The different development of the anisotropic upper critical field in MgB$_2$ by aluminum and carbon doping

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The temperature dependence of the upper critical field, $H_{c2}$, for both field directions in partially substituted polycrystalline MgB$_2$ was determined. Whereas the suppression of $T_c$ is similar for aluminum and carbon substituted samples, $H_{c2}$ is affected by the substitution in profoundly different ways. In the case of Al substitution changes can tentatively be described by intrinsic effects (shift of the Fermi level). In the C substituted samples, $H_{c2}$ is increased drastically, and extrinsic effects (disorder) have to play a major role. The strong contrast between the two substitutions is discussed, taking into account three relevant scattering rates.

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An unusual temperature dependence of the anisotropic upper critical field, $H_{c2}$, is one of the major consequences of two-band superconductivity as realized in magnesium diboride MgB$_2$. To further explore properties of a given compound it is often helpful to consider the effects of partial chemical substitutions. In the case of MgB$_2$, partial substitutions with many elements have been attempted, but only two elements are widely recognized to enter the structure: aluminum replacing magnesium and carbon replacing boron.

Both substitutions dope the material with additional electrons, which should similarly affect the superconducting properties, at least to the extent that a rigid band approximation works. According to the detailed band structure calculations, electron doping most drastically affects the $\sigma$ bands, which are nearly filled. Furthermore, any partial substitution by small amounts of an additional element increases chemical disorder, leading to increased scattering. In the two-band superconductor MgB$_2$, at least three different scattering rates have to be distinguished and the different substitution sites Mg (by Al) and B (by C) are likely to influence these scattering rates in drastically different ways. In general, the upper critical field, $H_{c2}$, is influenced by electron-phonon coupling (EPC), Fermi velocities, and by the mean free path, $\ell$. EPC and Fermi velocities are intrinsic properties altered by electron doping, while $\ell$ is a function of scattering. It will be interesting to compare the doping and temperature dependence of $H_{c2}$ with substitutions on either the Mg or the B site. This may help in separating electron doping and scattering effects of partial substitutions.

In the case of the B site substitution by carbon a number of studies have presented measurements of $H_{c2}$ on polycrystalline material and in a limited range on single crystals. All studies agree in significant enhancements of $H_{c2}$, and the studies on single crystals also indicate a decrease of the $H_{c2}$ anisotropy $\gamma_H \equiv H_{c2}^{\parallel c}/H_{c2}^{\parallel ab}$. Fewer $H_{c2}$ studies exist for Mg site substitution by aluminum, and there is a considerable spread of given values between them.

Here, we present a comparison of $H_{c2}^{\parallel c}$ and $H_{c2}^{\parallel ab}$ measured with the same technique on aluminum and carbon substituted polycrystalline MgB$_2$ with various substitution levels, prepared from the same Mg and (partly) B starting materials with similar procedures. As a function of electron doping, a similar decrease of both the transition temperature, $T_c$, and the upper critical field anisotropy, $\gamma_H$, contrasts with the dramatically different development of the magnitude of $H_{c2}$: Whereas the behavior of the upper critical field in the case of Al substitution can be understood as resulting from a shift of the Fermi level, an increase in scattering has to be taken into account to explain the large increase of $H_{c2}$ upon C substitution. We briefly discuss this different effect on scattering by C and Al substitution.

We investigated carbon substituted polycrystalline MgB$_2$ samples prepared in two different ways: We synthesized Mg$_x$(B$_{0.9}$C$_{0.1}$)$_2$ at 1200°C using Mg and B$_4$C as starting materials, as described in Ref. 2. For low C substitution levels, filaments already studied in Ref. 2 were ground to powder. In the case of aluminum substitution, chemical inhomogeneities are difficult to avoid. Inhomogeneities lead to transition broadening detrimentally particularly to the determination of $H_{c2}^{\parallel c}$. In order to maximize sample homogeneity, we tried several techniques, including pre-alloying Mg and Al, and using AlB$_2$ and AlB$_1$$_2$ as Al source. However, the best results were obtained with a two-step synthesis at high temperatures. First, synthesis at constant temperatures from 1000 to 1200°C from the elements in stoichiometric quantities for up to 10 days, followed by cooling to room temperature in streaming water produced material with large inhomogeneities as visible in x-ray diffraction pattern and particularly in the superconducting transition. In order to improve homogeneity, we finely ground and thoroughly mixed the products of the above synthesis, pressed them into pellets, and then heated them for a second time to 1200°C for 10 days.

