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Phase separation in carbon-doped MgB_2 studied by means of alternating current susceptibility measurements

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Abstract

Alternating-current susceptibility measurements were performed on ternary $MgB_{2-x}C_x$ ($0 \leqslant x \leqslant 0.1$) superconducting compounds. The results are consistent with the presence of macroscopic phase inhomogeneities at extremely low levels of carbon doping ($x > 0.04$) in agreement with high-resolution synchrotron x-ray powder diffraction measurements.

1. Introduction

The recent discovery of superconductivity in MgB_2 [1] has led to much excitement because of the remarkably high critical temperature, $T_c = 39$ K, for a binary system. To date, several attempts have been made to develop new MgB_2-based superconductors, improve their superconducting properties, and possibly increase their T_c by doping with either electrons or holes through chemical substitution for the Mg or B atoms [2–4]. Although in all cases the critical temperature decreases with increasing doping level at various rates for different substitutions, the study of these compounds remains of great interest for the understanding of the dependence of superconductivity on the crystal structure and the effect of doping on the electronic DOS and the Fermi surface details of the parent MgB_2.

We have reported that the electron-doped ternary $MgB_{2-x}C_x$ compounds adopt an AlB_2-type hexagonal structure, isostructural with MgB_2, in a relatively small range of nominal carbon concentration, $x < 0.1$, with their critical temperature decreasing almost linearly with increasing carbon content, x [3]. Powder x-ray diffraction (XRD) data indicate that carbon substitutes in the boron honeycomb layer without having much effect on the interlayer interactions and results in a monotonic contraction of the lattice parameter a with increasing x.

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However, high-resolution synchrotron XRD studies have revealed that the carbon miscibility in MgB_2 is very small and inhomogeneous phase-separated samples are obtained for $x > 0.04$ [5]. These multiphase samples appeared in dc susceptibility measurements to still show a one-step superconducting transition and full shielding [3].

The ac susceptibility at different dc magnetic fields and ac field amplitudes and frequencies reflects the flux dynamics in type II superconductors (such as the MgB_2-based series). It has been widely used in the case of the high-T_c superconducting cuprates to investigate their inhomogeneities, the possible loss mechanisms, the behaviour of superconductivity in the weak links between grains [6–8], and to estimate various superconducting properties such as the low-temperature energy gap and the flux diffusion barrier [9, 10]. By performing ac susceptibility measurements, Panagopoulos *et al* [11] have recently estimated the temperature dependence of the magnetic penetration depth, while Qin *et al* [12] obtained the flux creep activation energy as a function of the current density for the MgB_2 superconductor.

In the present work, we study in a systematic way the phase purity and/or possible phase inhomogeneities in the $MgB_{2-x}C_x$ ($0 \leqslant x \leqslant 0.1$) ternaries by carrying out ac susceptibility measurements at different ac amplitudes and dc magnetic fields as a function of temperature.

2. Experimental details

The samples investigated, of $MgB_{2-x}C_x$ ($x = 0$, 0.04, 0.06, 0.08, and 0.1), were prepared by heating mixed powders of amorphous boron, carbon black, and magnesium at 900 °C for 2 h. The ac susceptibility measurements were carried out on 30–40 mg samples sealed in gelatin capsules in the temperature range 5–60 K with a Quantum Design SQUID magnetometer (MPMS5). The magnetometer was equipped with a high-homogeneity 5 T superconducting magnet maintaining the samples in a homogeneous magnetic field. For the present ac susceptibility measurements, ac magnetic fields of amplitudes up to 3.5 Oe and a frequency of 333 Hz have been used under dc magnetic fields of 0, 100, 1000, and 10 000 Oe. After each temperature scan, nulling of the remnant field in the superconducting magnet was performed.

3. Results and discussion

In the powdered $MgB_{2-x}C_x$ samples studied, the absence of weak links was first confirmed by the linear dependence of the ac susceptibility on the amplitude and the frequency of the applied ac field [13]. This conclusion was also supported by the fact that no peak characteristic of intergranular losses was observed at low temperatures in the imaginary part (χ'') of the ac susceptibility [7]. In the case of pure MgB_2, magnetization and transport measurements have already shown that this superconducting material does not exhibit weak-link electromagnetic behaviour at the grain boundaries [14] or fast flux creep (motion of the vortices over pinning centres) phenomena [15]. Thus, in both pure and carbon-doped MgB_2, the inductive current flows coherently throughout the sample, unaffected by the grain boundaries.

