The effect of magnesium vacancies on the π intraband scattering in Mg_xB_2 as determined by point contact Andreev reflection

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In order to introduce structural defects into the π band with minimal distortions in the σ band, bulk samples of varying magnesium content were prepared. Point contact Andreev reflection measurements reveal that the density of states of the π band and the behavior of the energy gaps in field imply a relative increase of π band to σ band scattering with increasing magnesium deficiency. The results are consistent with the observed increase of the low temperature H_{c2} value in magnesium deficient MgB_2. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2786019]

The multiple band structure of the superconductor MgB_2 is responsible for a wide range of observed[1–3] and predicted[4] phenomena. Three sorts of scattering mechanisms are possible in this material:[5–8] intraband scattering within the π and σ bands and interband scattering between the two. Interband scattering is associated theoretically[5,9] and experimentally[5] with a reduction in the T_c of the material and a decrease in the energy separation between the two order parameters Δ_π and Δ_σ. It has been proposed that increasing intraband scattering in the three dimensional π band with respect to the more two dimensional σ band increases the low temperature H_{c2}.[10] Indeed, the diffusivity ratio ($\eta = D_\sigma / D_\pi$, with D_i the diffusivity in each band) can be determined directly from the $H_{c2}(T)$ curve.[10] Experimentally, various methods of increasing scattering or dirtying up this unusual superconductor have been attempted, although it has proved very difficult to selectively increase the scattering in one band only, with the exception of carbon doping.[11]

An independent measure of η can be extracted from point contact Andreev reflection (PCAR) spectra taken in applied magnetic field,[1] as shown recently by Szabo *et al.*[11] The model used to interpret the Andreev spectra has been set up only for H parallel to the crystallographic c axis.[6] However, as we and others have shown previously,[1,7,11] the π band is close to isotropic at low fields and, consequently, the study of the evolution of the energy gap and the density of states with respect to applied field should be insensitive to crystallite orientation up to fields $\lesssim 0.5$ T (at $T/T_c < 0.5$).[7] Here, we use both $H_{c2}(T)$ and PCAR to make an independent measurement of whether the increase of $H_{c2}(T)$ previously observed for Mg deficient samples is indeed related to increased π band scattering.

The samples used in this study were a series of magnesium deficient Mg_xB_2 bulk samples. Briefly, the samples were prepared by mixing crystalline magnesium powder (99.8% purity, 325 mesh) with amorphous boron powder (99.99% purity, 325 mesh). The powder was mixed in the ratio xMg:B (where $x = 1.0, 1.5$), pressed into pellets, wrapped in Ta foil without any excess Mg, and then heated to 900 °C for 15 min in an Ar–2% H_2 atmosphere. All of the samples were expected to be magnesium deficient (due to the rapid vaporization of magnesium at this temperature[12]), with the lowest x value sample ($x = 1.0$) being the most Mg deficient. It is important to stress that the x values are nominal in the sense that they are the mixing ratio, not the final value in the reacted sample. Precise x values are not possible to obtain from simple structural determination methods. The $x = 1.0$ sample contained some MgB_4, from x-ray diffraction, which was indicative of a Mg poor reaction environment. Raman spectroscopy and x-ray diffraction data indicated greater structural disorder with lower x values. Also, enhanced $H_{c2}/H_{irr}(T)$ and in-field J_c values were recorded for lower x, as described in detail elsewhere.[13] Magnetic susceptibility and resistivity data indicated that the T_c of the samples was basically unchanged as a function of magnesium content; 37.5 K for the $x = 1.0$ sample and 38 K for the $x = 1.5$ sample.[13] Point contact spectra were taken at 4.2 K using a mechanically sharpened Au tip, as described previously.[1]

The Δ_π and Δ_σ gap values extracted from a number of spectra (see inset of Fig. 1, for example) at different locations on the bulk surface are shown in the histogram in Fig. 1. There is a distribution of gap values but no evidence of merging of the two gaps which would indicate an increase of interband scattering. Previous observations of these samples also found that T_c remains constant across the sample series.[13]

Figure 2 shows the $H_{c2}(T)$ values determined resistively. The more magnesium deficient sample ($x = 1.0$) has H_{c2} at 5 K = 21 T whereas $x = 1.5$ has H_{c2} at 5 K = 16 T. On unnor-

