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Thermoelectric Power of MgB_2 Single Crystals Doped with Holes and Electrons

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The thermoelectric power of MgB_2 single crystals, non-substituted, single-substituted with C, and co-substituted with C and Li, was investigated in the temperature range from 10 to 300 K. Both the in-plane (S_{ab}) and the out-of-plane (S_c) thermoelectric powers are positive for non-substituted crystals and both S_{ab} and S_c change a sign for crystals doped with electrons when C is substituted for B in the amount larger than 6 at.%. The substitution of C, which supplies electrons mainly into the σ band, reduces the thermoelectric power anisotropy, most likely by increasing the interband scattering. When Li is additionally co-substituted for Mg, S_{ab} remains unchanged but S_c increases substantially. The Li substitution donates holes into the π band rather than into the σ band and in this way modifies the π band properties, including the possible increase in the intraband scattering.

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1. Introduction

Structure and electronic properties of MgB_2 can be modified in a controlled way by substitutional chemistry. The superconducting transition temperature, T_c, upper critical field and its anisotropy, gaps width, intra- and interband scattering, defect structure, etc., can be tuned in the wide range if the doping with holes and electrons is possible. Introducing Li, Al, Mn, Fe, and C into the melt, one can grow MgB_2 crystals where Mg and B are partially substituted and thus the crystals are doped with holes (Li) and electrons (Al, Fe, C) or they are substituted isovalently (Mn) [1–7]. The substituted crystals can be used to study the influence of doping and/or intra- and interband scattering on the anisotropic normal and superconducting properties of MgB_2. In this work we examine the temperature behavior of the thermoelectric power of MgB_2 single crystals with various substitutions. Both electron and hole doped crystals have been investigated, including crystals co-substituted with C–Li to study the possible effect of electron-hole compensation [7].

2. Experimental

Single crystals of C, Li, and C–Li substituted MgB_2 were grown under high pressure using a cubic anvil press. The applied temperature and pressure conditions for the growth of C substituted crystals were determined in our previous studies [3–5]. The successful method to obtain Li and C–Li substituted crystals was described in Ref. [7]. The C content in the MgB_2 crystals has been estimated from changes in the a lattice parameter. The amount of Li has been obtained from the structure refinement as described in Ref. [7]. Using the high pressure synthesis we have grown single crystals with dimensions up to $1.5 \times 1 \times 0.1$ mm^3 (see Fig. 1).

The thermoelectric power, S, has been measured for the temperature gradient, ΔT, applied both in the ab plane, S_{ab}, and along the c axis, S_c, of the MgB_2 crystal. The crystal was placed between two Cu blocks fitted with two heaters and two precisely calibrated Pt thermometers. The heaters kept a certain temperature difference between the Cu blocks and the potential difference between the top and the bottom of the sample was measured by the sensitive voltmeter. For ΔT from about 2 to 4 K, the thermoelectric power was gradient independent and the value of S for this gradient has been taken as a correct result. The measuring setup was tested with Sb and Pb standards and with a reference crystal of $YBa_2Cu_3O_7$. An error of the absolute value of S was estimated to be typically below 0.2 μV/K.

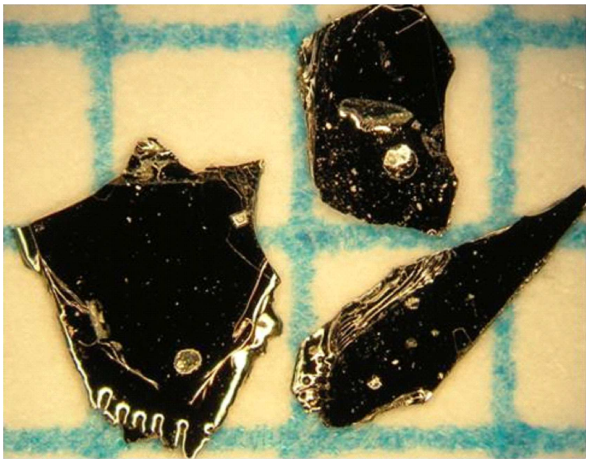

Fig. 1. MgB_2 single crystals (with various substitutions) grown in the high pressure and high temperature cubic anvil press. Scale is 1 mm.

3. Results and discussion

Single crystals of $Mg(B_{1-x}C_x)_2$ with C content changing from 2% to 7% have been studied as well as the crystals which were non-substituted, Li substituted, and C–Li co-substituted, for comparison. The influence of the C substitution on the

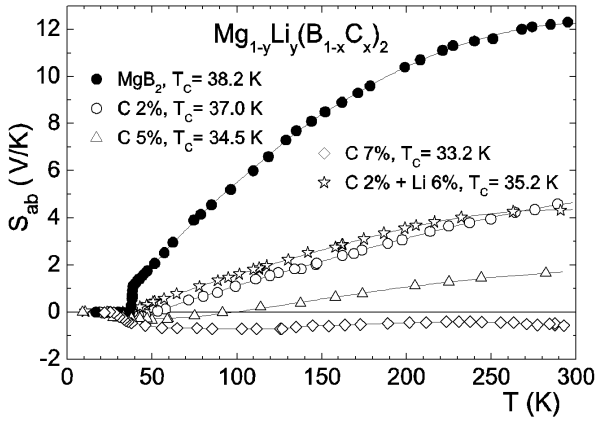

Fig. 2. Temperature dependence of the thermoelectric power S_{ab} of $Mg_{1-y}Li_y(B_{1-x}C_x)_2$ single crystals; non-substituted, carbon-substituted with $x = 0.02$, 0.05, and 0.07, and C–Li co-substituted with $x = 0.02$ and $y = 0.06$. S_{ab} is measured with the temperature gradient in the ab plane.