The temperature dependence of the real (χ') and the imaginary (χ'') parts of the ac susceptibility for $MgB_{2-x}C_x$ ($x = 0$, 0.04, 0.06, 0.08, and 0.1) is illustrated in figure 1. For these ac susceptibility measurements, an ac magnetic field (H_{ac}) of 1 Oe rms value with frequency $f = 333$ Hz has been used in the absence of a dc field (H_{dc}). Below the critical temperature, a sharp decrease in the real part of the ac susceptibility occurs, which reflects the diamagnetic shielding. In addition, below T_c a peak appears in χ'', representing losses. In general, in the case of a single-phase granular type II superconductor, two types of loss mechanism are observed in low-frequency ac susceptibility measurements, each associated

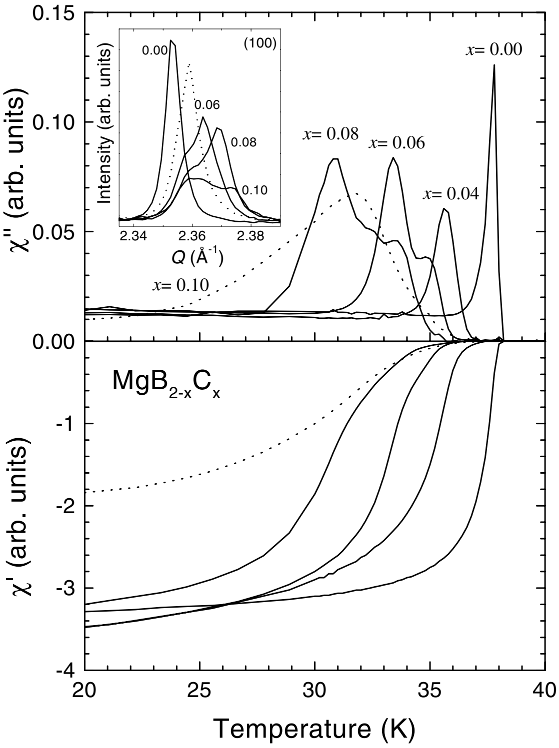

Figure 1. Temperature dependences of the χ'-and χ''-parts of the ac susceptibility for various MgB$_{2-x}$C$_x$ compositions (solid curves: $x = 0$, 0.04, 0.06, and 0.08; dotted curve: $x = 0.1$). The measurements were carried out at $H_{ac} = 1$ Oe (rms), $f = 333$ Hz, and $H_{dc} = 0$ Oe. Inset: synchrotron x-ray powder diffraction profiles at 16 K showing the (100) reflection of the MgB$_{2-x}$C$_x$ samples.

with a different loss peak in the χ''–T dependence:

(i) the intergranular peak, representing losses associated with flux penetrating the grain boundaries; and
(ii) the intragranular peak, reflecting losses related to the flux penetrating inside the grains [7, 16].

Since our samples are in powder form, the losses are mainly of intragranular nature. While in bulk MgB$_2$ samples, large critical currents have been observed since the grain boundaries act as strong pinning centres [12, 14, 15, 17], in powder samples the losses are weak due to weak pinning inside the grains and the presence of surface barrier. Then the presence of more than one peak in χ'' in our powder samples implies multiphase behaviour. The location of each peak occurs at the temperature value where the flux front of the applied ac magnetic field reaches the centre of the grains if pinning controls the irreversible behaviour. In the case of surface barrier control, the peak in χ'' occurs when the minor hysteresis loop (formed by the ac field) connects the ascending and descending branches of the hysteresis loop.

As can be seen in figure 1, the increase in carbon concentration, x, significantly affects the ac susceptibility of these materials. More specifically, as the carbon content increases, the onset of diamagnetic shielding in χ' and the peak position in χ'' shift to lower temperatures. In a constant applied dc field, this reflects the suppression of T_c with the carbon concentration.

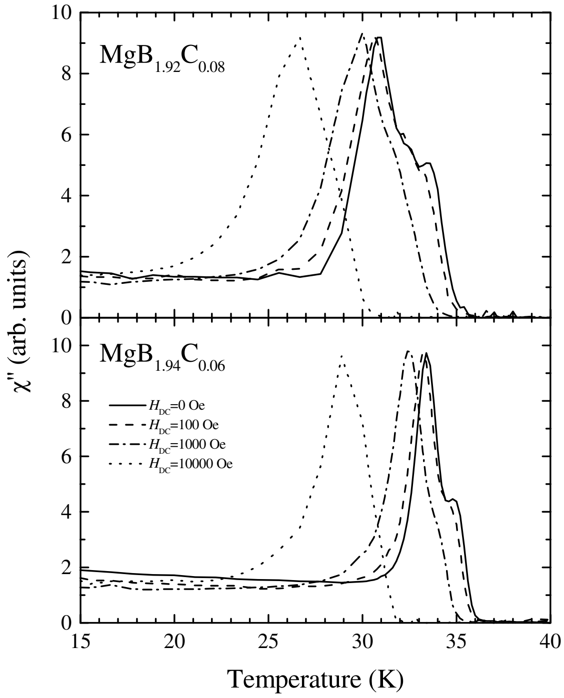

Figure 2. The temperature dependence of the χ''-part of the ac susceptibility for $MgB_{1.94}C_{0.06}$ and $MgB_{1.92}C_{0.08}$ at various dc fields up to 10 000 Oe. The measurements were carried out at $H_{ac} = 1$ Oe (rms) and $f = 333$ Hz.

