Tunnelling properties of Al doped MgB$_2$ thin film junctions

A G Zaitsev, R Schneider and J Geerk
Forschungszentrum Karlsruhe, Institut für Festkörperphysik, P.O. Box 3640
D-76021 Karlsruhe, Germany
E-mail: alexander.zaitsev@ifp.fzk.de

Abstract. Superconducting thin films with composition Mg$_{1-x}$Al$_x$B$_2$ (0 ≤ x < 0.5) were prepared in situ by simultaneous thermal evaporation of magnesium, rf sputtering of boron and dc sputtering of aluminium. The superconducting transition temperature decreased gradually with increasing doping from 34 K (undoped MgB$_2$) down to 7 K (Mg$_{0.53}$Al$_{0.47}$B$_2$). The films allowed a successful preparation of sandwich-type crossed-strip tunnel junctions suitable for reproducible low-noise tunnel measurements. The junctions were prepared using both artificial aluminium oxide barriers and natural barriers resulting from oxidation of the film surface. As counter-electrodes evaporated indium films were used. Differential conductance measurements at low-bias voltage allowed a direct determination of the energy gap on the Fermi surface π sheet. Conductance measurements at high-bias voltage revealed the energies of the electron-coupled phonons, which are responsible for the superconductivity in Mg$_{1-x}$Al$_x$B$_2$. Compared to the undoped MgB$_2$ significant changes in the phonon spectrum could be observed, e.g. a renormalisation of the optical phonons at the high-energy end, which is in agreement with the measurements on bulk samples by inelastic neutron scattering.

1. Introduction
The effect of doping on the superconducting properties of MgB$_2$, especially the substitution of B by C and of Mg by Al, remains a subject of continuous interest for both theory and application [1]. On the one hand, doping is considered as a possibility to improve the properties and the manufacturing technology of MgB$_2$ for various applications. On the other hand, it is expected to shed more light on the mechanism of superconductivity in this material. In particular, much experimental and theoretical work was invested to examine the effect of Al doping on the two-band structure of MgB$_2$ [2-7]. The values of the large gap (Δ$_e$) and the small gap (Δ$_o$) were estimated from specific heat [2], point contact [3,4] and scanning tunnelling [5] measurements on polycrystalline and single crystalline samples and described in terms of the band filling model [6] and the interband impurity scattering model [7]. For Δ$_o$ a monotonic decrease with doping was unambiguous, despite some scattering of the measurement data. However, the results for Δ$_e$ were controversial. Whereas the band filling model predicts the decrease of Δ$_e$ with doping, the interband scattering model predicts an increase of Δ$_e$ towards decreasing Δ$_o$, until both gaps merge. In the experiments the small gap was either found nearly constant for low doping levels (under 10% Al) and decreasing for high doping [2,3,5], or monotonically decreasing [4]. Such disagreements may result from experimental problems, like sample inhomogeneity and the differences of the experimental techniques, especially those of the gap estimation involving either fitting parameters, or sophisticated numerical data processing.

1 To whom correspondence should be addressed.
The aim of the present work was to prepare thin film samples of MgB$_2$ with various levels of Al doping and to prepare sandwich-type tunnel junctions, which enable precise and reproducible measurements of the current-voltage ($I$-$V$) characteristics and their derivatives both in the low-energy (gap) and high-energy (phonon) range. Thus both the energy gap values and the electron-coupled phonon energies of the samples could be obtained directly.

2. Experimental

Our Mg$_{1-x}$Al$_x$B$_2$ (MAB) thin films were prepared in situ in a 'direct growth' process using a combination of thermal evaporation of magnesium, rf magnetron sputtering of a planar boron target and dc sputtering of a planar aluminium target. Except for the Al target it was the same system, which we used for the preparation of high-quality MgB$_2$ films with high critical current density and low hf losses [8,9]. Applying to the Al target a dc power of 0 to 350 W it was possible to adjust the Al content in the Mg$_{1-x}$Al$_x$B$_2$ films from $x = 0$ to $x \approx 0.5$, as determined by Rutherford backscattering.

For the present work we deposited 300 nm thick films on $r$-plane and $c$-plane sapphire substrates of 10×20 mm$^2$ size. The films were not epitaxial, but $c$-axis textured. The superconducting transition temperature ($T_c$) was measured inductively. Both $T_c$ and the transition width $\Delta T_c$ are shown in Fig 1 as a function of the Al content. The $T_c(x)$ dependence is in good agreement with the literature data [2-5, 10-12], whereas our $\Delta T_c$ is usually lower compared to the available data on bulk single and polycrystalline MAB samples [10-12]. The latter suggests high homogeneity and overall quality of the examined MAB thin films.

The obtained films were further used for the preparation of sandwich-type crossed-strip tunnel junctions, see Fig. 2. This type of junctions was already successfully applied for tunnelling spectroscopy on pure MgB$_2$ films [8, 13]. The tunnel barrier on the surface of the MAB film was either natural or artificial. The natural barrier was formed just by exposing the surface of the freshly prepared film to oxygen. In order to form an artificial barrier, several Angstroms of Al were sputtered on the film surface before exposing it to oxygen. It was important to reach an electrical resistance of the barrier in the range between 10 $\Omega$ and 10 k$\Omega$, which was the most suitable range for our electric measurements and to assure, that the resultant tunnel characteristics were as noise-free as possible.

