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# Magnetic properties of Y-Ba-Cu-O superconductors

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The magnetic properties of polycrystalline and single-crystal samples of $YBa_2Cu_3O_7$ are compared. Transition temperatures are in the range of 85 to 89 K. The Meissner effect is below 30% of the diamagnetic shielding in all cases. Based on the high-temperature susceptibility it is suggested that an itinerant antiferromagnetic $3d$ band of the $Cu^{2+}$ is possible. Anisotropy occurs in the single crystal for applied fields above 200 Oe. There is a difference in the lower critical field of a factor of 20 where $H_{c1}$ is about 4000 Oe for $H$ parallel to the orthorhombic $c$ axis and 200 Oe for $H$ perpendicular to the $c$ axis of the crystal.

## INTRODUCTION

The original papers of Bednorz and Müller[1] and that of Wu *et al.*[2] have stimulated intense interest in oxide superconductors, most recently in single crystals.[3-5] In this paper we compare the magnetic properties of some polycrystalline samples of $YBa_2Cu_3O_x$ with that of a single crystal seeking those features which have a different behavior.

We report on three polycrystalline samples each made under slightly different conditions with volumes of about 0.02 $cm^3$ and on one single crystal. These samples are among the best of 30 or 40 samples that have been measured. The four samples called $A$,$B$,$C$ (polycrystalline), and $X$ (single crystal) are listed in Table I with selected data. Sample $A$ was prepared by mixing the constituent oxides in a mortar and pestle prior to cold pressing at 345 MPa to form a 1.25-cm-diameter pellet. Reaction occurred by heating the pellet in static air at 10 °C/min to 950 °C with a 12-h hold at that temperature before cooling to room temperature at 20 °C/min. Sample $B$ had $BaCO_3$ as one of the starting materials. Sample $B$ was prepared by firing at 925 °C for 12 h, cooling to room temperature at a rate of 40 °C/h. The entire process was carried out in a pure oxygen atmosphere. Sample $C$ was prepared by using the simple oxides which were mixed and sintered in air. The single crystal was grown[5] using a technique similar to that used by Iwazumi *et al.*[6] for La-Sr-Cu-O. In this method a mixed-phase pellet was fired in a slightly reducing atmosphere at 975 °C for 12 h during which time an oxidizing atmosphere was introduced to promote growth of $YBa_2Cu_3O_7$ crystallites already present in the pellet.

Magnetic measurements are made using a superconducting quantum interference device (SQUID) magnetometer which covers the temperature range 4.5–300 K with applied fields from 1 to 40000 Oe. High-temperature susceptibility measurements are made with a force balance magnetometer.

Polycrystalline samples are prepared in the form of small cylinders whose density, as given in Table I, can easily be determined. The density of the single crystal is not known but is assumed to be theoretical ($\approx 6.4$ g/$cm^3$). It has the approximate size of $0.35\times0.35\times0.17$ $mm^3$ with the $c$ axis along the shorter length for the measurements with $H$ parallel to the $c$ axis and about 0.15 mm for the $c$ axis for $H$ perpendicular to the $c$ axis because part of the sample split off in orientation. Samples $A$ and $C$ are cut in the form of parallelopiped, while sample $B$ is ground to spherical shape. From x-ray analysis these samples all had the orthorhombic structure. In addition, the polycrystalline samples are over 95% single phase.

## RESULTS AND DISCUSSION

Magnetic moment per unit volume ($M$) (emu/$cm^3$ or gauss) is measured as a function of temperature and magnetic field. Values for $M$ at 4.2 K in a field of approximately 14 Oe are listed in Table I. In Fig. 1 is plotted the temperature dependence of a normalized susceptibility for the three polycrystalline samples. The normalized susceptibility is the ratio of $\chi_m$ (measured) to $\chi_t$ (theory), where $\chi_t$ is calculated from the sample shape and $\chi_m$ is from

TABLE I. Selected data for samples $A$, $B$, $C$, and $X$.

