PHYSICAL REVIEW B, VOLUME 64, 012507

High-pressure study on MgB_2

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(Received 14 February 2001; published 12 June 2001)

The hydrostatic pressure effect on the newly discovered superconductor MgB_2 has been determined. The transition temperature T_c was found to decrease linearly at a large rate of -1.6 K/GPa, in good quantitative agreement with the ensuing calculated value of -1.4 K/GPa within the BCS framework by Loa and Syassen, using the full-potential linearized augmented plane-wave method. The relative pressure coefficient $d \ln T_c/dp$ for MgB_2 also falls between the known values for conventional sp and d superconductors. The observation, therefore, suggests that electron-phonon interactions play a significant role in the superconductivity of the compound.

DOI: 10.1103/PhysRevB.64.012507 PACS number(s): 74.60.$-$w, 74.62.Fj, 74.25.Fy, 74.25.Ha

The recent discovery[1] of superconductivity in MgB_2 at temperatures as high as 40 K has generated great interest. MgB_2, which exhibits an AlB_2 structure with honeycomb layers of boron atoms, appears to be electrically three dimensional[2] and its grain boundaries have a far less detrimental effect on superconducting current transport.[3] The new compound may provide a new way to a higher superconducting transition temperature T_c and an easier avenue for devices. Two models[2,4] were subsequently advanced to account for the observation. While both have attributed the superconductivity observed mainly to the conduction bands derived from the boron sublattice, they propose different mechanisms responsible for the superconducting pairing. Based on band calculations, Kortus *et al.*[2] suggest that it results from the strong electron-phonon interaction and the high phonon frequency associated with the light boron element. A relatively large boron isotope effect on T_c has recently been observed,[7] consistent with the suggestion. However, Hirsch[4] offers an alternate explanation in terms of his ''universal'' mechanism, conjecturing that superconductivity in MgB_2, similar to that in cuprate superconductors, is driven by the pairing of the heavily dressed holes in bands that are almost full to gain enough kinetic energy to overcome the Coulomb repulsion. A positive pressure effect on T_c has also been predicted by Hirsch if the pressure can reduce the B-B intraplane distance. We have therefore decided to determine the hydrostatic pressure effect on T_c. The T_c was found to decrease linearly and reversibly with pressures at a relatively large rate of $dT_c/dP \sim -1.6$ K/GPa up to 1.84 GPa. The observation is in good quantitative agreement with the ensuing calculated result of -1.4 K/GPa by Loa and Syassen,[5] using the full-potential linearized augmented plane-wave method. The observed value of $d \ln T_c/dP$ also falls within those of conventional sp and d superconductors. The results therefore suggest that electron-phonon interactions play a major role in the superconductivity of this compound.

The polycrystalline MgB_2 samples examined in the present study were prepared by the solid-state reaction method.[7] Small Mg chips (99.8% pure) and B powder (99.7%) with a stoichiometry of Mg:B = 1:2 were sealed inside a Ta tube in an Ar atmosphere. The sealed Ta ampoule was in turn enclosed in a quartz tube. The ingredients were heated slowly up to 950 °C and kept at this temperature for 2 h, followed by furnace cooling to room temperature. The samples so prepared were granular and porous and were used for measurements without further treatment. The structure was determined by powder x-ray diffraction (XRD), using a Rigaku DMAX-IIIB diffractometer. The resistivity was determined by the standard four-lead technique and the ac magnetic susceptibility by an inductance method with a Linear Research Model LR-700 Bridge. The dc magnetization was measured using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The thermoelectric power was determined employing a home made apparatus using a sensitive ac measurement technique. The hydrostatic pressure environment was generated inside a Teflon cell filled with 3M Fluorinert FC 77 acting as the fluid pressure medium and housed in a Be-Cu high-pressure clamp.[8] The pressure was estimated using a Pb manometer situated next to the sample. The temperature was measured by a Chromel-Alumel thermocouple located next to the sample above ~ 45 K and by a germanium thermometer housed at the bottom of the high-pressure clamp below ~ 45 K.

