Electron transport properties of MgB$_2$ in the normal state

M. Putti, E. Galleani d’Agliano, D. Marrè, F. Napoli, M. Tassisto,
INFM/CNR, Dipartimento di Fisica, Via Dodecaneso 33, 16146 Genova, Italy

P. Manfrinetti, A. Palenzona,
INFM, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31,
16146 Genova, Italy

C. Rizzuto,
Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146
Genova, Sincrotrone di Trieste, Trieste

S. Massidda
INFM Dipartimento di Fisica, Università di Cagliari, S.P.
Monserrato-Sestu Km 0.700, I-09042 MONSERRATO (CA), Italy

(March 22, 2022)
Abstract

We have measured the resistivity and the Seebeck coefficient of a MgB$_2$ sintered sample. The temperature dependence of resistivity is fitted well by a generalized Bloch-Grüneisen equation with a Debye temperature $\Theta_R$ of 1050 K. The Seebeck coefficient is given by the sum of a diffusive and a phonon drag term and the behavior in the temperature region $T_c < T < 0.1\Theta_R$ follows a relationship $AT + BT^3$ where the two terms are proportional to the electron and to the phonon specific heat, respectively. The phonon drag term, here emphasized for the first time, is rather large, indicating a strong electron-phonon interaction. The diffusive term is positive and increases with Al doping. The comparison of the experimental values with calculations including precise electronic structure suggests that $\sigma$ bands give the main contribution to the Seebeck effect.

The discovery of 40 K superconductivity in MgB$_2$ [1] has stimulated a large discussion on the nature of the pairing and many evidences suggest a BCS-type mechanism: the isotope effect on $T_c$ [2], energy gap [3] and specific heat measurements [4] and a negative pressure coefficient of $T_c$ [5] [6].

Electron transport properties may give insight into the normal state conduction process and on the electronic structure, to understand whether MgB$_2$ can be considered a "simple" metal in which electron-phonon interactions play the most important role, or electron correlation has to be taken into account. From this point of view some measurements indicate that MgB$_2$ behaves indeed like a metal: magnetoresistivity is large and follows a generalized Kohler’s rule [7], the Seebeck effect [8] [8] [8] is small, positive and nearly linear; on the other hand, some Hall effect measurements [8] look very similar to those of cuprates decreasing as $1/T$ with temperature. Therefore, for a better understanding of basic properties of MgB$_2$, new measurements are required possibly on high quality samples because, in sintered samples, the presence of grain boundaries can affect the transport properties. This is not the
case of the Seebeck effect, which, as far as the scattering processes at the grain boundaries may be considered elastic, is not affected by granularity, as well proved in cuprates [10]; thus, measurements of thermoelectric power (TEP) $S$ can be an useful tool to provide information on the electronic structure of MgB$_2$, as shown in ref. [6] and [8], where a dependence of $S$ on the pressure and on Al doping was observed; these authors, however, did not consider the phonon drag contribution, which in the case of strong electron-phonon coupling has to be important.

In this paper we present resistivity and Seebeck effect measurements on a sintered MgB$_2$ sample. The compound MgB$_2$ was prepared by direct synthesis from the elements: Mg and crystalline B were well mixed together and closed by arc welding under pure argon into outgassed Ta crucibles which were then sealed in quartz ampoules under vacuum. The samples were slowly heated up to 950 °C and maintained at this temperature for 1 day. X-ray diffraction shows values of the lattice parameters, $a = 3.087(1)$, $c = 3.526(1)$ Å, and the absence of extra reflections. The specimen for transport measurements, $(2 \times 3 \times 12$ mm$^3$), has been prepared by pressing the powders in a stainless-steel die into a pellet which was then sintered by heat treatment at 1000 °C for 2 days.

The resistivity measurements were performed using a standard four probe technique and the TEP was measured using an a.c. technique described elsewhere [11] with sensitivity of 0.5% and accuracy of 1.5%. The gradient applied to the sample was varied from 1 to 3 K/cm and the frequency from 0.003 to 0.008 Hz; the data were acquired with a slowly rising temperature (1 mK/sec).

