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Property studies of MgB_2 superconductor directly synthesized using high pressure

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Abstract

Polycrystalline MgB_2 with a sharp superconducting transition at 39 K was directly synthesized from the elements using high pressure. The sample showed high critical current densities. The electron energy-loss spectrum of B shows the peaks of σ and antibonding bonds, in good agreement with the hole-doping theoretical calculations. The pressure dependences of the sound velocities were measured up to 0.5 GPa, and subsequently elastic moduli, the Debye temperature and the specific heat were calculated. The isothermal Murnaghan equation of state of MgB_2 is established. Also, the pressure coefficient of the phonon frequency and the volume dependence of the electron–phonon coupling constant are calculated.

1. Introduction

The discovery of superconductivity at 39 K in MgB_2 intermetallic compound [1] opens a new way to search for novel superconductors with higher T_c. The rather higher T_c of the MgB_2 superconductor raises a challenge to mechanism studies, and brings new hope of both finding applications of superconducting compounds and finding new superconducting materials, particularly in the boride system. The theoretical works suggested that the superconductivity arises in the boron honeycomb layer and could be understood in the phonon-mediated BCS framework. During the past few decades, high-pressure synthesis has proven to be a very effective method for fabricating new solid phases which are either unavailable or hard to approach at ambient conditions. In particular, high-pressure synthesis plays a very important role in building up novel high-T_c superconductors. Recently Takano *et al* [2] reported high-pressure sintering of commercial MgB_2 powder, which significantly improved the superconducting properties of the materials. Li *et al* [3] succeeded in achieving direct synthesis of MgB_2 superconductor from Mg and B elements, yielding 39 K MgB_2 superconductor. The pressure effect on T_c is of special interest, since the dressed hole theory predicted an increase of T_c with pressure [4]. First high-pressure measurements revealed

negative pressure coefficients of $dT_c/dP \sim -1.6$ K GPa^{-1}, [5]. Subsequent band structure calculations could account for the decrease of T_c within the BCS model via a pressure-induced change of the density of states and the phonon frequency [6]. Here we present results on the MgB_2 bulk superconductor directly synthesized from elements using high pressure, and studies of properties including critical current density measurements, EELS, ultrasound measurements and calculations of related physical parameters.

2. Experimental details

Stoichiometric Mg (80 mesh, 98.5% or above purity) and B (360 mesh, above 5 N purity) powders in the molar ratio 1:2 were carefully mixed in the protection of a N_2 atmosphere. The mixture was installed into a BN tube and then inserted into a graphite sleeve which serves as the electric heater in the following high-pressure synthesis. The high-pressure synthesis was carried out on a cubic-anvil-type high-pressure apparatus with pyrophyllite being the pressure-transmitting medium. The pellet shaped sample was sintered under 3.0–5.0 GPa and at temperature $\sim$1000 °C for $\sim$10 min; this was followed by a temperature quench and pressure release. Details of the sample preparation were published elsewhere [3]. The structure and composition details of the compounds were checked by means of powder x-ray diffraction using a Rigaku rotating-anode diffractionmeter (RINT2000), and by morphology observation and qualitative EDAX detection using a field-emission scanning electron microscope (AMRAY1910F). The superconducting properties were studied by measuring the dc magnetic susceptibility using a SQUID magnetometer (Quantum Design) and electric conductivity using the four-probe method. HRTEM observations and EELS studies were performed on a Philips CM 200-FEG electron microscope equipped with a Gatan Imaging Filter system. The acoustic velocities and their pressure dependence for the sample were measured at room temperature by using the pulse-echo-overlap method. The travel time for ultrasonic waves propagating through the sample with a 10 MHz carrying frequency was measured using the MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. High-pressure experiments were carried out in a piston–cylinder high-pressure apparatus at room temperature. The pressure was calibrated by a manganin resistance gauge. The changes in density and length of the sample under pressure were modified by the Cook method. Electric insulation oil was used as the pressure-transmitting medium to provide hydrostatic pressure.