The powder XRD pattern of the samples displayed the hexagonal MgB_2 phase but with a very weak trace of MgO. The deduced lattice parameters are $=3.084$ Å and $c = 3.523$ Å in excellent agreement with the powder diffraction database.[9]

The Seebeck coefficient (S) of MgB_2 is positive and relatively small and decreases with decreasing temperature, as shown in Fig. 1, similar to a metal with effective hole-type carriers. It also exhibits a rapid drop at 38.9 K and vanishes at 38.1 K, signaling the appearance of a narrow superconducting transition and consistent with the electrical and magnetic results to be described below. The temperature dependence of the resistivity (ρ) is shown in the inset to Fig. 1. It decreases like a metal on cooling, with a resistivity ratio $\rho(300\ \mathrm{K})/\rho(40\ \mathrm{K}) \sim 3$, much smaller than the ~ 20 reported.[3] We attributed the resistivity-ratio difference to the porosity and the grain boundary effect of our samples. The ρ starts to drop rapidly at ~ 39 K with a rather narrow transition of 0.35 K, defined as the difference between the temperatures at 10% and 90% drops of $\rho(40\ \mathrm{K})$. Shown in another inset to the same figure is the dc magnetic susceptibility (χ_{dc}) of the sample, measured at 50 Oe as a

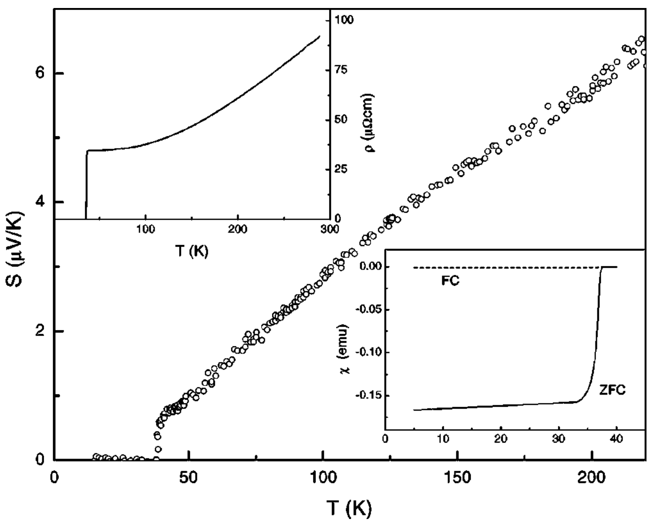

FIG. 1. S vs T of MgB_2. Upper left inset: ρ vs T. Lower right inset: χ_{dc} vs T.

function of temperature, in both the zero-field-cooled (ZFC) and the field-cooled (FC) modes. The ZFC χ_{dc} shows a sharp superconducting transition starting at $\sim$38.5 K with a width of $\sim$1 K and with more than 100% superconducting shielding at 5 K prior to correction of the demagnetization factor. Similar to ZFC χ_{dc}, FC χ_{dc} demonstrates unambiguously a diamagnetic shift at $\sim$38.5 K, but the magnitude of the signal is only $\sim$1% of that for the ZFC χ_{dc}. This is ascribed to the granular nature of the sample and the possible strong pinning of the compound.

To determine the pressure effect on T_c, we chose to measure the ac magnetic susceptibility (χ_{ac}) of the sample in a peak-to-peak field of $\sim$2 Oe. At ambient pressure, similar to χ_{dc}, χ_{ac} undergoes a drastic diamagnetic shift with an onset temperature at $\sim$38.5 K, characteristic of a superconducting transition with a midpoint temperature of $\sim$37.4 K, as shown in Fig. 2. Under pressure, the superconducting transition is shifted toward a lower temperature. The pressure

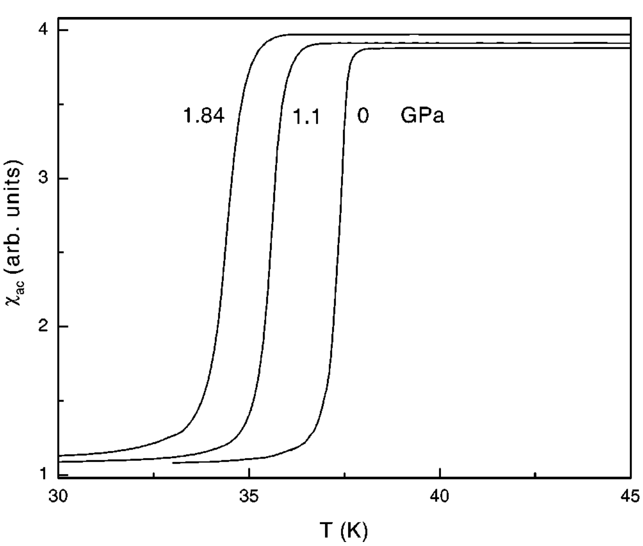

FIG. 2. χ_{ac} vs T at various pressures.

