Influence of carbon doping in the vortex matter properties of MgB$_2$

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We have studied the vortex-matter phase diagram of low C doped MgB$_2$ superconductor. The significant finding is the appearance of a peak effect, which, as both our global magnetization and local ac susceptibility measurements revealed, is placed well below the $H_{c2}$-line. The absence of significant bulk pinning below the onset line $H_{on}(T)$ of the peak effect implies that the Bragg glass phase is present for $H < H_{on}(T)$. Interestingly, the unexpected absence of bulk pinning above the end point line $H_{ep}(T)$ of the peak effect implies the presence of a slightly pinned vortex phase in the regime $H_{ep}(T) < H < H_{c2}(T)$. In addition, the observed increase of the $H_{c2}(0)$ since the carbon doped MgB$_2$ becomes more dirty and the reduced anisotropy, in comparison to the pure MgB$_2$, makes the C-doped MgB$_2$ more favorable for practical applications.

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In spite of the rich physics of recently discovered MgB$_2$, due to the multi component order parameter, the potential of MgB$_2$ for applications is limited by comparatively low upper critical fields $H_{c2}(0)$ $\approx$ 30 kOe. Atomic substitutions may influence the basic properties of a superconductor making it appropriate for practical applications, by increasing the $H_{c2}(T)$ line and/or the critical current that can sustain without losses. On the other hand, atomic substitutions may help in the clarification of a number of issues related with the basic mechanism which is responsible for the superconductivity in the particular compound. It has been theoretically proposed that the $H_{c2}(T)$ line can be increased by adding nonmagnetic impurities to the MgB$_2$ crystall structure consists of alternating close packed Mg$^{+2}$ layers and honeycomb-like boron sheets. $T_c$ was found to gradually decrease upon substitution of Mg for Al and B for C, consistent with a decrease in the density-of-states at the Fermi level induced by electron doping and reduced lattice volume. Although both Al and C reduce the $T_c$, the filling of the $\sigma$-band may reduce the anisotropy of the pristine MgB$_2$, helping this way the tuning of the basic properties of MgB$_2$.

Single crystals were grown by a high-pressure technique previously developed for the growth of pristine MgB$_2$ phase using precursors with a nominal composition of Mg(B$_{1-x}$C$_x$)$_2$ $x = 0.02 - 0.20$. The residual resistivity ratio at $T_c$, of crystals from the same batch, as used in the present work is $\rho_{ab}(300)/\rho_{ab}(T_c) \approx 2.2$ while the residual resistivity increases by a factor of 3-4 in comparison to the pristine MgB$_2$, indicating a degreasing of the mean free path by a factor of 3-4.

Local ac susceptibility measurements were carried out on a MgB$_{1.96}$C$_{0.04}$ single crystal by means of a GaAsIn Hall chip (active area of $50 \times 50 \mu$m$^2$). The dimensions of the crystal are $750 \times 350 \times 40 \mu$m$^2$ with the shorter length along the c-axis. The crystals have $T_c$ of 35.6 K at zero dc field ($H_{dc} = 1$ Oe) and a transition width of 0.3 K (10%-90% criterion). In order the small ac field to be measured, under the presence of a large dc magnetic field, a second sensor of the same size was connected opposite to the first one by means of an ac bridge. The real and imaginary parts ($V' = V' + iV''$) of the modulated Hall voltage, which is proportional to the local magnetic moment ($V \propto m \propto B - H_{ac}$) at the surface of the crystal, were measured by means of two lockin amplifiers. DC magnetization measurements were performed (SQUID) magnetometer.

![Image](image_url)

FIG. 1: Zero field and field cooled temperature variation of the global magnetic moment of MgB$_{1.96}$C$_{0.04}$ crystal for $H || c$-axis. The inset shows the temperature variation of the magnetic moment for $H = 5$ Oe. The small positive peak at the region of $T_{ep}$ is an artifact due to field inhomogeneity.

Figure II shows the temperature variation of the bulk magnetic moment of the MgB$_{1.96}$C$_{0.04}$ for several mag-
netic fields ($H \parallel c$) as it was measured by the SQUID magnetometer. For small fields (1-32 kOe) the $m(T)$ curves don’t show any special feature and are terminated at the $m = 0$ axis in a parallel fashion. The diamagnetic onset temperature is identified with $T_{c2}(H)$ that is determined by extrapolating the low temperature curve to $m = 0$. As one can see the irreversibility is negligible, and only when the temperature is reduced enough, irreversible behavior is appeared. Measurements in higher fields ($H > 32$ kOe) clearly show a negative peak whose its height and width increase as the magnetic field increases. We define the temperatures where the peak effect starts as $T_{on}(T)$, takes its minimum value as $T_p(T)$ and finally ends as $T_{ep}(H)$. It is interesting to note that in the interval $T_p < T < T_{c2}(H)$, the magnetization is nearly reversible (see the curve measured at $H = 35$ kOe) while for $T_{on}(H) < T < T_{ep}(H)$ the magnetic moment presents hysteretic behavior which increases as the magnetic field increases.