![Figure 1](image.png)

**Figure 1.** Critical temperature (midpoint) versus Al content $x$ in Mg$_{1-x}$Al$_x$B$_2$ films (left axis) and 90% (onset) to 10% (offset) transition width, $\Delta T_c$, versus $x$. The dashed lines are guides to the eye.
Once the film and the barrier were prepared, the thick dielectric layer was immediately painted on the surface by diluted GE7031 low-temperature varnish and the counterelectrode was made by thermal evaporation of indium through a shadow mask. The resultant junction area was \( \sim 0.1 \text{ mm}^2 \). Finally, the junction was contacted, as shown in Fig. 2. When indium was superconducting \((T < 3.4 \text{ K} \text{ and zero applied magnetic field})\) such a junction was of S-I-S (superconductor-insulator-superconductor) type. When the superconductivity in indium was suppressed, either by \( T > 3.4 \text{ K} \), or by applying a field of \(-100 \text{ mT}\), the junction was of S-I-N (superconductor-insulator-normalconductor) type.

3. Results and Discussion

The junctions were characterised by measuring their \( I-V \) characteristic and its derivatives. The differential conductance \((dI/dV)\) at low bias voltage was measured at 1.2K in a zero field as a response of the junction to a small ac \((f = 485 \text{ Hz})\) constant-voltage wobble signal of 32 \( \mu \text{V} \), in dependence of the dc bias voltage applied across the junction barrier. These measurements usually indicated high quality S-I-S junctions, see the sample curve in Fig. 3, with a clear BCS-like gap, low leakage current of less than 1% and two sharp conductance peaks. The distance between these two peaks corresponds to the sum of the energy gaps of the MAB film and the indium counterelectrode \((\Delta_0 = 0.54 \text{ meV})\). Thus, the examples shown in Fig 3 reveal the energy gap of Mg\(_{0.6}\)Al\(_{0.4}\)B\(_2\) to be 1.10 meV and the energy gap of Mg\(_{0.89}\)Al\(_{0.11}\)B\(_2\) to be 2.25 meV. As expected by the band filling model [6], the gap is smaller for the film with higher Al content and lower \( T_c \). These values are determined with relatively high accuracy of \( \pm 0.02 \text{ meV} \) and without using any fit parameters.
The obtained gap values are apparently related to the small, or $\sigma$-gap, of MAB. The difficulty to observe the large, or $\sigma$-gap, in MgB$_2$-based thin film junctions is likely related to the directional tunnelling along the $c$-axis of the film, as discussed earlier [13]. In the present work we did not observe any indication of the $\sigma$-gap for any composition of the examined MAB films.

Measuring $dI/dV$ of S-I-N junctions to higher dc bias voltages one obtains the information on the energies of the electron-coupled phonons of the superconducting films [13]. It is important to point out that features induced by coupling of electrons to phonons appear in the superconductive tunnelling conductance only if they are responsible for the Cooper pairing mechanism. However, in case of MAB the phonon induced structures are expected to be very weak (a factor of $10^{-4}$ compared to the background). They get even weaker for the films with increased Al doping and reduced $T_c$, since the strength of the phonon-induced effect scales with the square of the energy gap. Furthermore, the phonon energies of magnesium diboride are spread up to a high energy of 100 meV [13,14]. The application of such high voltages to the thin insulating barrier of the junction may easily increase the noise level, which makes the precise measurements to be a challenging task. In the present work we measured the differential resistance ($dV/dI$) by a high resolution bridge circuit [15] as a response of the junction to an ac ($f = 485$ Hz) constant-current wobble signal, in dependence of the dc bias voltage applied across the junction barrier. Then the data were inverted numerically to $dI/dV$.

Fig. 4 and Fig 5 show a sample set of characteristics obtained for a Mg$_{0.6}$Al$_{0.4}$B$_2$ based junction. In Fig. 4 we compare the $dI/dV$ data of this junction with the MAB film in the superconducting (measured at 4.2 K) and normal (measured at 22 K) state. As expected, the phonon induced structures are very weak and mainly disappear within the line width on the large scale of Fig 4. In the inset two parts of the figure are enlarged in order to make the difference between the curves visible. However, the phonon-induced structures are clearly seen as peaks in the second derivative, $-d^2I/dV^2$, see Fig. 5 a. For the sake of comparison we also show the $d^2I/dV^2$ data of an undoped MgB$_2$ film [8], see Fig 5 b. Basically, the phonon spectrum of MgB$_2$ consists of three broad regions, although within each region a fine structure may be resolved as well. The low-energy region slightly below 40 meV is associated with three acoustic phonons where vibrations of the Mg sublattice are predominantly involved. The mid-energy region and the high-energy region above $\sim$80 meV are associated with the optical phonons due to the out-of plane and in-plane movements of the B atoms, respectively. The mid-energy region contains peaks resulting from the $\pi$-$\sigma$ interband pairing interaction, that is mainly responsible for the superconductivity in the $\pi$ sheet [13]. As we can see from Fig 5, the Mg$_{0.6}$Al$_{0.4}$B$_2$ film exhibited more distinct structure within the low-energy region compared to the pure MgB$_2$. The peak at $\sim$31 meV, which is present just as a shoulder in the MgB$_2$ spectrum (Fig 5b), is fully resolved in the MAB spectrum (Fig 5a). Then, the doping enhances the high-energy end of the spectrum, and a new high-energy peak at $\sim$96 meV appears. Such a spread of the phonon spectra towards higher energies due to Al-doping is in good agreement with inelastic neutron scattering results for the phonon density of states in bulk MAB samples [14]. The mid-energy peaks are still clearly present, indicating that both $\sigma$ and $\pi$ sheets are still present and the interband pairing interaction is crucial for the superconductivity of 40% Al doped MAB. The features in the mid-region seem to be weakened.