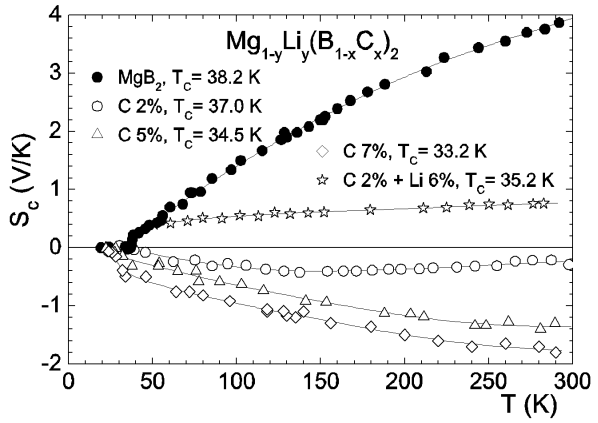

Fig. 3. Temperature dependence of the thermoelectric power S_c of $Mg_{1-y}Li_y(B_{1-x}C_x)_2$ single crystals; non-substituted, carbon-substituted with $x = 0.02$, 0.05, and 0.07, and C–Li co-substituted with $x = 0.02$ and $y = 0.06$. S_c is measured with the temperature gradient along the c axis.

thermoelectric power is shown in Figs. 2 and 3, for measurements performed with a temperature gradient in the ab plane and along the c axis, respectively. For the non-substituted MgB_2, S_{ab} decreases smoothly with decreasing temperature down to $T_c = 38.2$ K, then S_{ab} drops sharply to zero, as expected. Similar temperature dependence has been observed for S_c, however the absolute value of S_c is much lower. The thermoelectric power anisotropy, defined as S_{ab}/S_c, changes from 3 to 5 when temperature decreases from 300 K to T_c. The raise of the anisotropy with decreasing temperature means that S_c drops faster than S_{ab} suggestive of

the interband-scattering reduction. When C is substituted for B, both S_{ab} and S_c become smaller with the C content and, for a larger amount of C, both of them change the sign to negative. For S_{ab}, the substitution of 7% of C is necessary to observe the negative values. For S_c, however, the only 2% substitution of C is enough to modify the Fermi surface, change the charge cariers distribution significantly, and in this way change the sign of S. Thus, the substitution of C for B, which donates electrons mostly into the 2D σ band, strongly influences the electronic structure and results in substantial changes of the thermoelectric properties in both directions, parallel and perpendicular to the *ab* plane. The difference between S_{ab} and S_c decreases with the C content, so we conclude that the C substitution not only alters the σ band filling but probably also increases the interband scattering noticeably. Both S_{ab} and S_c saturate with the C content and the extrapolated saturation values of $S_{ab} \approx -2$ μV/K and $S_c \approx -3$ μV/K have been observed at 300 K.

As we mentioned above, Li substitutes for Mg and dopes MgB_2 with holes. Thus, an intriguing question arises if it is possible to compensate the effect of C substitution, which dopes MgB_2 with electrons, by the C–Li co-substitution. For this reason, the thermoelectric power of the C–Li co-substituted crystals has been also studied and the results are included in Figs. 2 and 3. The substitution of 2% of C reduces T_c slightly from 38.2 K to 37 K. The co-substituted crystal with 2% of C and 6% of Li shows additional reduction of T_c to 35.2 K. However, the thermoelectric power S_{ab} for crystals substituted with 2% of C and co-substituted with 2% of C and 6% of Li is practically the same. Thus, Li does not influence the thermoelectric properties of the *ab* plane, that can be explained assuming that holes coming from Li occupy almost entirely the π band. This is supported by the results of first-principles calculations, which show that only a small amount of the Li-introduced holes may dope the σ band [8]. On the other hand, S_c for the crystal co-substituted with 2% of C and 6% of Li is distinctly larger than S_c for the crystal single-substituted with 2% of C. Thus the anisotropy of S for the C–Li co-substituted crystal is smaller than for the C single-substituted one. Assuming that Li donates holes mainly into the π band, this feature may be explained as a result of changes in the electronic properties of this 3D band only, including the intraband scattering. The interband scattering, however, seems not to be influenced by the Li co-substitution (up to 6%) in any substantial degree. This speculation has to be verified by additional experiments with crystals single--substituted with various amount of Li, which are under way. Preliminary results show that 6% of Li single-substituted for Mg changes (if any) both T_c and S only slightly.

4. Conclusions

In conclusion, availability of sizeable MgB_2 crystals doped with electrons and holes enabled us to perform advanced studies of the anisotropic thermoelectric properties of the two-band superconductor. The thermoelectric power is strongly influenced by doping when C is substituted for B. This substitution, which introduces electrons into the σ band, results in a substantial decrease in both S_{ab} and S_c, leading to the change of their sign to negative for the C content equal to about 7 and 2%, respectively. The observed decrease in S indicates more metallic and electron-conducting character of the C substituted crystals. The substitution of C reduces the thermoelectric power anisotropy, most likely by increasing the interband scattering. When 6% of Li is additionally introduced into the crystal with 2% of substituted C, S_{ab} practically does not change, however S_c increases. This effect suggests that holes, which dope most likely the π band, change the conducting features of this band only. The electron- and hole-doping effects seem to be asymmetric for the thermoelectric normal-state properties, similarly as observed for the superconducting properties [7]. In order to fully understand the relation between doping and the intra- and interband scattering, additional experiments are necessary with crystals single-substituted with Li and Al, and crystals co-substituted with Li–Al. Such crystals have been recently successfully grown.

Acknowledgments

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