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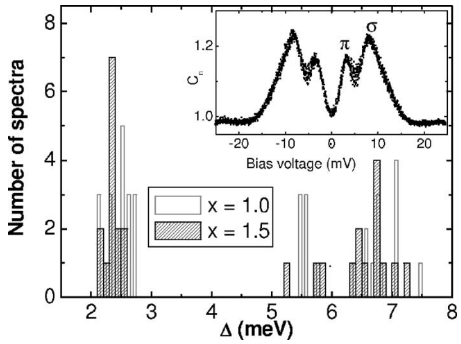

FIG. 1. Distribution of gap energies for $x=1.5$ and $x=1.0$ samples. The inset shows a PCAR spectrum at 4.2 K in zero field for the $x=1.5$ sample clearly showing peaks in the spectra owing to the two gaps, marked on the inset.

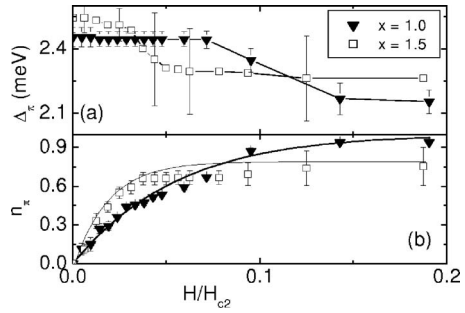

FIG. 3. (a) Values of Δ_π for the $x=1.5$ (□) and $x=1.0$ (▼) extracted from the fit, (b) n_π extracted from the PCAR as a function of field for $x=1.5$ (□) and $x=1.0$ (▼), the lines are guides for the eye only. The x scale has been normalized by the H_{c2}(5 K) value for each sample.

malized axes, it appears that there is a slight upturn in H_{c2} at low temperature for the more deficient sample as indicated by the departure from the dashed line in Fig. 2. However, on normalized axes (see lower left hand inset of Fig. 2) to compare directly with predictions in Ref. [10] the possibility that this feature has any significance is very weak. Note also that the absolute values of H_{c2} are low compared to doped bulk samples or thin films, indicating that in our samples the scattering rates are low. We have fitted the $H_{c2}(T)$ curves at $T \sim T_c$, to the Gurevich model[10] following Putti *et al.*,[14]

$$\left.\frac{dB_{c2,ab}}{dT}\right|_{T_c} \sim \frac{8\phi_0 k_B}{\pi^2\hbar}\frac{1}{a_1 D_\sigma/\gamma + a_2 D_\pi}, \tag{1}$$

where ϕ_0 is the flux quantum, a_i are parameters related to the band coupling,[9,10,14] D_i are the diffusivities in each band, and γ can for most cases[14] be associated with the anisotropy. The diffusivities can be further estimated from the residual resistivity ρ_0, as described in Ref. 14, when

$$\frac{1}{\rho_0} = e^2 \sum_{\alpha=\sigma,\pi} N_\alpha D_\alpha, \tag{2}$$

where N_α is the density of states in each band α.

It is not possible to extract the diffusivity ratio accurately using this expression because we do not know γ, the anisotropy of H_{c2}. Nevertheless if we assume that $2<\gamma<5$, we find that for the $x=1.0$ sample, $\eta=0.022\pm0.013$ and for the $x=1.5$ sample, $\eta=0.017\pm0.010$. We note that the absolute values of η are extremely low compared to those of previous studies on films where a very strong upturn in $H_{c2}(T)$ at low temperatures was observed.[15] The values of η we have observed are consistent with the previous studies of bulk materials.[16,17] The slopes of H_{c2} near T_c for the two samples are also rather similar which leads to only subtle differences in η between samples.

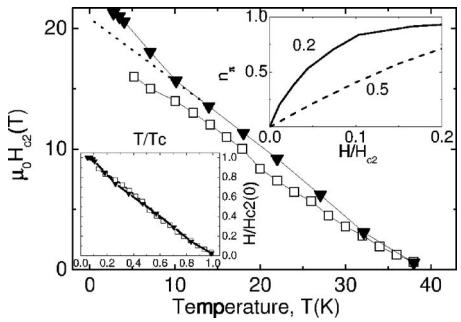

FIG. 2. H_{c2}(T) for $x=1.5$ (□) and $x=1.0$ (▼). The inset shows the theoretically calculated DOS averaged over the vortex lattice as a function of reduced field (Refs. 16 and 20) for two diffusivity ratios $\eta=0.2$ (solid line) and $\eta=0.5$ (dashed line). Lower left inset shows reduced field versus reduced temperature for the two samples.