3. Results and discussion

Figure 1 shows the x-ray diffraction pattern of a MgB_2 sample, consisting of an AlB_2-type major phase, with a small amount of MgO impurity which is believed to be most probably derived from the raw material of the magnesium powder. The inset of figure 1 shows a schematic view of the crystal structure of MgB_2. The selected-area electron diffraction patterns and convergent beam electron diffraction patterns indicate that MgB_2 has a hexagonal structure with space group $P6/mmm$, consistent with the results from x-ray diffraction. Figure 2 shows the HRTEM image of the MgB_2 along the [001] zone axis, clearly showing the image of a hexagonal array, which reflects the constituent atoms. An electron diffraction pattern corresponding to the HRTEM image is presented in the inset in figure 2. Figure 3 shows the dc magnetic susceptibility measurements of the sample in 100 Oe applied field, indicating a very sharp superconducting transition with $T_c^{mag} = 39$ K and an almost temperature-independent diamagnetic signal up to 35 K, which implies an improved bulk superconductivity primarily due to the compacted intergrain links of the high-pressure-synthesized MgB_2 sample,

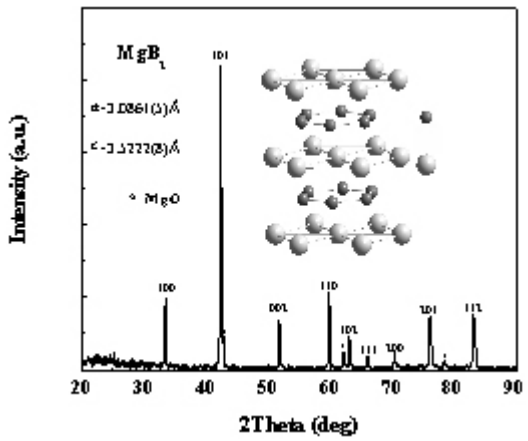

Figure 1. The x-ray diffraction pattern of the MgB_2 compound synthesized under high pressure. The major phase is MgB_2, but a MgO impurity phase (asterisk) is also presented. The inset shows a schematic view of the crystal structure of MgB_2.

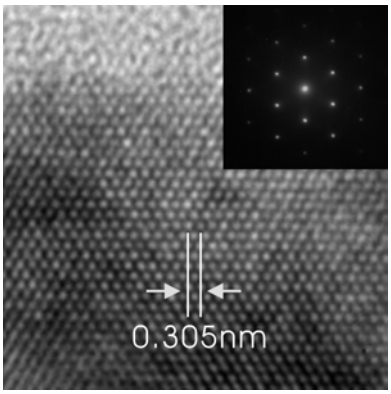

Figure 2. A HRTEM image of MgB_2 crystal along the [001] zone axis. The inset shows the corresponding ED pattern.

as is revealed from SEM-EDAX analysis. It is noted that the high-pressure-synthesized MgB_2 samples are very hard, showing mirror-like surfaces after polishing. The magnetic hysteresis loops were measured at 5, 10, 15, 25, 30 and 35 K. Accordingly, the critical current density of the sample has been calculated on the basis of Bean's critical state model: J_c (A cm^{-2}) $= 30\,\Delta M$ (emu cm^{-3})$/d$ (cm), where ΔM is the difference in the magnetic moment occurring during increasing and decreasing the magnetic field and d is the average dimension of the sample. Figure 4 plots the calculated J_c-values as a function of the magnetic field at various temperatures. The sample shows a higher bulk J_c over the temperature and field range; for example, $J_c > 10^4$ A cm^{-2}, which is believed to be the threshold for practical application, was obtained at 0.8 T and 30 K. This is quite different from the results usually observed for the high-T_c cuprates where the intergrain weak links of the ceramics lead to a very low bulk critical current density at high temperature and field.