Powder x-ray measurements on MgB$_2$ samples substituted with up to 20% Al indicate no phase separation, shifts in the lattice parameters close to liter-
FIG. 1: a) Magnetization $M$ vs temperature $T$ in 20 Oe (both zero field cooled and field cooled) of Al or C substituted polycrystalline MgB$_2$ samples. b) Transition temperature $T_c$ vs number of additional electrons per unit cell due to Al (full symbols) or C (open symbols) substitution. The open square is from Ref. 14.

ature values$^{19}$ and a moderate peak broadening suggesting small variations in the Al content throughout the samples. The broadening becomes significant for Mg$_{0.7}$Al$_{0.3}$B$_2$. For this composition, additional small peaks suggest the presence of MgB$_2$ and MgAlB$_4$ minority phases. The superconducting transition in zero field was measured resistively (on the 60 to 70% dense pellets) and by magnetization measurements in 20 Oe (after powdering the samples and mixing with epoxy). The magnetization measurements on isolated powder particles makes any $T_c$ variations within the sample well visible as an onset broadening [Fig. 1b)]. The effective $T_c$ was defined as the crossing point of the steepest slope of the field cooled $M(T)$ with the $M = 0$ axis [Fig. 1b)]. The height of the “sliver” in the onset above this temperature is a measure for the amount of material with higher $T_c$ due to locally less Al substitution. Such a variation is present in Al substituted samples, but rather small.

The polycrystalline upper critical field, which corresponds to $H^c_{c2}$, was determined from resistivity and magnetization in applied fields up to 140 kOe and 70 kOe, respectively. In the overlapping field region, the results agree within error bars. The results on the C substituted samples are also in agreement with the results of Refs. 3 and 8. The “minimum upper critical fields” ($H^c_{c2}$) were established with a method developed by Bud’ko and coworkers. On unsubstituted polycrystalline MgB$_2$, this method yielded similar results on the temperature dependent anisotropy as measurements performed on single crystals. Materials were ground to a fine powder and mixed with epoxy. The minimum upper critical field is then visible as pronounced features in the derivatives of the magnetization as a function of temperature or field (see inset of Fig. 2). As an example, the resulting upper critical field of Mg$_{0.9}$Al$_{0.1}$B$_2$ is shown in Fig. 2. For this sample, $H^c_{c2}(0) \approx 29$ kOe is slightly higher than $H^c_{c2}(0) \approx 25$ kOe measured with the same method on an unsubstituted sample. The significance of the increase is questionable, taking into account that even on unsubstituted single crystals from the same source $H^c_{c2}(0)$ with values of 28 kOe (Ref. 21) up to 31 kOe (Ref. 22) were observed. We note that our result is significantly lower than the value of 52 kOe reported for a Mg$_{0.88}$Al$_{0.12}$B$_2$ single crystal.\(^{15}\) The upper critical field parallel to the layers on the other hand, $H^c_{ab}(0) \approx 127$ kOe, is significantly lower than corresponding measurements on unsubstituted MgB$_2$. Our result is moderately higher than the results reported in Refs. 17 and 18, significantly higher than those reported in Ref. 16. Parts of the discrepancies might be related to different amounts of impurity scattering (see discussion below), whereas other parts may originate from different inhomogeneities in the Al distribution.

The analysis on the aluminum doped samples with up to 20% Al substitution yields the following picture:
Al substitution first slightly increases, then slightly decreases $H_{\text{c2}}^{\text{lc}}$ (essentially constant), whereas $H_{\text{c2}}$ parallel to the layers monotonically decreases (Fig. 3, closed symbols). The decrease of $H_{\text{c2}}^{\text{ab}}$ is roughly linearly, extrapolating to 0 for $\sim 30\%$ Al substitution.