In addition, the increase in x leads to broadening of the peak in χ'', while the superconducting transition, reflected by the onset in χ', becomes more rounded. This behaviour is related to the reduction in the superconducting volume fraction.

The most pronounced effect for $x > 0.04$ is, however, the appearance of at least one additional peak in the χ''–T dependence of $MgB_{2-x}C_x$. In the case of single crystals, the observation of more than one intrinsic peak in χ'' is connected with the misalignment of the crystal axes with respect to the magnetic field or to the non-monotonic variation of screening current with magnetic field, while in powder samples, it is related to the existence of multiphase compositions [7]. Thus the fact that for $x = 0.06$ and 0.08 at least two clearly resolved peaks are observed in the imaginary part of the ac susceptibility implies the coexistence of at least two phases with different T_c. This is in excellent agreement with the high-resolution synchrotron XRD data (inset in figure 1), which reveal that for these nominal carbon doping levels at least two phases coexist in the samples with different carbon concentration [5]. In our case, the phase with the lower transition temperature is expected to be richer in carbon than that with the larger T_c. Additionally, the $x = 0.1$ sample exhibits a considerably broadened peak in the χ''–T dependence, denoting the superposition of several phases, again in agreement with the results of the XRD measurements [5]. We also note that although earlier dc susceptibility measurements showed single-step superconducting transitions, well-defined discontinuities are present in the temperature dependence of $\mathrm{d}\chi'/\mathrm{d}T$ of the present samples, consistent with the multipeak behaviour of χ''.

The temperature dependence of the imaginary part of the ac susceptibility for $MgB_{1.94}C_{0.06}$ and $MgB_{1.92}C_{0.08}$ is presented in figure 2. For these measurements, an ac magnetic field of

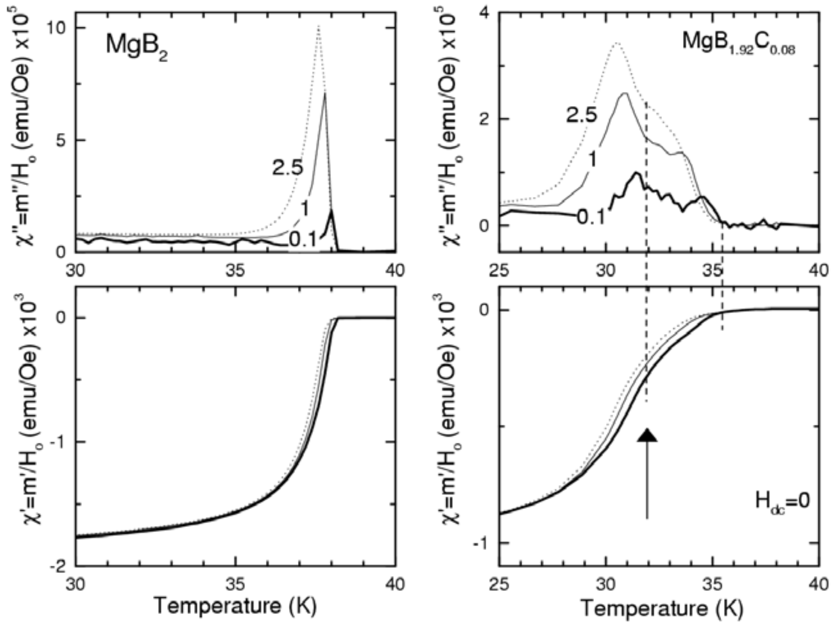

Figure 3. Temperature dependences of the χ'-and χ''-parts of the ac susceptibility for MgB$_2$ and MgB$_{1.92}$C$_{0.08}$ at 0.1, 1, and 2.5 Oe rms amplitudes of the ac field. The measurements were carried out at $H_{dc} = 0$ and $f = 333$ Hz.

1 Oe rms value with $f = 333$ Hz was used, under dc fields of 0, 100, 1000, and 10 000 Oe. The increase of the applied dc field shifts the χ''-peaks to lower temperatures, but at a rate smaller than that in the Y–Ba–Cu–O superconductor [12, 18]. Detailed study of the MgB$_{1.94}$C$_{0.06}$ and MgB$_{1.92}$C$_{0.08}$ magnetic response in different dc external fields shows that the peak positions in χ'' change at different rates with applied magnetic field. This difference combined with the broadening of the peaks in high dc fields makes separation of the different phases impossible at high field (figure 2).