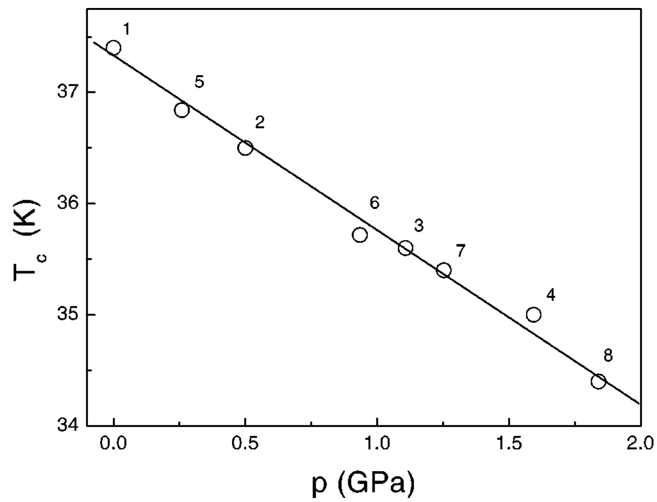

FIG. 3. T_c vs P. The numbers represent the sequential order of the experimental runs.

effect on T_c is summarized in Fig. 3. It is evident that T_c is suppressed reversibly and linearly at a rate of $T_c/dP = -1.6$ K/GPa up to 1.84 GPa. The numbers in the figure represent the sequential order of the experimental runs.

According to BCS theory, $T_c \propto \omega \exp\{-1.02(1+\lambda)/[\lambda(1-\mu^*)-\mu^*]\}$, where ω is the characteristic phonon frequency, μ^* the Coulomb repulsion, and λ the electron-phonon interaction parameter,[10] which is equal to $N(0)\times\langle I^2\rangle/M\langle\omega^2\rangle$ with $N(0)$ being the density of states at the Fermi energy, $\langle I^2\rangle$ the averaged square of the electronic matrix element, M the atomic mass, and $\langle\omega^2\rangle$ the averaged square of the phonon frequency. The relative pressure effect on T_c is $d\ln T_c/dP = d\ln\omega/dP + 1.02/[\lambda(1-\mu^*)-\mu^*]^2(d\lambda/dP)$. Recent band calculations by Kortus *et al.*[2] showed that MgB_2 is electronically isotropic, the $N(0)$ derived mainly from the B atoms near the Fermi surface is large, and the phonon frequency is high due to the low mass of B, resulting in a large λ. Pressure is expected to increase ω, broaden the density of states, and it may reduce $N(0)$, resulting in a relatively strong decrease in T_c. Following the high-pressure experiment, Loa and Syassen[5] as well as Vogt *et al.*[6] carried out the full-potential linearized augmented plane-wave calculation. Loa and Syassen found that MgB_2 is isotropic both electronically and mechanically and found that pressure suppresses $N(0)$ with $d\ln N(0)/dP = -0.31\%/\mathrm{GPa}$ and enhances ω with $d\ln\omega/dP = +0.71\%/\mathrm{GPa}$. By assuming μ^* and I to be pressure independent and by adopting the usual numerical values $\mu^* = 0.1$ and the zero-pressure $\lambda = 0.7$, they obtained within the BCS framework $d\ln T_c/dP \sim -3.6\%/\mathrm{GPa}$ or $dT_c/dP \sim -1.4$ K/GPa for $T_c = 39$ K. The calculated value may be considered as a crude estimate; however, it is in good quantitative agreement with our measured $dT_c/dP = -1.6$ K/GPa. Vogt *et al.* calculated a similar pressure coefficient $d\ln N(0)/dP = -0.4\%/\mathrm{GPa}$ and argued that the pressure effect on T_c can be explained within the BCS theory and their band structure calculations, assuming reasonable parameters for μ^* (0.1) and λ (1.0). It is interesting that in both calculations the pressure-induced change of $N(0)$ is relatively small compared with the estimated increase of ω, indicating that the main source of the decrease of T_c with pressure is its effect on ω.

