High Pressure Study on MgB$_2$

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Abstract

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, $dlnT_c/dp$, for MgB$_2$ also falls between the known values for conventional $sp$- and $d$-superconductors. The observation, therefore, suggests that electron-phonon interaction plays a significant role in the superconductivity of the compound.

74.60.-w, 74.62.Fj, 74.25.Fy, 74.25.Ha
The recent discovery 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 and its grain boundaries have a far less detrimental effect on superconducting current transport. The new compound may provide a new way to a higher superconducting transition temperature $T_c$ and an easier avenue for devices. Two models 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. 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 consistent with the suggestion. However, Hirsch 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 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 interaction plays a major role in the superconductivity of this compound.

Polycrystalline MgB$_2$ samples examined in the present study were prepared by the solid-state reaction method. 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 hours, followed by furnace-cooling to room
temperature. The samples so-prepared were granular and porous and were used for measure-
ments 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 SQUID magnetometer. The thermoelectric power was determined employ-
ing 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. The pres-
sure 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 $a = 3.084$ Å and $c = 3.523$ Å
in excellent agreement with the powder diffraction database.

The Seebeck coefficient ($S$) of MgB$_2$ is positive and relatively small and decreases with
decomposing 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 ($\rho$)
is shown in the inset to Fig. 1. It decreases like a metal on cooling, with a resistivity-ratio
$\rho(300 \text{ K})/\rho(40 \text{ K}) \sim 3$, much smaller than the $\sim 20$ reported. We attributed the resistivity-
ratio difference to the porosity and the grain boundary effect of our samples. The $\rho$ starts to
drop rapidly at $\sim 39$ K with a rather narrow transition of 0.35 K, defined as the difference
between the temperatures at 10% and 90% drops of $\rho(40 \text{ K})$. Shown in another inset to
the same figure is the dc magnetic susceptibility ($\chi_{dc}$) of the sample, measured at 50 Oe
as a function of temperature, in both the zero-field-cooled (ZFC) and the field-cooled (FC) modes. The ZFC-$\chi_{dc}$ 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-$\chi_{dc}$, FC-$\chi_{dc}$ 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-$\chi_{dc}$. 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 ($\chi_{ac}$) of the sample in a peak-to-peak field of $\sim 2$ Oe. At ambient pressure, similar to $\chi_{dc}$, $\chi_{ac}$ undergoes a drastic diamagnetic shift with an onset temperature at $\sim 38.5$ K, characteristic of a superconducting transition with a mid-point temperature of $\sim 37.4$ K, as shown in Fig. 2. Under pressure, the superconducting transition is shifted toward a lower temperature. The pressure effect on $T_c$ is summarized in Fig. 3. It is evident that $T_c$ is suppressed reversibly and linearly at a rate of $\frac{d ln T_c}{d P} = -1.6$ K/GPa up to 1.84 GPa. The numbers in the figure represent the sequential order of the experimental runs.

According to the BCS theory, $T_c \propto \omega \exp\{-1.02(1 + \lambda)/[\lambda(1 - \mu^*) - \mu^*]\}$, where $\omega$ is the characteristic phonon frequency, $\mu^*$ the Coulomb repulsion, and $\lambda$ the electron-phonon interaction parameter, which is equal to $N(0) < I^2>/M<\omega^2>$ with $N(0)$ being the density of states at the Fermi energy, $<I^2>$ the averaged square of the electronic matrix element, $M$ the atomic mass, and $<\omega^2>$ the averaged square of the phonon frequency. The relative pressure effect on $T_c$ is $\frac{d ln T_c}{d P} = \frac{d ln \omega}{d P} + 1.02/[\lambda(1 - \mu^*) - \mu^*]^2(d \lambda/d P)$. Recent band calculations by Kortus et al. 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 $\lambda$. Pressure is expected to increase $\omega$, 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 as well as Vogt et al. 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 \( d\ln N(0)/dP = -0.31\%/\text{GPa} \) and enhances \( \omega \) with \( d\ln \omega/dP = +0.71\%/\text{GPa} \).