The point contact spectral analysis we perform has been described in detail previously.[1] The conductance spectra of MgB_2 can be fitted to a modified BTK model[18] with five parameters: Δ_π, Δ_σ, Z the interface barrier between the tip and the sample, ω the smearing of the contact, and f the weighting between conductance contribution to the spectra of the two bands. In an applied magnetic field, a model that accounts for the mixed state density of states (DOS) can be used to fit the spectra.[19] The expression for modeling the conductance (G) of the contact then becomes

$$\frac{G(V)}{G_N} = f[n_\pi + (1-n_\pi)g_\pi] + (1-f)[n_\sigma + (1-n_\sigma)g_\sigma], \tag{3}$$

where n_i is the fractional number of normal conducting channels. As described in Ref. 1, $n_{\pi,\sigma}$ can be directly identified with the zero energy DOS averaged over the vortex lattice, as used in Ref. 6. As in previous studies, in order to reduce the number of parameters in the fit, it is assumed that the weighting function f and the interface barrier Z determined in the zero applied field spectrum are invariant with field.[19] Figure 3(a) shows the behavior of Δ_π as a function of reduced field $h=H/H_{c2}$, while Fig. 3(b) shows the DOS extracted using Eq. (3), for representative contacts on both samples. The H_{c2} values used for the normalization are taken from Fig. 2. The resistivity measurements are most likely weighted to $H_{c2}\sim H_{c2}\|ab$, i.e., the higher H_{c2} value for both samples.

The inset of Fig. 2 shows the predicted[6,20] variation of n_π $(H\|c)$ for two values of $\eta=0.2$ and 0.5. Comparing the inset of Fig. 2 with the data shown in Fig. 3(b), it can be seen that both samples have relatively low values of η; however, the more stoichiometric sample $(x=1.5)$ has a steeper gradient (lower η) than the sample with a high concentration of magnesium vacancies $(x=1.0)$. These observations are consistent with the information extracted from fitting $H_{c2}(T)$.

The change in η suggested by the n_π DOS should also be reflected in definite, but subtle, differences in the behavior of the order parameter values, particularly Δ_π, as a function of field.[6] Cleaner samples (lower η) should show a more rapid initial suppression in field $(h\leqslant 0.25)$ than dirtier

(higher η) samples.[6] Figure 3(a) shows the behavior of $\Delta_\pi(h)$ extracted from representative point contact spectra taken from both the samples. The more stoichiometric sample indeed shows behavior characteristic of lower η than the sample with more magnesium deficiency, although the effect is much less apparent than the changes in the n_π DOS. The behavior of the gaps with field supports the hypothesis that the $x=1.5$ sample shows less π band scattering than the $x=1.0$ sample relative to the respective σ band properties.

The data obtained from the field behavior of both the DOS and the gaps suggest that deliberately introducing Mg deficiency into the structure dirties the π band without introducing significant interband scattering. This result explains the higher H_{c2} values found in samples prepared in a more Mg-deficient environment in terms of the intraband scattering in the MgB_2.[10] It is not possible to extract a diffusivity ratio directly from the PCAR measurement for polycrystalline, randomly oriented samples but the behavior of the samples is certainly qualitatively consistent with the diffusivity ratio values extracted from the Gurevich model.[10]

In summary, we have completed a point contact Andreev reflection spectroscopy study on samples of Mg-deficient MgB_2. Resistive measurements indicated that the H_{c2} of the sample with greater magnesium deficiency was higher than that of the more stoichiometric sample. Point contact measurements in zero field confirmed that there was no significant increase in interband scattering between the two samples, while measurements in field have allowed us to extract the DOS of the π and σ bands and the behavior of $\Delta_{\pi,\sigma}$ as a function of field. The data indicate that the less Mg-deficient sample has less π band scattering relative to the σ band than the Mg-deficient sample but the changes are subtle. These results suggest that careful control of the magnesium stoichiometry of MgB_2 might selectively alter the π intraband scattering while minimally affecting the σ intraband scattering and the π-σ interband scattering.

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