It has also been demonstrated[11] that, within the framework of BCS theory, the volume effect on T_c can be expressed as $\ln(T_c/\omega)/dV \equiv \phi \ln(\omega/T_c)$, where ω is the phonon frequency, V the volume, and ϕ a material-dependent parameter. For sp superconductors, $\phi \sim 2.5$, while for the d superconductors, $\phi < 2.5$ and can become negative. The lack of knowledge on ϕ and on the compressibility of MgB_2 prevents us from making a direct comparison between our observation and the predicted ϕ. However, by examining all available data on the relative pressure effect on the T_c of conventional low-temperature noncuprate superconductors,[11–13] we found that, in general, $d\ln T_c/dP < -8 \times 10^{-2}$ GPa for sp superconductors, but $> -2 \times 10^{-2}$/GPa for the d superconductors, and the value is not sensitive to impurities except for cases where the Fermi surface topology changes due to the applied pressure or impurity content. For MgB_2, $d\ln T_c/dP \sim -4.2 \times 10^{-2}$/GPa, which lies between the values for the two groups of conventional superconductors. It is interesting to note that $d\ln T_c/dP \sim -5 \times 10^{-1}$/GPa for K_3C_{60},[14] in which electron-phonon interaction is considered to play an important role.

In an alternate approach, regarding the cuprate high-temperature superconductors, Hirsch[4] proposed that MgB_2 is a hole-doped superconductor with a conduction band almost completely filled. The T_c varies with carrier concentration nonmonotonically and peaks at an optimal doping level. Pressure is expected to enhance the T_c resulting from the reduction of the B-B intraplane distance. Unfortunately, we found that the T_c of MgB_2 is greatly suppressed by pressure even though MgB_2 is mechanically isotropic[5] and the B-B intraplane distance is expected to decrease under pressure. It should be noted that a negative pressure coefficient is possible only if the pressure can induce a large change in the carrier concentration and MgB_2 is overdoped. The positive S observed by us appears to be consistent with the hole-doped scenario of MgB_2 suggested, although Hall data and the doping state are still unavailable.

In conclusion, the T_c of MgB_2 has been found to decrease linearly and reversibly up to 1.84 GPa at a large rate of -1.6 K/GPa, in good quantitative agreement with the values based on band calculations by Kortus *et al.* and Loa and Syassen within the BCS framework. The large relative pressure effect on T_c of MgB_2 also falls within those of the conventional sp and d superconductors. The observation favors the proposition that electron-phonon interactions play a significant role in the superconductivity of this compound. Unless the pressure can induce a large hole transfer in a possibly overdoped MgB_2 to compensate for the predicted positive pressure effect on T_c, the ''universal'' mechanism cannot account for the observation.

ACKNOWLEDGMENTS

The authors wish to thank J. Cmaidalka, J. Lenzi, and Y. S. Wang for assistance in sample synthesis, thermoelectric power, and magnetic measurements, respectively. This work was supported in part by NSF Grant No. DMR-9804325, the T. L. L. Temple Foundation, the John J. and Rebecca Moores Endowment, and the State of Texas through the Texas Center for Superconductivity at the University of Houston; and at the Lawrence Berkeley Laboratory by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Material Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).

[2] J. Kortus, I.I. Mazin, K.D. Belashchenko, V.P. Antropov, and L.L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001).

[3] D.K. Finnemore, J. E. Ostenson, S. L. Bud'ko, G. Lapertot, and P. C. Canfield, Phys. Rev. Lett. **86**, 2420 (2001).

[4] J.E. Hirsch, cond-mat/0102115 (unpublished).

[5] I. Loa and K. Syassen, Solid State Commun. (to be published).

[6] T. Vogt, G. Schneider, J.A. Hriljac, G. Yang, and J.S. Abell, Phys. Rev. B **63**, 220505 (2001).

[7] S.L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. **86**, 1877 (2001).

[8] C.W. Chu and L.R. Testardi, Phys. Rev. Lett. **32**, 766 (1974).

[9] Powder Diffraction File, Set 38, p. 509 (JCPDS, 1988).

[10] W.L. McMillan, Phys. Rev. **167**, 331 (1968).

[11] M. Levy and J.L. Olsen, *Physics of High Pressures and Condensed Phase* (North-Holland, Amsterdam, 1964), Chap. 13.

[12] N.E. Brandt and N.I. Ginzburg, Usp. Fiz. Nauk **12**, 344 (1969) [Sov. Phys. Usp. **8**, 202 (1964)].

[13] T.F. Smith, in *Superconductivity in d- and f-Band Metals*, edited by David H. Douglass, AIP Conf. Proc. No. 4 (AIP, New York, 1972), p. 293; J. Low Temp. Phys. **6**, 171 (1972).

[14] G. Sparn *et al.*, Science **252**, 1839 (1991).