By assuming \( \mu^* \) 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

\[
\frac{d\ln T_c}{dP} \sim -3.6\%/\text{GPa} \quad \text{or} \quad \frac{dT_c}{dP} \sim -1.4 \text{ K/GPa} \quad \text{for} \quad T_c = 39 \text{ K}.
\]

The calculated value may be considered as a crude estimate, however, it is in good quantitative agreement with our measured \( dT_c/dP = -1.6 \text{ K/GPa} \). Vogt et al. calculated a similar pressure coefficient \( d\ln N(0)/dP = -0.4\%/\text{GPa} \) 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 \( \mu^*(0.1) \) and \( \lambda (1.0) \). It is interesting that in both calculations the pressure induced change of \( N(0) \) is relatively small compared with the estimated increase of \( \omega \) indicating that the main source of the decrease of \( T_c \) with pressure is its effect on \( \omega \).

It has also been demonstrated\(^1\) that, within the framework of the BCS theory, the volume effect on \( T_c \) can be expressed as \( \ln(T_c/\omega)/dV \equiv \phi \ln(\omega/T_c) \), where \( \omega \) is the phonon frequency, \( V \) the volume, and \( \phi \) 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 \( \phi \) and on the compressibility of MgB\(_2\) prevents us from making a direct comparison between our observation and the predicted \( \phi \). However, by examining all available data on the relative pressure effect on the \( T_c \) of conventional low temperature noncuprate superconductors,\(^2\)\(^3\) we found that, in general, \( d\ln T_c/dP < -8 \times 10^{-2} \text{GPa} \) for \( sp \)-superconductors, but \( > -2 \times 10^{-2} \text{GPa} \) for the \( d \)superconductors, and the value is not sensitive to impurity except for cases where the Fermi surface topology changes due to applied pressure or impurity content. For MgB\(_2\), \( d\ln T_c/dP \sim -4.2 \times 10^{-2} \text{GPa} \), which lies between the values for the two groups of conventional superconductors. It is interesting to note that \( d\ln T_c/dP \sim -5 \times 10^{-1} \text{GPa} \) for K\(_3\)C\(_{60}\)\(^4\), 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 non-monotonically 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 B-B intraplane distance is expected to decrease under pressures. It should be noted that a negative pressure coefficient is possible only if 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 MgB2 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 $\approx$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 interaction plays a significant role in the superconductivity in 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.

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REFERENCES

1 J. Akimitsu, Symposium on Transition Metal Oxides, Sendai, Japan, January 10, 2001.

2 J. Kortus et al., cond-mat/0101446, 30 January 2001.

3 D. K. Finnemore et al., cond-mat/0102114, 6 February 2001.

4 J. E. Hirsch, cond-mat/0102115, 8 February 2001.

5 [Preprint received after initial submission of our manuscript] I. Loa and K. Syassen, cond-mat/0102462, 26 February 2001.

6 [Preprint received after initial submission of our manuscript] T. Vogt, G. Schneider, J. A. Hriljac, G. Yang, and J. S. Abell, cond-mat/0102480, 27 February 2001.

7 S. L. Bud’ko et al., cond-mat/0101463, 3 February 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, Ch. 13 (Amsterdam: North Holland, 1964).

12 N. E. Brandt and N. I. Ginzburg, Sov. Phys.-Uspekhi 8 202 (1964); ibid. 12, 344 (1969).

13 T. F. Smith, AIP Conf. Proc. 4, 293 (1992); J. Low Temp. Phys. 6, 171 (1972).

14 G. Sparn et al., Science 252, 1839 (1991).
FIGURES

FIG. 1. $S$ vs. $T$ of MgB$_2$. Upper left inset: $\rho$ vs. $T$. Lower right inset: $\chi_{dc}$ vs. $T$.

FIG. 2. $\chi_{ac}$ vs. $T$ at various pressures.

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