As is well known, the crystal structure of MgB_2 consists of graphite-like boron honeycomb layers interlaced with the magnesium element. The studies by Ravindran *et al* [7] show that

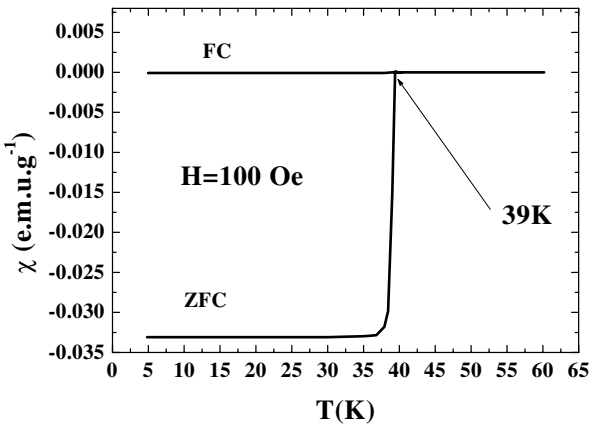

Figure 3. The experimental results of the dc susceptibility measurements for the MgB_2 superconductor, in both zero-field-cooling (ZFC) and field-cooling (FC) modes at 100 Oe applied field, using a SQUID magnetometer.

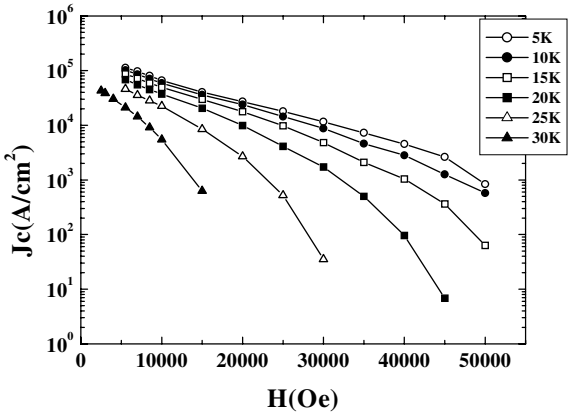

Figure 4. The calculated critical current density (J_c) based on Bean's critical state model. The sample shows a quite large J_c-value at an elevated temperature.

the B s states are hybridized with the B p state and show strongly bonded sp^2 hybrids ($\sigma(p_{x,y})$ bonds) in the *ab*-plane. Mg donates electrons to the boron layers and shows full ionization in the compound. The bonds of B along the *c*-direction, which is perpendicular to the *ab*-plane, are $\pi(p_z)$ bonds. The bonds between Mg and B are ionic. Their calculation indicates that the B–B bond is much stronger than the Mg–B bonds and suggests that there is an appreciable degree of metallic bonding between Mg atoms. Thus MgB_2 is a mixed-bond solid containing ionic, covalent and metallic bondings. A series of electronic structure calculations on MgB_2 and related isoelectronic systems by An [8] indicate that the B $\pi(p_z)$ bands are lower than the bonding $\sigma(sp^2)$ bands from the influence of Mg^{2+}-ion layers compared with graphite, causing $\sigma \rightarrow \pi$ charge transfer and σ band hole doping, which drives superconductivity in MgB_2. The special electronic structure of MgB_2 could be reflected in the EELS spectra. Figure 5(a) is the spectrum of MgB_2, which shows the B K edge. For comparison, we also present in figure 5(b) the standard spectrum of pure B from the database of the EELS Atlas, in which the B K edge is at 188 eV in pure B. It is clearly seen that the shape of the B peak in MgB_2 is different from that in figure 4(b). There is a small peak at about 188 eV (marked by *a*) and a highest

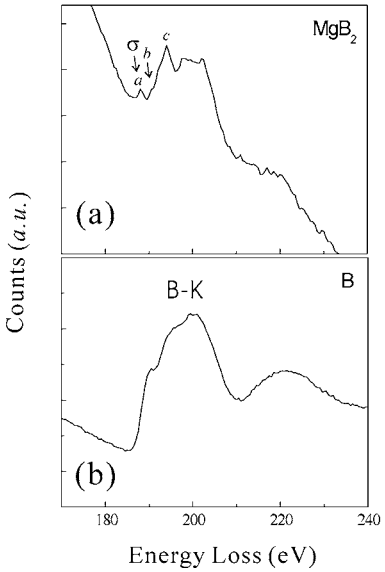

Figure 5. EELS spectra of (a) MgB_2 and (b) B crystals.