Our conclusion of multiphase behaviour is further supported by measurements in different ac field amplitudes. As an example, figure 3 shows χ' and χ'' for $x = 0$ and 0.08 samples in 0.1, 1, and 2.5 Oe rms ac field (the dc field is zero), where one can compare directly the differences. Indeed, the imaginary part shows the two-peak behaviour for $x = 0.08$ with both the onset and the point at which the second peak begins to develop not depending on the ac field amplitude. Moreover, the corresponding χ'-curves exhibit a clear change in slope at an ac-field-independent point, marked by an arrow in figure 3. The non-linear dependence of χ' and χ'' at the peak regime implies that either bulk pinning or surface barrier control the response. Similar measurements in non-zero dc field (not shown) show the same behaviour with the only difference being that the characteristic points move to lower temperatures and broaden slightly. Finally, we note that the polycrystalline character of the samples and the presence of anisotropy make identification of the mechanism (bulk pinning or surface barrier) which controls the irreversibility (non-linear behaviour in the ac susceptibility) difficult.

Leaving out complicated contributions to the χ''-peak profiles, such as differing superconducting properties and loss mechanisms [19] in the various carbon-doped phases, the peak areas in the multiphase samples could be related to the relative percentage of each phase present. For this estimation, only the measurements at relatively low applied magnetic field were taken into account when the peaks were clearly distinguishable. We find that the volume

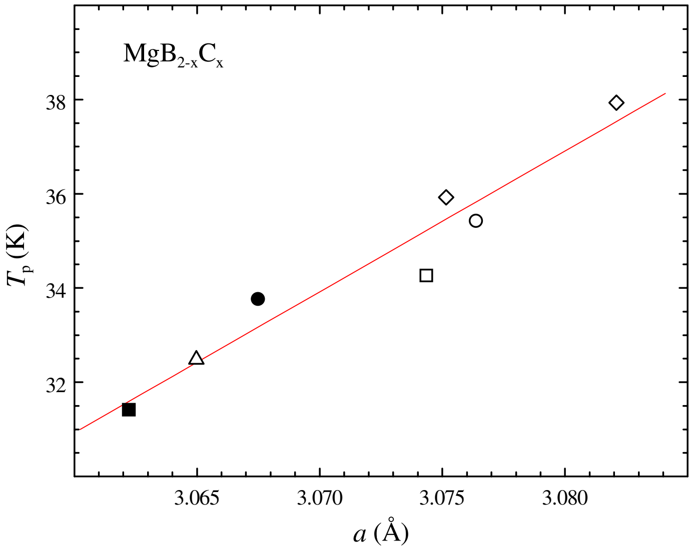

Figure 4. χ''-peak positions, T_p, versus lattice parameter, a, for $MgB_{2-x}C_x$. Diamonds correspond to $x = 0$ and 0.04, while the triangles correspond to $x = 0.1$. The open (solid) circle and square correspond to the carbon-poor (carbon-rich) phase in the samples with nominal overall composition $x = 0.06$ and 0.08, respectively.

(This figure is in colour only in the electronic version)

fractions of the phase containing lower carbon concentration (higher T_c) in $MgB_{1.94}C_{0.06}$ and $MgB_{1.92}C_{0.08}$ are of the order of 15 and 25%, respectively. Although these results represent only rough estimates, they are close to the volume fractions obtained by Rietveld refinement of the synchrotron XRD profiles [20]. The broader distribution of carbon compositions in the $x = 0.1$ sample prevents us from extracting individual fractions reliably.

The T_cs of superconducting materials can be extracted from the onset of χ' and χ''. As for the present multiphase samples we cannot identify the onset for each phase, we have used the peak positions, T_p, in χ'' after extrapolation to zero ac amplitude in the absence of a dc field in order to obtain estimates of the transition temperatures. The validity of our assumption that the phase-separated samples comprise superconducting compositions with different carbon (i.e. electron) doping is evident from figure 4 which shows the evolution of T_p with the hexagonal lattice parameter a, after taking into account the structural results [5]. T_p decreases quasilinearly as the lattice contracts on increasing carbon doping at a rate, $\mathrm{d}T_p/\mathrm{d}a$, of 300 K $Å^{-1}$.

4. Conclusions

In conclusion, we have performed ac susceptibility measurements on $MgB_{2-x}C_x$ at various ac and dc magnetic fields. The existence of more than one peak in the χ''–T dependence and of discontinuities in the $\mathrm{d}\chi'/\mathrm{d}T$ versus T plots at doping levels $x > 0.04$ can be attributed to the coexistence of distinct superconducting phases containing different carbon concentrations. Single-phase $MgB_{2-x}C_x$ solid solutions are thus very difficult to achieve and multiphase behaviour is encountered even at small doping levels ($x < 0.06$) in analogy with the trends encountered in the $Mg_{1-x}Al_xB_2$ series [2].

Acknowledgments

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