| Samples | $T_c$ (K) | $Ms^a$ (G) | $\chi_m$ | $\chi_t$ | $H_{c1}$ (Oe) | $J_C$ ($10^5$ A/$cm^2$) | $\rho$ (gm/$cm^3$) |
|---|---|---|---|---|---|---|---|
| $A$ | 89 | 0.56 | 0.04 | 0.08 | 400 | | 3.74 |
| $B$ | 88 | 1.55 | 0.11 | 0.119 | 500 | 0.15 | 4.18 |
| $C$ | 89 | 1.14 | 0.076 | 0.09 | 400 | | 3.20 |
| $X_\parallel{}^b$ | 90 | 2.40 | 0.15 | 0.145 | 4000 | 24.0 | $6.4^c$ |
| $X_\perp{}^b$ | 81 | 1.37 | 0.09 | 0.09 | 200 | 1.0 | $6.4^c$ |

[a]At 14 Oe.
[b]$H$ parallel or perpendicular to $c$ axis of crystal.
[c]Assumed to be theoretical.

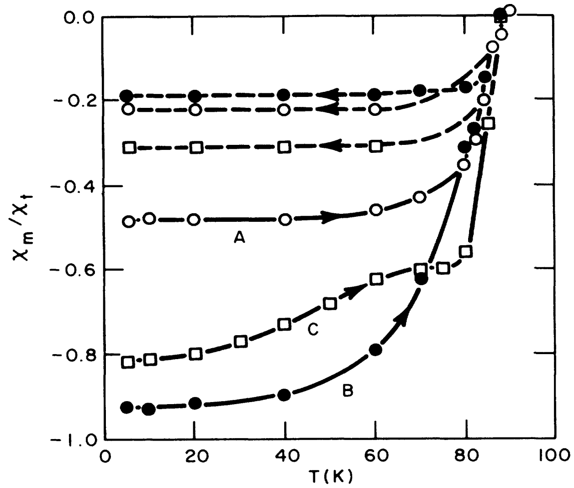


FIG. 1. Normalized volume susceptibility $\chi_m$ (measured) divided by $\chi_t$ (theory) vs temperature for the three polycrystalline samples $A$, $B$, and $C$ (see Table I). The measurements made in increasing temperature gives the diamagnetic shielding while those for decreasing temperature gives the Meissner effect. The applied field is $H=14$ Oe.

$M=\chi_m H$. When $\chi_m/\chi_t=1$ then a complete diamagnetic shielding (or Meissner) effect is observed. In Fig. 1 the curve that is marked with an arrow indicating measurements made in increasing temperature is the diamagnetic shielding and the arrow indicating decreasing temperature is on the Meissner effect curve. The susceptibility becomes about $10^{-6}$ at the superconducting transition temperatures ($T_c$) and values of $T_c$ (Table I) are in the 85–90-K range. From Table I and Fig. 1 it is noted that the flux exclusion due to the diamagnetic shielding is 50–92% of theoretical, while the Meissner effect is only 20–30% of that theoretically possible.

Figure 2 shows the field dependence of magnetic moment for two of the polycrystalline samples at 4.4 K. The initial slope gives $\chi_m$ and where the $M$ vs $H$ data depart from linearity is a measure of the lower critical field ($H_{c1}$) which is listed in Table I. For sample $B$ which is spherical $H_{c1}\approx 500$ Oe, which corrected for demagnetization is about 750 Oe. This value is obtained by dividing the measured $H_{c1}$ by $(1-n)$, where $n$ is the demagnetization coefficient, in this case $n=\frac{1}{3}$. When the applied field is reduced, magnetic flux which has penetrated the sample, remains frozen in and a positive value of $M$ is found. From the largest $\pm M$ values using an approximate relationship given by Fietz and Webb[7] [$J_C=30M/R$, where $R$ is the (cylinder) sample radius in cm and $J_C$ is the current density in A/cm$^2$] values of current density in polycrystalline superconductors of 15000 A/cm$^2$ are calculated.