The resistivity measurements are presented in Fig. 1 up to 300 K; the transition region is enlarged in the inset. The critical temperature defined at half of the transition is $T_c = 38$ K with amplitude $\Delta T_c \sim 0.3$ K. The room temperature resistivity has a value of 130 $\mu$Ωcm, whereas the resistivity at $T = 40$ K is 40 $\mu$Ωcm.

We fit the temperature dependence of the normal state resistivity to the expression:

$$\rho(T) = \rho_0 + \rho_{ph}(T),$$

(1)
where \( \rho_0 \) is the temperature-independent residual resistivity and \( \rho_{ph}(T) \) the phonon-scattering contribution assumed of the generalized Bloch-Grüneisen form:

\[
\rho_{ph}(T) = (m - 1) \rho' \Theta_R \left( \frac{T}{\Theta_R} \right)^m \frac{\Theta_R/T}{\int_0^z \frac{z^m dz}{(1 - e^{-z})(e^z - 1)}},
\]

(2)

where \( \Theta_R \) is the Debye temperature, \( \rho' \) is the temperature coefficient of resistivity for \( T \gg \Theta_R \) and \( m = 3 – 5 \). Eq. (2) reduces to \( \rho(T) = \rho_0 + \text{const} \times T^m \) for \( T \ll \Theta_R \); indeed we see that from 40 to 100 K the resistivity is well fitted by a power law \( \rho(T) = \rho_0 + \text{const} \times T^3 \) [7]. The best fit to our data is obtained with \( m = 3, \rho_0 = 39.7 \, \mu\Omega cm, \Theta_R = 1050 \, K, \rho' = 0.49 \, \mu\Omega cm/K \) and is shown in Fig.1 as a continuous line. The \( \Theta_R \) value is in fair agreement with \( \Theta_D \) obtained from heat capacity measurements [12] although lower values have also been reported [4]. \( \rho' \) which is proportional to the dimensionless \( \lambda_{tr} \) coupling coefficient, has the same value that in A15 [13], consistent with a moderately strong coupling. The low temperature \( T^3 \) behavior, common in transition metals [14] where is related to inter-band scattering processes, suggests that also in MgB\(_2\) the main contribution to the electrical conductivity comes from a more mobile band, whose carriers are scattered into empty states of another less mobile band.

The TEP measurements are shown in Fig. 2, where we see the transition around 37 K and a continuous increase from 45 K, with curvature changing from positive to negative above 150 K. Above the transition region the TEP appears in excellent agreement with the literature data [5] [6] [8] both in value and in behavior. This contrasts with the wide spread of resistivity data available in the literature, which indicates a smaller influence of disorder or granularity on TEP.

The observed temperature behavior can be analyzed considering first the diffusive contribution to \( S \) given by the Mott formula:

\[
S_d = \frac{\pi^2 K_B^2 T \sigma'}{3 e \sigma},
\]

(3)

where \( e \) is charge of carriers, \( \sigma \) is the electrical conductivity and \( \sigma' = \frac{\partial \sigma}{\partial \varepsilon} |_{\varepsilon = \varepsilon_F} \). Note that \( \varepsilon_F \) must be counted upward for electrons and downward for holes. In the isotropic case
and if the relaxation time $\tau$ is independent of the energy (this is the case for scattering with grain boundaries), $\sigma'/\sigma = 3/2\varepsilon_F$, independent of the scattering processes and equation (3) becomes:

$$S_d = \frac{\pi^2 K_B^2 T}{2e \varepsilon_F},$$

(4)

