unit cell volume V on the applied pressure. There is a significant difference between the contraction rates of the intraplanar periodicity a and the interplanar periodicity c, the latter reduces about 1.4 times as fast as the former, signifying that the structure is more compressible in the c direction than in the a/b direction. A least-square linear fitting of the experimental data yielded a value for the bulk modulus $B_0 = 172$ GPa while a value of $B_0 = 174$ GPa was obtained using a least-square fitting of the Murnaghan equation. The volume compressibility, defined as $\kappa = 1/B_0 = -(1/V_0)dV/dP$, can be deduced from the experimental data and showed a weak dependence on the pressure.

The boron-isotope effect has indicated that the superconductivity in the MgB_2 material is phonon-mediated that can be described within the framework of the BCS theory.[10] Using the McMillan formula,[11] the transition temperature T_c within the framework of the BCS theory can be approximated with

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp\left[-\frac{1.02(1+\lambda)}{\lambda - \mu^*(1+\lambda)} \right],$$

where ω is the characteristic phonon frequency, μ^* is the Coulomb pseudopotential describing the repulsive interac-

tion between electrons, and $\lambda = N(0)\langle I^2\rangle / M\langle \omega^2\rangle$ denotes the electron-phonon coupling constant, in which $N(0)$ is the electronic density of states at the Fermi level, $\langle I^2\rangle$ the averaged electron-ion matrix element, and M the atomic mass.

The value of dT_c/dP can be estimated from the McMillan formula. Since it is difficult to obtain experimentally the value of $d\ln N(0)/dP$, we used a theoretically calculated value, -0.0031/GPa (Ref. 8) for $d\ln N(0)/dP$ and the value of $d\ln\omega/dP$ is obtained from the lattice dependence on the applied pressure through the equation $\omega/\omega_0 = (V_0/V)^{\gamma}$, where γ is the Gruneisen parameter, which is typically close to unity and we here assumed $\gamma = 1$ to obtain $d\ln\omega/dP = -d\ln V/dP$.

The values of $d\ln V/dP$ is deduced from the x-ray data (Fig. 3) and therefore we obtained $d\ln\omega/dP \approx 0.00576\,\mathrm{GPa}^{-1}$. Incorporating these values for $d\ln\omega/dP$ and $d\ln N(0)/dP$ as well as $\mu^* = 0.1$ and $\lambda = 0.7$ (Ref. 2) to the McMillan formula, we can obtain $dT_c/dP \approx -1.22$ K/GPa, which is very close to our experimental value of -1.03 K/GPa. However, we should note here that since the McMillan formula was deduced for isotropic structures, given the anisotropic nature of the MgB_2 structure, the above analysis has limit in its validity.[12]

On the other hand, the electrical resistivity was found to be well proportional to temperature, i.e., $\rho = C_0 + C_1(P)T$, above 220 K as shown in the inset of Fig. 4. The value of dT_c/dP can also be estimated from an alternative method basing on the temperature coefficient of electrical resistivity, $C_1(P)$, that is deduced from the experimental data. Under the assumption that the electrical resistivity, ρ_{ph}, at high temperature is due to phonon scattering, we can therefore have $\rho_{\mathrm{ph}} \propto T/M\omega_D^2$, where ω_D is the Debye frequency. Furthermore, if we assume $d\ln\omega_D/dP \approx d\ln\omega/dP$, we can then estimate the value of $d\ln\omega/dP$ from the pressure dependence of the temperature coefficient of electrical resistivity given in Fig. 4. The value of $d\ln\omega/dP$ thus obtained is $0.008\ \mathrm{GPa}^{-1}$, from which $dT_c/dP \approx -1.58$ K/GPa is obtained. This estimated value is reasonable in light of the experimental uncertainties and the many approximations in particular involved in the calculations leading to the result. In addition, comparing our result with a recently available Raman data,[13] we obtain that $d\omega/dP \approx 6.0\,\mathrm{cm}^{-1}$/GPa using the averaged frequency $\omega_0 \approx 752\,\mathrm{cm}^{-1}$. It is in good agreement with the Raman result ($d\omega/dP \approx 5.4\,\mathrm{cm}^{-1}$/GPa) for this frequency.

With the availability of more experimental data reported by different authors, we have noticed that there are discrepancies in the reported values of the transition width and the decreasing rate of T_c with pressure in particular. We suggest that the discrepancies arise mainly from the differences in the microstructure of the various materials, as they have been synthesized under different conditions. This has been demonstrated clearly by Monteverde *et al.* as they compared the differences in the superconducting behavior under pressure of several MgB_2 materials prepared under different conditions.[14] On the other hand, it should be noted that there has been no significant difference observed in the onset transition temperature. A most recent study[15] reported a T_c reducing rate of 1.03 K/GPa on pressure, close to the value we reported here.

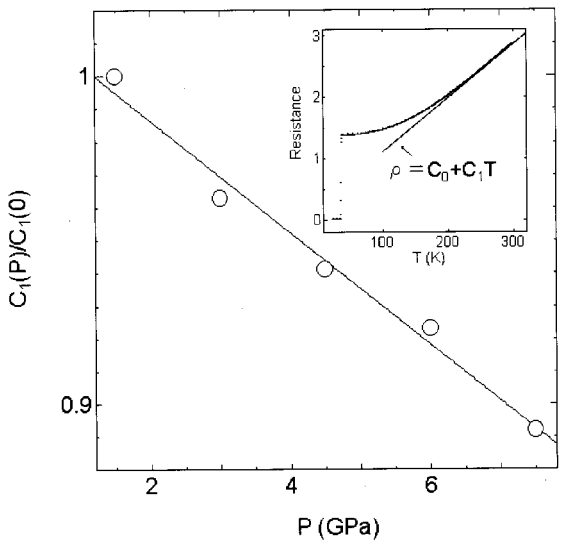

FIG. 4. Ratio of the temperature coefficient of electrical resistivity, $C_1(P)/C_1(0)$, as a function of pressure. The inset shows the relationship between electrical resistivity and temperature where a linear range exists at high temperature.

In summary, the MgB_2 material synthesized under high pressure and high temperature shows improved superconducting performance characterized by (a) sharp transition from normal state to superconducting state, (b) lower decreasing rate (~ 1.03 K/GPa) of transition temperature T_c with increasing pressure, and (c) lower ratios of electrical resistivity $\rho(300\ \mathrm{K})/\rho(40\ \mathrm{K})$. These characteristics in transport properties are preserved under pressure to at least up to 10 GPa and the pressure effect on T_c is well explained within the framework of the classical BCS theory based on the electron-phonon coupling mechanism.

The authors wish to thank Dr. J. P. Lu of the University of North Carolina at Chapel Hill for helpful discussions.

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