peak at about 194 eV (marked by *c*) followed by broad complex peaks. A small shoulder (marked by *b*) is seen on the left of the highest peak (*c*). According to the MgB_2 band structure calculations [8–15], the σ band is doubly degenerate and crosses the Fermi surface; therefore hole states are caused in the σ bands. It is supposed that the small peak *a* corresponds to 1s $\rightarrow$ partially filled 2p ($\sigma(p_{xy})$) as marked by σ. The antibonding B π bands and B σ bands are above the Fermi surface around the Γ point, so part of energy-loss peak *c* and shoulder *b* can be regarded as the antibonding bands σ^* and π^*. The energy difference between peaks *a* and *c* is about 6 eV, which is in good agreement with the calculated value of the gap between the doubly degenerate σ bonding and antibonding bands. From the above analyses, the EELS result gives evidence that there are hole states at the top of the bonding σ bands which may play a very important role in the superconductivity of MgB_2. The EELS result shows a good agreement with the theoretical prediction and calculation.

The measured longitudinal and shear velocities V_l, V_s and the density ρ of the sample at ambient conditions are 10.55, 7.17 km s^{-1} and 2.66 g cm^{-3}, respectively. V_l, V_s are much higher than for general materials, almost coming close to those of hard materials, such as SiC ($V_l = 12.1$ km s^{-1}, $V_s = 7.6$ km s^{-1}) and Al_2O_3 ($V_l = 10.5$ km s^{-1}, $V_s = 6.2$ km s^{-1}). The Young's modulus *E*, shear modulus *G*, bulk modulus *B* and Poisson's radio σ were calculated to be 292.8, 136.6, 114.0, 0.072 GPa, respectively. The Debye temperature Θ_D and specific heat C_v were calculated using the following formulae to be 1096 K and 13.5 J mol^{-1} K^{-1}, respectively [16]:

$$\Theta_D = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{\frac{1}{3}}\left(\frac{1}{v_l^3}+\frac{2}{v_s^3}\right)^{-\frac{1}{3}} \tag{1}$$

$$C_v = 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\Theta_D/T}\frac{e^x x^4\,dx}{(e^x-1)^2}, \qquad x = \frac{\hbar\omega}{kT} \tag{2}$$

where *V*, *N*, *h* and *k* are the unit-cell volume, number of atoms in the unit cell, Planck constant and Boltzmann constant, respectively. The bulk modulus *B* is less than that obtained by the

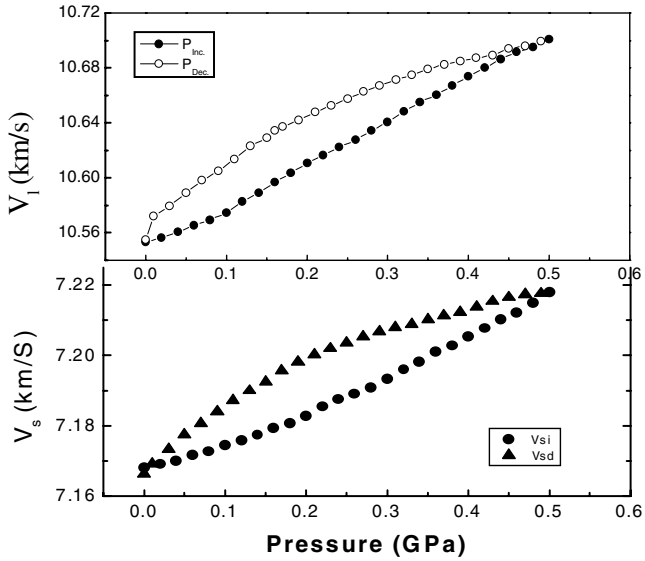

Figure 6. Variation of the longitudinal and shear velocities of MgB_2 with pressure.

x-ray diffraction experiment [17]. This is due to the fact that a polycrystalline sample is used in the ultrasonic measurements. Thus, a smaller B is reasonable and Θ_D is close to that calculated by Ravindran *et al*.