For a type-II superconductor, near $H_{c2}$ line is expected that the magnetization varies as $4\pi M = -(H_{c2}(T) - H)/(2\kappa_0^2 - 1)\beta_A \approx (H_{c2}(T) - H)/(2\kappa_0^2\beta_A)$, where $\beta_A$ is determined by the geometrical arrangement of fluxoids in the mixed state and $\kappa_0(T)$ is the second Ginzburg-Landau-Maki parameter. The isofield $M(T)$ slope, near $T_{c2}$ is determined by two factors: $\partial M/\partial T|_{H_{dc}} = -(1/2\kappa_0^2(T)\beta_A) dH_{c2}(T)/dT - +1/\kappa_0(T) d\kappa_0(T)/dT(H_{c2}(T) - H)$. Since $\kappa_0 \approx 20 - 30$ one can ignore the second term, consequently, the slope of the magnetization curves near $T_{c2}$ is mainly determined from the $H_{c2}(T)$ line slope. The observed reduction of the magnetization slope as the field increases means that the $H_{c2}(T)$ line goes to $T = 0$ with decreasing slope.

Fig. 2 shows the real and imaginary parts of the local fundamental ac-susceptibility $(\chi' = (B' - H_{dc})/H_{ac}, \chi'' = (B'' - H_{dc})/H_{ac})$, as function of temperature, measured under several dc magnetic fields $10 \leq H_{dc} \leq 42.5$ kOe for an ac-field $H_{ac} = 8.8$ Oe. The measurements have been taken during cooling and heating. As the measurements are made in higher magnetic fields both $\chi'$ and $\chi''$ form a peak. Moreover, the location of the peak temperature $T_p(H)$ and the end point $T_{ep}(H)$ do not depend on the amplitude of the ac-field. Our local Hall measurements enabled us to detect the peak effect in much lower fields than the global SQUID measurements. In addition, below a characteristic point $(T_1, H_1) \approx (24.5$ K, 20 kOe) the peak effect could not be observed. Below this characteristic point the peak effect turned into a sharp drop which we define it by its onset $T_{on}$ and its end point $T_{ep}$. This feature also could not be observed below a second characteristic point $(T_2, H_2) \approx (26$ K, 12 kOe) (see Fig. 4 below). Comparing the temperature where the diamagnetic signal appears in our local ac susceptibility measurements to the corresponding bulk dc measurements we find out that this doesn’t correspond to the $T_{c2}$. Here, we would like to emphasize that for the case of a type-II superconductor in the mixed state with negligible pinning, as the $H_{c2}$ line is approached one expects that the local ac-susceptibility is mainly in-phase to the ac field (for sufficiently low frequencies) and positive (paramagnetic) $\chi' = 4\pi (dM/dH)_{H_{ac}} \propto 1/2\kappa_0^2(T)\beta_A > 0$. We did not observe paramagnetic ac moment for $T > T_{ep}$ probably due to the fact that, either the paramagnetic moment is below our sensitivity limit, or we have a superposition of a paramagnetic and a diamagnetic ac moment (due to a small critical current) of equal size giving a zero net ac-moment.

![FIG. 2: Real ($\chi'$) and imaginary ($\chi''$) local fundamental ac-susceptibility as a function of temperature, for $H_{ac} = 8.8$ Oe and ($H_{dc} = 10 - 42.5$ kOe). For $H > 20$ kOe the peak effect is always observed.](image-url)
influence of the amplitude of the applied ac field on the hysteretic response. In Fig. 3 we present the temperature variation of the real and imaginary part of local ac-susceptibility under 40 kOe dc-magnetic field, for appreci-ate large amplitudes of the ac-field. We see that the detected hysteresis progressively reduces as we apply higher ac fields. For high enough ac fields the hysteresis is confined only in the regime between the onset of the peak and a new characteristic point, at which the in-phase signal presents a kink. These results may be explained as follow-ing: The fact that the zero field cooled vortex state ex-hibits zero screening current in the regime $T < T_{on}$ suggests that no metastable states are present in this regime and that the so-called Bragg glass state [10] is a true equilibrium phase. Furthermore, we performed relaxation and partial loop measurements in the regime between the onset point and the peak effect. Those measurements, which will be presented elsewhere[17], revealed that partial sub-loops are always present and that the field cooled vortex state exhibits strong relaxation, while the zero field cooled one doesn’t relax even in long experimental times. These results indicate that the zero field cooled vortex state is an equilibrium state while the field cooled phase is a supercooled metastable one. In addition, these two vicinal vortex states (namely the disordered and the Bragg glass) coexist in the finite temperature interval $T_{on} < T < T_p$ around the transition regime. All the above mentioned results indicate that the detected transition is of first order. Recently, the same behavior was detected in YBa$_2$Cu$_3$O$_7$, Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, HgBa$_2$CuO$_{4+\delta}$, NbSe$_2$, and V$_3$Si single crystals.