4. Summary and Outlook

In summary, thin superconducting Mg$_{1-x}$Al$_x$B$_2$ films ($0 \leq x < 0.5$) were prepared successfully by the combination of thermal evaporation and sputtering. These films allowed the preparation of high-quality sandwich-type tunnel junctions suitable for low-noise tunnelling measurements, which enabled direct and precise measurements of the current-voltage ($I$-$V$) characteristics and their derivatives both in the low-energy (gap) and high-energy (phonon) range. Differential conductance measurements at low bias-voltages allowed a direct determination of the energy gap on the Fermi surface $\pi$ sheet. The systematic investigation of the dependence of the $\pi$-gap on Al-doping is currently under way. The measurements in the phonon-energy range are believed to provide reliable data for further computation of the tunnelling density of states and the Eliashberg function of the electron-phonon coupling similarly to the computation performed earlier for pure MgB$_2$ [13] in order to contribute to the understanding of the effect of Al-doping on the electron-phonon coupling in MAB.
Figure 4. Differential conductance of a Mg$_{0.6}$Al$_{0.4}$B$_2$ based S-I-N junction measured at 4.2 K with superconducting MAB (bold line) and at 22 K with normal conducting MAB (thin line). The insets enlarge the details.

Figure 5. Second-derivative data, $-d^2I/dV^2$, of superconducting Mg$_{0.6}$Al$_{0.4}$B$_2$ (a) compared with $-d^2I/dV^2$ data of pure superconducting MgB$_2$ (b) [8]. In both cases the normal-state background is subtracted.
References

[1] Lee S 2007 Phys. C \textbf{456} 14
[2] Putti M, Affronte M, Manfrinetti P and Palenzona A 2003 Phys. Rev. B \textbf{68} 094514
[3] Szabó P, Samuely P, Pribulova Z, Angst M, Bud’ko S, Confield P C and Marcus J 2007 Phys. Rev. B \textbf{75} 144507
[4] Daghero D, Deleuse D, Calzolari A, Tortello M, Ummarino G A, Gonnelli R S, Stepanov V A, Zhigadlo N D, Katrych S and Karpinski J 2008 J. Phys.: Condens. Matter \textbf{20} 085225
[5] Giubileo F, Bobba F, Scarfato A, Cucolo A M, Kohen A, Roditchev D, Zhigadlo N D and Karpinski J 2007 Phys. Rev. B \textbf{76} 024507
[6] Kortus J, Dolgov O V and Kremer R K 2005 Phys. Rev. Lett. \textbf{94} 027002
[7] Erwin S C and Mazin I I 2003 Phys. Rev. B \textbf{68} 132505
[8] Schneider R, Geerk J, Zaitsev A G and v. Löhneysen H 2007 Appl. Phys. Lett. \textbf{91} 022509
[9] Zaitsev A G, Schneider R, Hott R, Ratzel F, Linker G and Geerk J 2006 J. Phys. Conf. Series \textbf{43} 309
[10] Li J Q, Li L, Liu F M, Dong C, Xiang J Y and Zhao Z X 2002 Phys. Rev. B \textbf{65} 132505
[11] Bianconi A, Agrestini S, Di Castro D, Campi G, Zangari G, Saini N L, Saccone A, De Negri S, Giovannini M, Profeta G, Continenza A, Satta G, Massidda S, Cassetta A, Pifferi A and Calapietro M 2002 Phys. Rev. B \textbf{65} 174515
[12] Karpinski J, Zhigadlo N D, Schuck G, Kazakov S M, Batlogg B, Rogachi K, Puzniak R, Jun J, Müller E, Wägli P, Gonnelli R, Daghero D, Ummarino G A and Stepanov V A 2005 Phys. Rev. B \textbf{71} 174506
[13] Geerk J, Schneider R, Linker G, Zaitsev A G, Heid R, Bohnen K-P and v. Löhneysen H 2005 Phys. Rev. Lett. \textbf{94} 227005
[14] Renker B, Bohnen K-P, Heid R, Ernst D, Schober H, Koza M, Adelmann P, Schweiss P and Wolf T 2002 Phys. Rev. Lett. \textbf{88} 067001
[15] Adler J G and Jackson J E 1966 Rev. Sci. Instrum. \textbf{37} 1049