Second, we must consider a phonon drag term $S_g$, arising for temperatures lower than the Debye temperature, when the phonon relaxation time for interaction with other phonons and impurities is much longer than the relaxation time for phonon-electron interactions. For pure isotropic metals and considering only electron-phonon normal processes, an upper bound for $S_g$ can be estimated to be of the order [13]

$$S_g = \frac{C_{ph}}{3ne},$$

(5)

where $C_{ph}$ is the phonon specific heat per unit volume. Thus, for $T \ll \Theta_D$, and assuming $S_g$ to really reach this upper bound, the total TEP $S$ will take the form:

$$S = S_d + S_g = AT + BT^3,$$

(6)

where:

$$A = \frac{\pi^2 K_B^2}{2e \varepsilon_F} \frac{1}{n_a},$$

(7)

$$B = \frac{\beta_3}{3ne} = \frac{K_B}{e} \frac{4\pi^4}{n_a} \frac{1}{5 \Theta_D^3}.$$

(8)

Here $\beta_3 = \frac{9NK_B}{e\Theta_D^3}$ is the coefficient of the low temperature phonon specific heat, $N$ is the number of atoms per unit volume, and $n_a$ is the number of valence electrons which is 4/3 in MgB$_2$. Equation (6) can be compared with the experimental TEP of MgB$_2$ in the temperature range $T_C < T < 0.1\Theta_D \sim 100K$ which overlaps for a large amount with our measurements range.

The inset of Fig. 2 shows the ratio $S/T$ as a function of $T^2$ for $40 K < T < 100 K$. The data show a linear behavior up to a $T^2$ value of 8000 ($T = 90 K$) and then begin to bend.
The best fit performed in the range $2000 \, K^2 < T^2 < 8000 \, K^2$ is plotted as a continuous line and the fit parameters are $A = 1.76 \times 10^{-2} \, \mu V/K^2$ and $B = 1.26 \times 10^{-6} \, \mu V/K^4$.

In Fig. 2 eq. (6) with $A$ and $B$ given by the fit is plotted as a continuous line, while the diffusive term $S_d = AT$ is plotted as a dashed line. The experimental curve is well fitted by eq. (6) up to 100 K, above which the data change curvature and tend to increase linearly, with nearly the same slope of $S_d$. The experimental phonon drag term defined as $S - S_d$, plotted as a dotted line, tends to saturate above 250 K. This is exactly what it is expected for $S_g$; in fact, increasing the temperature, phonon-impurity and phonon-phonon processes become more important, and the phonon drag falls, causing a peak in the TEP. In metals as Cu, Ag, Au, Al, the phonon drag peak occurs at about $\Theta_D/5$ [15], while in our case the peak is not yet reached at $\Theta_D/4$ giving a further evidence of the importance of the electron-phonon coupling in MgB$_2$.

We therefore find that the diffusive and phonon drag terms contribute nearly equally to the TEP. This was not recognized both in ref. [6] and [8] because only a diffusive term, even not vanishing at $T = 0$, was considered in order to fit the data.

To further verify the consistency of the model, let us try now to relate the coefficient $A$ and $B$ with some microscopic parameters. We first start neglecting the multi-band character of MgB$_2$ and we pursue in our naive model of isotropic free electrons. Its reliability will be discussed afterwards in the light of the band structure effects.

The coefficients $A$ and $B$ of our sample, and those extrapolated from data in literature for pure [6] and Al doped MgB$_2$ [8], are summarized in table I. The Fermi energy $\varepsilon_F$ and the Debye temperature $\Theta_D$ are obtained directly from $A$ and $B$ (eq.s (7) and (8)): the Debye temperature of about 1400 $K$, is only the 30% higher than $\Theta_R$ and $\varepsilon_F$ for pure MgB$_2$ is of the order of 2 eV and becomes 1.2 eV for Al doped samples: since the Al doping raises the Fermi level, the decreasing of $\varepsilon_F$ with Al doping is a further evidence (in addition to the positive sign) that $S_d$ is dominated by holes.