The decrease of $H_{\text{c2}}^{\text{ab}}$ and the almost constant behavior of $H_{\text{c2}}^{\text{lc}}$ suggests that disorder may not be important in determining the $H_{\text{c2}}$ development with Al substitution. In unsubstituted MgB$_2$, clean limit (two-band) theoretical calculations$^{25,26}$ compare rather favorably with experimental data$^{26,27}$. These calculations as well as phenomenological considerations$^{19}$ indicate that in the low temperature limit the $\pi$ bands are not important for determining $H_{\text{c2}}$: $H_{\text{c2}}(0)$ is mostly determined by the $\sigma$ bands, as first suggested by Bud’ko and coworkers.$^{28}$ The upper critical field is related to the coherence length, $\xi$, through $H_{\text{c2}} \propto \xi^{-2}$. In the clean limit at zero temperature, ignoring the difference between GL and BCS coherence length, $\xi$ is related to the superconducting gap and Fermi velocities by $\xi \propto v_F/\Delta$, and the Fermi velocity anisotropy determines the anisotropy of $\xi$. Here, $v_F$ ($\Delta$) is defined as the root-mean-squared wave vector dependent Fermi velocity (superconducting gap), averaged over the Fermi surface (in the case here over the $\sigma$ sheets of the Fermi surface). We may then approximate

$$H_{\text{c2}}^{\parallel}(0) \propto \left(\Delta_\sigma(0)/v_{F,\sigma}^{\parallel}\right)^2, \quad \gamma_H(0) = v_{F,\sigma}^{\parallel}/v_{F,\sigma}^{\parallel}. \quad (1)$$

Apart from disorder effects due to the partial substitution, Al doping modifies charge distribution and decreases the lattice constants ($c$ in particular).$^{29}$ The main effect, however, is to dope the system with additional electrons, resulting in a shift of the Fermi level, $E_F$, to higher energies. For substitution levels well below 30%, where $E_F$ reaches the $\sigma$ band edge at the $\Gamma$ point$^{26}$ the changes in the electronic structure are well approximated within a rigid band model. The increase of $E_F$ decreases the density of states (DOS) at $E_F$ and modifies the band averaged Fermi velocities, primarily in the $\sigma$ bands.$^{28}$ For moderate substitution levels, the out-of-plane $\sigma$ Fermi velocity, $v_{F,\sigma}^{\parallel}$, remains approximately constant, whereas the in-plane $\sigma$ Fermi velocity, $v_{F,\sigma}^{\parallel}$, substantially decreases. According to Eq. (1) this lowers the $H_{\text{c2}}$ anisotropy and increases $H_{\text{c2}}^{\parallel}$. However, the decreased DOS at $E_F$ weakens the electron-phonon coupling, resulting in decreased superconducting gaps and $T_c$ (c.f. Fig. 1). The additional effects of the substitution on the phonons$^{29}$ complicate the theoretical analysis of the development of $\Delta_\sigma$ and $\Delta_\pi$ with substitution level, and experimental reports on the gap development are sparse as of yet.$^{17,19,23}$ As an approximation, we can use the experimental values of the transition temperature shown in figure 1 and assume $\Delta_\sigma \propto T_c$.

The combination of the decreased $\Delta_\sigma$ and also decreased $v_{F,\sigma}^{\parallel}$ results in little change of $H_{\text{c2}}^{\parallel}$ as estimated by Eq. (1), in accordance with the experiment. The calculation also yields the substantial decrease of $H_{\text{c2}}^{\parallel}$ and of the anisotropy $\gamma_H$ observed experimentally. For the out-of-plane upper critical fields of Mg$_{1-x}$Al$_x$B$_2$ at a similar, but slightly more detailed analysis was recently presented by Putti and coworkers.$^{28}$ The fact that the experimental development of the upper critical field can be accounted for by the clean limit formula$^{10}$ clearly suggests that effects of increased scattering are not relevant in our samples of Mg$_{1-x}$Al$_x$B$_2$ at low substitution levels. This is different from recently presented results on single crystal samples, where scattering in the $\pi$ bands seems to be larger.$^{18}$

The development of $H_{\text{c2}}$ with partial carbon substitution is also shown in Fig. 4 (open symbols). Our results, which agree qualitatively with the limited results on single crystals available$^{10,11,13,14,15}$, show a drastic increase of $H_{\text{c2}}$ both parallel and perpendicular to the layers, in contrast to the Al substitution case. The increase of $H_{\text{c2}}^{\parallel}$ is monotonous in the substitution range measured, whereas $H_{\text{c2}}^{\parallel}$ peaks somewhat below 400 kOe for C substitution levels around 5%. Figure 4 displays the temperature dependent $H_{\text{c2}}$ anisotropy for C substituted, Al substituted, and unsubstituted MgB$_2$. Where

![Graph showing zero temperature upper critical field vs number of additional electrons per unit cell](image-url)
Different scattering rates have to be taken into account: interband scattering and intraband scattering in the $\sigma$ and $\pi$ bands. We note that the observation of constant $\Delta_\sigma / \Delta_\pi$ ratios by spectroscopic means\textsuperscript{25,26} indicate that the interband scattering rate is hardly affected by moderate levels of C substitution and may be neglected as in unsubstituted MgB$_2$. However, a recent point contact study on MgB$_2$ crystals containing high C substitution levels suggest that the interband scattering rate may be important, particularly for high substitution levels.\textsuperscript{35,36} Calculations within “intraband dirty limit”\textsuperscript{25,26} can indeed explain very drastic increases of $H_{c2}$, much larger than in single band superconductors.