Figure 4 summarizes our results in the form of $T - H$ phase diagram of the mixed state of MgB$_{1.96}C_{0.04}$. A similar phase-diagram has been also determined for the $x = 0.05$ sample. The main differences with $x = 0.02$ sample are the larger characteristic fields $H_{c1}^{ab}$, $H_{on}$, $H_{ep}$, and $H_p$. Remarkably, the $H_1$ ($\sim 15$ kOe) field does not change between the pristine and carbon doped crystals. For completeness the $H_{c2}^{ab}(T)$-line was added, permitting the estimation of the $H_{c2}$ anisotropy which is depicted in the inset. This part of the anisotropy curve is well below the corresponding curves reported in the literature[3] for the pristine MgB$_2$[21]. In the results presented in Fig. 4 there is a remarkable experimental finding. The end point line as defined from the end point of the peak effect doesn’t coincide to the upper-critical field line as that defined from the bulk magnetization measurements. In addition, the portion of the mixed state occupied by the peak effect shrinks and the magnitude of the critical current is reduced as the field decreases. The peak effect disappears at $(T_1, H_1)$ and is transformed to a very narrow diamagnetic step, up to the point $(T_2, H_2)$. As the field is further reduced, the local $\chi'$ shows a monotonic conventional behavior. However, the line defined by the diamagnetic onset points of the $\chi'$ curves is also placed below the $H_{c2}$ line and only at a particular point $(T_3, H_3)$ changes slope and coincides to the $H_{c2}$ line. Based on our results and with what al-
ready is known in other compounds the onset peak-effect line concerns an order-disorder transition, most probably of first-order, so the \((T_2, H_2)\) is a tricritical point where a first order transition is terminated. One could claim that \((T_2, H_2)\) point is a critical point. However a critical point can exist only for phases such that the difference between them is purely quantitatively. Therefore, these vortex solid phases cannot be continuously transformed into each other and a termination of the phase transition line, separating these phases, can terminate only on another phase transition line. This fact may not be valid in our case, since the Bragg glass phase is also qualitatively different from the phase that occupies the region between the \(H_{c2}^e\) and the end-point line. This region of the phase diagram may be related with an amorphous vortex phase. We would like to stress that in this regime the critical current is very low (normally one expects that the critical current reduces smoothly towards the zero values at \(H_{c2}^e\)) and is an important new experimental finding which needs a theoretical explanation. A critical point therefore cannot exist for such phases, and the equilibrium curve must either go to \(T_c(H = 0)\) or terminate by intersecting the equilibrium curves of other phases. Consequently, the onset line below \((T_2, H_2)\) may concern a curve of second-order phase transitions in the \(T - H\) plane that separates phases of different symmetry, namely a transition line from a Bragg glass to an amorphous vortex phase. Alternatively, if one supposes that the diamagnetic onset of the local susceptibility (for \(H < H_2\), see Fig. 4) does not represent a phase transition but simply marks an irreversibility line, then the point \((T_2, H_2)\) is a critical point with the consequence of a reentrance of the Bragg glass phase below the \((T_2, H_2)\) point in the regime \(H_{cr} < H < H_{c2}^e\). At the end, we would like to comment on the presence of the characteristic point \((T_3, H_3) \approx (33 \text{ K}, 5 \text{ kOe})\). As we observe in Fig. 4 for magnetic fields below \(H_2\) the onset of the diamagnetic local ac response coincides to the onset of the diamagnetic global dc magnetic moment. Although tunnelling data are not available at the presence, we know that in pristine MgB\(_2\) near \(T_c(H = 0)\) the \(\pi\) gap closes at about 4-5 kOe. Therefore, it is interesting to correlate this point with the closing of the \(\pi\) gap.

In summary, we experimentally estimated the vortex matter phase diagram for MgB\(_{1.98}\)C\(_{0.04}\) single crystal superconductor which exhibits half the anisotropy of the pristine MgB\(_2\) one. The peak effect is observed in our local Hall and in bulk SQUID measurements. The respective line \(H_p(T)\) and even the end point line \(H_{cr}(T)\) are placed well below the upper-critical field line \(H_{c2}(T)\). The \(H_p(T)\) line doesn’t terminate on the \(H_{c2}(T)\) line but disappeared at \((T_2, H_2)\). The peak effect line concerns an order-disorder transition of first-order. This line probably is terminated at the tricritical point \((T_2, H_2)\) continuing as a line of second order transitions up to \(T_c\). The \(H_{c2}(0)\) is obviously increased in the C doped MgB\(_2\) crystal, implying a decreased mean free path of the charge carrier.

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