Let us now turn to the TEP as resulting from the band structure of MgB$_2$. Two types bands contribute to the conduction [17] [18]: two $\sigma$ bands, deriving from the $p_{x,y}$ states of
B and two \( \pi \) bands deriving from the \( p_z \) states. The two sets of bands have very different dimensional character, the \( \sigma \) bands being of hole-type and nearly 2D, and the 3D \( \pi \) bands mainly of electron-type. Great relevance in the discussion of the pairing mechanism has been given to the \( \sigma \) bands \[18\], and the positive sign of the Hall coefficient and of the TEP, as well as the increasing of the latter with Al doping, confirm the importance of these bands in the transport properties. Starting from the precise electronic structure calculations described in Ref. \[17\], we have computed the Seebeck tensor \( S_d \), as a function of the chemical potential shift, to reproduce within a rigid band scheme the Al doping. These calculations are performed using the the scheme described, e.g., in ref. \[17,19\]. Because of hexagonal symmetry, the independent components are \( S_{xx} = S_{yy} \) and \( S_{zz} \). Briefly, if \( \Omega \) is the unit cell volume and \( v_i(\mathbf{k}, n) \) are the cartesian components of the Fermi velocities for the \( n-th \) band, we obtain the TEP components \( S_{ii} \) as:

\[
S_{ii}(T) = \frac{K_B}{e} \int \frac{d\varepsilon}{e \varepsilon - \mu} \sigma_{ii}(\varepsilon)(-\frac{df}{d\varepsilon}) \int d\varepsilon \sigma_{ii}(\varepsilon)(-\frac{df}{d\varepsilon})
\]

where

\[
\sigma_{ij}(\varepsilon) = \frac{e^2}{\Omega} \sum_{k,n} v_i(\mathbf{k}, n)v_j(\mathbf{k}, n)\tau(\mathbf{k}, n)\delta(\varepsilon(\mathbf{k}, n) - \varepsilon)
\]

If we consider \( \tau \) to be isotropic and independent of energy, it will not affect the final result. As pointed out in Ref. \[19\], \( S_{ii} \) vanishes in the approximation \( -\frac{df}{d\varepsilon} = \delta(\varepsilon - \mu) \), and it would therefore be appropriate to include the energy dependence of \( \tau \) as well. Unfortunately, it is not easy to obtain a consistent \( \tau(\varepsilon) \) approximation, and we therefore use the most conservative, \( \tau = const \), approach.

\( S_d \) shows the expected linear behavior as a function of temperature, and we therefore plot in Fig.3 \( S_d/T \), as a function of the electron doping, in a rigid band scheme. Fig. 3(a) gives the tensor components, while to compare with experiment we show in Fig. 3(b) the average of \( S_d/T \) over directions, \( \overline{S_d}/T \). Since both numerator and denominator in the definition of \( S_d/T \) contain a band summation, there is no clear cut distinction between the \( \sigma \) and \( \pi \) contributions (in fact, when we consider the \( \sigma \) bands alone, the resulting \( S_d/T \) reproduces
the free-electron results along the $x$ and $y$ directions, and is zero along $z$, up to the 2D to 3D crossover when $\mu$ crosses the $\sigma$ band top at $\Gamma$, and $S_{zz}$ grows to finally give isotropic results). With this warning, in order to better understand our results, we decompose $S_d/T$ in terms of $\sigma$ and $\pi$ bands contributions (i.e. we decompose the numerator of eq. (9)). We notice that for small values of doping the dominant, positive contribution comes from $\sigma$ bands; when the chemical potential goes beyond the $A$ point maximum this contribution disappears and the resulting $S_d/T$ is much smaller and negative, identical to the $\pi$ contribution. The smallness of the latter relative to the $\sigma$ contribution can be easily understood: the numerator of eq. (9) essentially monitors the $\sigma_{ii}(\varepsilon)$ derivative with respect to $\varepsilon$, and this quantity is much larger for the $\sigma$ bands. As a function of the doping $x$, $S_d/T$ initially grows, and then it bends down, especially when $\mu$ goes beyond the 2D to 3D crossover, but also because of the change the $\pi$ contribution.