The single-crystal temperature dependence data are given in Fig. 3 in the normalized susceptibility units $\chi_m/\chi_t$ for an applied field of about 14 G. Two different directions are marked as parallel (‖) to the $c$ axis and perpendicular ($\perp$) to the $c$ axis. At this low field the shielding curves are similar but show a displacement at $T_c$ of about 4 K. On cooling from above $T_c$ to 4.5 K the Meissner effect is a smaller fraction of the diamagnetic shielding than in the polycrystalline materials. In the single crystal the Meissner effect is anisotropic with a much smaller value perpendicular to the $c$ axis as compared to parallel to the $c$ axis as seen in Fig. 3. It will be also noticed that a measurement made at $H=500$ Oe with $H$ perpendicular to $c$ indicates a strong effect of $H$ in this direction.

When the crystal is measured as a function of field at 4.5 K the anisotropic properties are clearly evident as shown in Fig. 4. The linearity of $M$ vs $H$ extends to 4000 Oe for $H$ parallel to the $c$ axis (about 7000 Oe corrected for demagnetization) but only to 200 Oe for $H$ perpendicular to the $c$ axis (240 corrected for demagnetization). The value of $H_{c1,\perp}$ given here is somewhat lower than reported by Dinger, Worthington, Gallagher, and Sandstrom[5] possibly because of crystal quality or because of the criticality of mounting in this direction. In addition, the value of $M$ differs by a factor of 50. Since the sample radius is different for the two directions the values calculated for $J_C$ as listed in Table I differ by a factor of 24 using the relation $J_C=30M/R$. For $H$ parallel to the $c$ axis a value of $J_C$ of $2.4\times 10^6$ A/cm$^2$ is calculated.

High-temperature susceptibility measurements, i.e.,

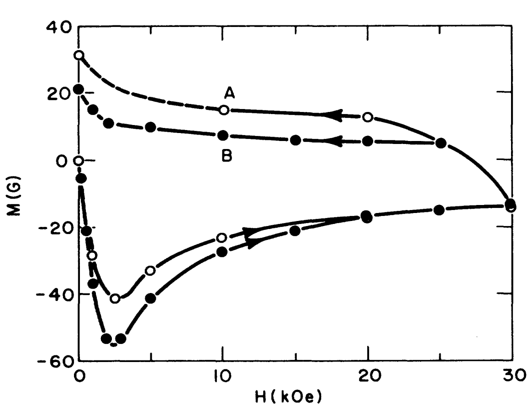


FIG. 2. The magnetic moment in gauss vs the applied field in kOe at 4.4 K for polycrystalline samples $A$ and $B$.

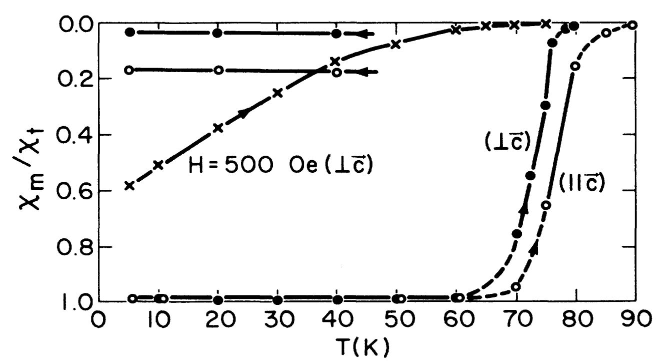


FIG. 3. The normalized susceptibility for the single crystal parallel and perpendicular to the $c$ axis at an applied field of 14 Oe. The data points marked with an $\times$ are for an applied field of $H=500$ Oe with the field perpendicular to the $c$ axis of the crystal.

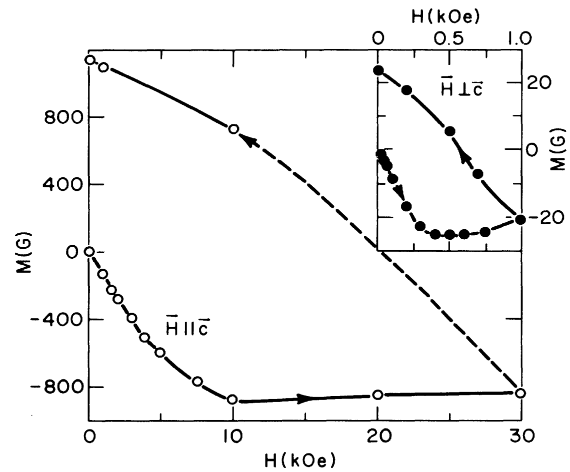


FIG. 4. Magnetic moment in gauss of the single crystal as a function of magnetic field at a temperature of 4.5 K. The main plot is for $H$ parallel to the $c$ axis of the crystal while the inset plot is for $H$ perpendicular to the $c$ axis.