These dirty limit calculations also yield a temperature dependent $H_{c2}$ anisotropy, like the clean limit calculations do. However, here the $T$ dependence of $\gamma_H$ also depends on the ratio of the scattering in the anisotropic $\sigma$ and in the nearly isotropic $\pi$ bands. If the intraband scattering is much larger in the $\sigma$ bands than in the $\pi$ bands, a decreasing $\gamma_H(T)$ dependence is expected, whereas the opposite case results in an increasing $\gamma_H(T)$ dependence. Starting from the unsubstituted MgB$_2$ with a decreasing $\gamma_H(T)$ dependence, a low level partial substitution mainly increasing the $\sigma(\pi)$ bands scattering, should lead to a more (less) pronounced $\gamma_H(T)$ dependence. As we can see from Fig. 4, the $\gamma_H(T)$ dependence becomes less pronounced upon increasing the substitution level. Comparing C and Al substitution, the decrease of the $T$ dependence seems rather similar, indicating that it is mostly due to the intrinsic changes discussed above, rather than disorder. For the same electron doping levels, the $\gamma_H(T)$ variation is somewhat less strong for the carbon substitution case. This indicates that upon C doping the scattering is increased more in the $\pi$ bands than in the $\sigma$ bands. A similar conclusion was reached for a 6.3% C substituted single crystal and for thin films containing carbon.\textsuperscript{37,38} For a more quantitative analysis, a theory treating clean-limit (electron doping) and dirty-limit (scattering) effects on an equal footing would be highly desirable.

The effect of higher $\pi$ band scattering also manifests itself in the form of the $H_{c2}$ curves, most visibly for $H_{c2}{\parallel c}$. In extreme cases this leads to a positive curvature of $H_{c2}{\parallel c}(T)$ at low $T$.\textsuperscript{37,38} In contrast to “dirty films” result\textsuperscript{37,38} we did not observe such a positive curvature, but compared to unsubstituted MgB$_2$, the negative curvature of $H_{c2}{\parallel c}(T)$ was significantly decreased for the C substituted samples. For 10% C substituted MgB$_2$, $H_{c2}{\parallel c}(T)$ was found to be almost linear at low temperatures. The tendency of decreased negative curvature of $H_{c2}{\parallel c}$ with increasing C substitution is also seen in single crystal measurements\textsuperscript{11,14,15} and supports the conclusion of mainly additional scattering in the $\pi$ bands causing the $H_{c2}$ enhancement. In contrast, in the Al substituted samples, the $H_{c2}(T)$ curvature is not significantly affected (cf.
The irreversibility field, related to the upper critical field, variations of the significance of to the aluminum substitution case, where considerable intrinsic property of C substitution. This is in contrast to conclude that an increase of the mean free path in the T dependence disorder effects, found a larger reduction Into account into the electronic structure study for different samples. A recent first principles electronic structure study on C substituted MgB₂ taking into account disorder effects, found a larger reduction of the mean free path in the σ bands, which is in contrast to our analysis. However, there are a variety of effects that are more involved to include in a calculation, e.g., carbon induced local distortions in the structure, as suggested by a single crystal x-ray diffraction study. Since the large increase of H_{c2} in C substituted MgB₂ and related scattering rates are important for potential applications, additional theoretical studies are clearly desirable, as would be a clear experimental demonstration of a procedure boosting scattering mainly in the σ bands.

In conclusion, whereas the development of H_{c2} with partial aluminum substitution can be understood within a simple rigid band picture, disorder effects are responsible for the large enhancement of the H_{c2} magnitude of carbon substituted MgB₂. In contrast, the development of the H_{c2} anisotropy and T_{c} are remarkably similar for the two substitutions. Scattering within the π bands is increased much more by carbon than by aluminum substitution, and more than scattering in the σ bands. The origin of this is yet to be resolved.

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