Figure 6 shows the pressure dependence of the longitudinal and shear velocities of MgB_2 at room temperature. The data are reproducible for several pressure load–unload cycles. V_l and V_s increase roughly linearly with increasing pressure. The calculated $\mathrm{d}V_l/\mathrm{d}P$ and $\mathrm{d}V_s/\mathrm{d}P$ are 0.27 and 0.04 km s^{-1} GPa^{-1}, respectively, and show much larger hysteresis effects under hydrostatic pressure. We speculate that this is the effect of relaxation between the Mg layer and the B layer.

The variations $\Delta Y(P)/Y(P_0) = [Y(P) - Y(P_0)]/Y(P_0)$ of the elastic constants ($Y = E$, G, B and σ) are shown in figure 7 as a function of pressure. The monotonic increase of the elastic constants with applied pressure indicates continuous stiffness of the elastic constants under hydrostatic pressure. Among them, the bulk modulus B exhibits the largest increase up to 0.5 GPa.

The bulk modulus B_0 and its pressure derivative B_0' can be obtained from the corrected density and the measured pressure dependences of V_l and V_s up to 0.5 GPa. The calculated B_0 and B_0' for MgB_2 are 113.95 GPa and 7.40, respectively, so the isothermal Murnaghan equation of state can be written as follows [18]:

$$P = (B_0/B_0')[(V_0/V)^{B_0'} - 1] = 15.40[(V_0/V)^{7.40} - 1]. \tag{3}$$

Here V and V_0 are the volumes under high pressure and at ambient pressure, respectively.

According to the change of the sound velocities with pressure, $\mathrm{d}\ln\langle\omega^2\rangle^{1/2}/\mathrm{d}P \approx +0.014$ GPa^{-1} is obtained by means of the formula

$$\omega = \left(\frac{18\pi^2 N}{V}\right)^{\frac{1}{3}} \left(\frac{1}{v_l^3} + \frac{2}{v_s^3}\right)^{-\frac{1}{3}} \tag{4}$$

which is in good agreement with the value estimated by Vogt *et al*. Therefore it is also consistent with the results of the band structure calculations within the BCS model.

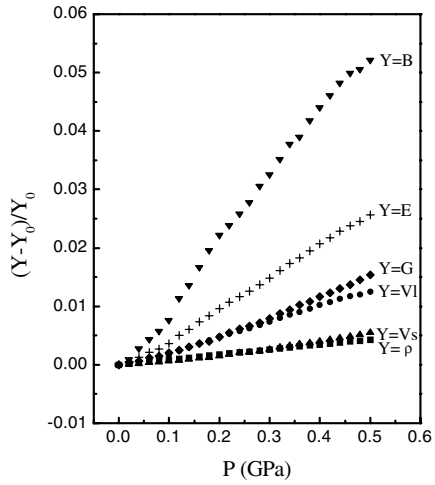

Figure 7. Variation of elastic constants Y of MgB_2 ($Y = E, G, B, \sigma$) with pressure P. Y is normalized by $(Y - Y_0)/Y_0$, where Y_0 is a normal modulus at ambient P_0.

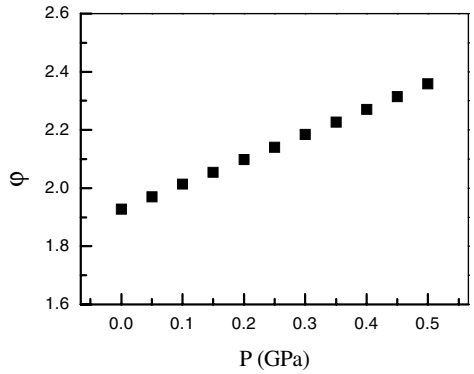

Figure 8. The change of φ with pressure.