The calculated values are smaller, by a factor of about 1.7-2, than the experimental values of table I. The trend as a function of doping, however, is similar in experiment and theory; it would be interesting, in this respect, to obtain the experimental values for larger doping. While the agreement between theory and experiment is not quantitatively good, it may considered to be satisfactory based on the fact that our calculations do not include the energy dependence of $\tau$, which may result into quantitative differences [19]. As a speculation, we may say the following: our understanding of MgB$_2$ indicates a strong electron-phonon coupling for the $\sigma$ band top (mostly with the $E_{2g}$ phonon mode). Very likely, such a strong coupling will depend on the energy location, relative to the $\sigma$ band top, resulting into an energy dependent $\tau(\varepsilon)$. We also stress that our calculations do not contain any form of renormalization; it has been a controversial question, in the literature [20], whether renormalization should affect the bare band-structure results. If this would be the case, the strong electron-phonon coupling in MgB$_2$ would bring the theoretical value into agreement with experiment. We may speculate that the presence of contributions to TEP from different bands, having different electron-phonon couplings, should prevent a complete cancellation of renormalization effects in the final result.
In summary, we analyzed in detail the resistivity and the thermoelectric power in the normal state and we showed that these transport properties can described within an independent electron framework, by taking into account the high phonon frequencies and the strong electron-phonon coupling. In particular the TEP is the sum of a diffusive and a phonon drag terms which contribute nearly equally to it. The phonon drag term was not previously recognized, in fact its peak is shifted above room temperature by the high Debye temperature and the strong electron-phonon interaction. The diffusive term is positive and increases with Al doping. The comparison of the experimental values with the theoretical ones, calculated starting from the precise electronic structure suggests that $\sigma$ bands give the main contribution to the TEP. Further investigation will be necessary to verify this result; in particular transport properties on samples with higher level of Al doping will be a useful tool to better investigate the role of the $\sigma$ bands, whose relevance in the pairing mechanism has been strongly advocated.
REFERENCES

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

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

[3] G.Karapetrov, M.Iavarone, W.K.Kwok, G.W.Crabtree and D.G.Hiuks, Phys.Rev.Lett. 86, 4374 (2001); A.Sharoni, I.Felner and O.Millo, cond-mat/0102325.

[4] R.K.Kremer, B.J.Gibson, K.Ahn, cond-mat/0102432.

[5] B. Lorenz, R. L. Meng, C. W. Chu, cond-mat/0102264.

[6] E. S. Choi, W. Kang, J.Y.Kim, Min-Seok Park, C.U.Jung, Heon-Jung Kim, Sung-Ik Li, cond-mat/0104454.

[7] D. K. Finnemore, J. E. Ostenson, S. L. Bud’ko, G. Lapertot, P. C. Canfield, cond-mat/0102114.

[8] B. Lorenz, R. L. Meng, Y. Y. Xue, C. W. Chu, cond-mat/0104041.

[9] R.Jin, M.Paranthaman, H.Y.Zhai, H.M.Christen and D.Mandrus, cond-mat/0104411.

[10] J.L.Tallon, J.R.Cooper, P.S.I.P.N. de Silva, G.V.M.Williams and J.W.Loram, Phys.Rev.Lett. 75, 4114 (1995).

[11] M.Putti, A.Canesi, M.R.Cimberle, C.Foglia, A.S.Siri, Phys. Rev. B 58, 12344 (1998).

[12] F.Bouquet, R.A.Fisher, N.E.Phillips, D.G.Hinks, J.orgensen, cond-mat/0104206.

[13] F.Nava, O.Bisi, K.N.Tu, Phys. Rev. B 34, 6143 (1986).

[14] G.T. Meaden Electrical resistance of metals Heywood Books, London, 89 (1966)
[15] J.M.Ziman, *Electrons and phonons*, Oxford, Clarendon Press (1960); R.D.Barnard, *Thermoelectricity in metals and alloys*, Taylor & Francis Ltd, London, 136 (1972).

[16] V.N.Kang, C.U.Jung, Kijon H.P.Kim, Min-Seok Park, S.Y.Lee, Hyeong-Jin Kim, Eun-Mi Choi, Kyung Hee Kim, Mun-Seog Kim, Sung-Ik Lee, cond-mat/0102313; V.N.Kang, Hyeong-Jin Kim, Eun-Mi Choi, Kijon H.P.Kim, Sung-Ik Lee, cond-mat/0105024.

[17] G.Satta, G.Profeta, F.Bernardini, A.Continenza, S.Massidda, in print on Phys. Rev. B.

[18] J.Kortus, I.I.Mazin, K.D.Belashenko, V.P.Antropov, L.L.Boyer, cond-mat/0101446; J.M.An, E.W.Pickett, Phys. Rev. Lett. 86, 4366 (2001).

[19] P.B. Allen, W.E. Pickett, H. Krakauer, Phys. Rev. B 37, 7482 (1988).

[20] G. Grimvall, *The electron-phonon interaction in metals*, Ed. E.P. Wohlfarth, in Selected Topics in Solid State Physics Vol. XVI, North-Holland, 1981; A.B.Kaiser, Phys. Rev. B 29, 7088 (1984); A.B.Kaiser, Phys. Rev. B 35, 4677 (1987), and references therein.

**Figure captions**

Figure 1: $\rho$ as a function of temperature; the transition region is enlarged in the inset. The best fitting curve obtained with $\rho_0 = 39.7 \mu\Omega cm$, $\Theta_R = 1050 K$, $\rho' = 4.95 \times 10^{-1} \mu\Omega cm/K$ is reported as a continuous line.

Figure 2: $S$ as a function of temperature; the continuous line is given by eq. (6) with $A = 1.76 \times 10^{-2} \mu V/K^2$ and $B = 1.26 \times 10^{-6} \mu V/K^4$; the dashed line is the diffusive term $S_d = AT$; the dotted line is the experimental phonon drag term defined as $S - S_d$. In the inset it is shown $S/T$ as a function of $T^2$; the continuous line is the best fit performed in the range $2000 K^2 < T^2 < 8000 K^2$.

Figure 3: $S_d/T$ as a function of doping, estimated in a rigid band scheme from the integrated DOS. (a) Tensor components and average; (b) Average $S_d/T$ and its band decomposition, as explained in the text.

**Table captions**
Table 1: The coefficients $A$ and $B$ obtained by fitting $S/T$ vs. $T^2$ (eq.(6)); $\Theta_D$ as obtained by eq. (8); $\varepsilon_F$ as obtained by eq. (7).

|         | $A$ ($\mu V/K^2$) | $B$ ($\mu V/K^4$) | $\Theta_D$ ($K$) | $\varepsilon_F$ (eV) |
|---------|-------------------|-------------------|-----------------|-------------------|
| MgB$_2$ | $1.76 \times 10^{-2}$ | $1.26 \times 10^{-6}$ | 1430            | 2.1               |
| (a)MgB$_2$ | $1.70 \times 10^{-2}$ | $1.30 \times 10^{-6}$ | 1430            | 2.2               |
| (b)MgB$_2$ | $2.00 \times 10^{-2}$ | $1.30 \times 10^{-6}$ | 1430            | 1.8               |
| (a)Mg$_{0.95}$Al$_{0.05}$B$_2$ | $2.88 \times 10^{-2}$ | $1.41 \times 10^{-6}$ | 1390            | 1.3               |
| (b)Mg$_{0.9}$Al$_{0.1}$B$_2$ | $2.99 \times 10^{-2}$ | $1.49 \times 10^{-6}$ | 1360            | 1.2               |

(a) ref. [5]; (b) ref. [8].
$S (\mu V/K)$ vs $T (K)$

Inset: $S T$ vs $T^2$ ($K^2$)

$S = 0.020, 0.025, 0.030$
The diagrams illustrate the temperature dependence of the thermoelectric power $S/T$ in a rigid band scheme. Figure (a) shows $S_{d,xx}/T$ and $S_{d,yy}/T$ as well as $S_{d,zz}/T$, with the average indicated by a solid line. Figure (b) presents the total $S_d/T$, along with the contributions from $\sigma$ and $\pi$ channels.