The volume dependence of λ within the BCS theory has been characterized using

$$\frac{\mathrm{d}\ln(T_c/\Theta_D)}{\mathrm{d}\ln V} = \ln\frac{\Theta_D}{T_c}\frac{\mathrm{d}\ln\lambda}{\mathrm{d}\ln V} \equiv \ln\frac{\Theta_D}{T_c}\varphi \tag{5}$$

where φ is a material-dependent parameter describing the electron–phonon interaction. For superconducting sp metals, one generally finds $\varphi \approx 2.5$. We calculated $\varphi \approx 1.9$ for MgB_2 based on the change of the Debye temperature (calculated from our experimental data), phase transition temperature [5] and volume [18] under pressure. The value is reasonable because of the high Debye temperature of MgB_2. The change of φ under pressures is plotted in figure 8.

4. Summary

We address here the advantages of using high-pressure synthesis to fabricate the new intermetallic MgB_2 superconductor, including the merits of preventing Mg from volatilizing, isolating from air to avoid oxidization and substantially enhancing the reaction rate. Thus-obtained MgB_2 shows a sharp superconducting transition at $T_c = 39$ K and higher critical

current density. Parallel EELS studies indicate that hole states exist in the $\sigma(p_{xy})$ bands. Experimentally, the pressure dependences of the elastic constants and thermal dynamics parameters of MgB_2 were determined. Its isothermal equation of state is established in terms of the Murnaghan formula. The change of the vibration frequency of the atoms with applied pressure is calculated using the measured sound velocities; it is in good agreement with the estimated theoretical value. The change of the electron–phonon interaction parameter with volume under pressure is obtained as well.

Acknowledgments

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References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63–4
[2] Takano Y, Takeya H, Fujii H, Kumakura H, Hatano T and Togano K 2001 *Appl. Phys. Lett.* **78** 29 134–6
[3] Li S-C, Zhu J-L, Yu R-C, Li F-Y, Liu Z-X and Jin C-Q 2001 *Chin. Phys.* **10** 338–9
[4] Hirsch J E 2001 *Phys. Lett.* A **282** 392
[5] Lorenz B, Meng R L and Chu C W 2001 *Phys. Rev.* B **64** 12 507
[6] Loa I and Syassen K 2001 *Preprint* cond-mat/0102462
[7] Ravindran P, Vajeeston P, Vidya R, Kjekshus A and Fjellvg H 2001 *Preprint* cond-mat/0104253
[8] An J M and Pickett W E 2001 *Preprint* cond-mat/0102391
[9] Kurmaev E Z, Lyakhovskaya I I, Kortus J, Miyata N, Demeter M, Neumann M, Yanagihara M, Watanabe M, Muranaka T and Akimitsu J 2001 *Preprint* cond-mat/0103487
[10] Medvedeva N I, Ivanovskii A L, Medvedeva J E, Freeman A J and Novikov D L 2001 *Preprint* cond-mat/0104346
[11] Belashchenko K D, van Schilfgaarde M and Antropov V P 2001 *Preprint* cond-mat/0102290
[12] Medvedeva N I and Ivanovskii A L 2001 *Preprint* cond-mat/0103157
[13] Hirsch J E and Marsiglio F 2001 *Preprint* cond-mat/0102479
[14] Reyes-Serrato A and Galván D H 2001 *Preprint* cond-mat/0103477
[15] Wan Xiangang, Dong Jinming, Weng Hongming and Xing D Y 2001 *Preprint* cond-mat/0104216
[16] Knopoff L 1963 *High Pressure Physics and Chemistry* vol 1, ed R S Bradley (London: Academic)
[17] Vogt T, Schneider G, Hriljac J A, Yang G and Abell J S 2001 *Phys. Rev.* B **63** 220505
[18] Gerward L 1985 *J. Phys. Chem. Solids* **46** 925