above $T_c$ on the polycrystalline samples are presented in Fig. 5. Only sample $A$, which has the lowest diamagnetic shielding, shows a paramagnetic moment. Sample $B$ (and also $C$, not illustrated) have almost flat $\chi_m$ vs $T$ curves showing a slight increase in $\chi_m$ with $T$. If $\chi_m$ for sample $B$ is subtracted from that for sample $A$, a Curie-Weiss behavior is found with a molar Curie constant ($C_M$) of 0.006 for the $Cu^{2+}$ in the material. Comparing this value of $C_M$ with theoretical $C_M = \frac{3}{8}$ for $YBa_2Cu_3O_7$ with one unpaired spin per Cu ion gives a $Cu^{2+}$ impurity of 1.6% which is well within the range of possible second phase products in the sample. It thus seems that one of the interesting features of $YBa_2Cu_3O_x$ superconductors is that there is an absence of any localized moment on the copper or that it is in an antiferromagnetic state with the copper having a small magnetic moment of $0.1\mu_B$ or $0.2\mu_B$.

Of many models that can be considered concerning the absence of a localized moment associated with the copper we suggest that an antiferromagnet itinerant $3d$ band

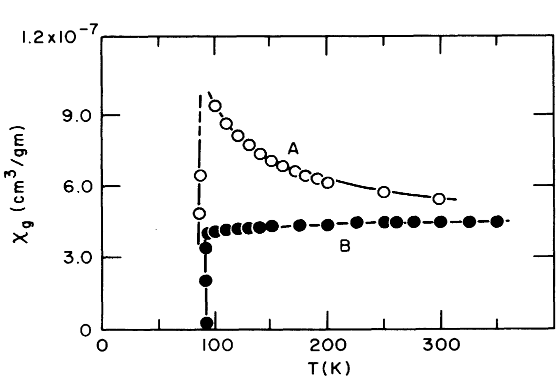


FIG. 5. The gram susceptibility of samples $A$ and $B$ as a function of temperature above the superconducting transition temperature.

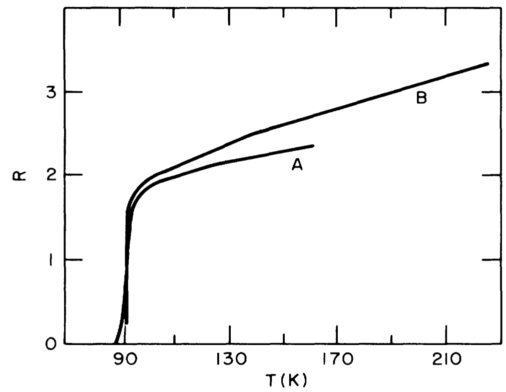


FIG. 6. Resistance in arbitrary units as a function of temperature for samples $A$ and $B$. At 150 K the absolute values of resistivity is 1.68 mΩcm for sample $A$ and 1.97 mΩcm for sample $B$.

forms similar to that found in metallic Cr.[8,9] This could also explain the shape of the $\chi_m$-$T$ curve in Fig. 5 for sample $B$ since antiferromagnetic susceptibility increases with temperatures below the antiferromagnetic ordering temperature, which could be at some temperature around 200 K where the susceptibility starts to become flat. In addition, an itinerant $3d$ band would be compatible with the shape of resistivity-temperature curves as shown in Fig. 6. Here $s$-$d$ scattering would decrease with decreasing temperature in the antiferromagnet region since there would be a diminished scattering as the ordering of the $3d$ band became more pronounced. This would account for the extended temperature region where the resistivity shows a nonlinear decrease prior to the onset of superconductivity at $T_c$. Another approach to the shape of the resistivity curves is superconducting fluctuations above $T_c$ as proposed by Freitas, Tsuei, and Plaskett.[10]

The nature of the superconductivity in these oxide superconductors is the subject of current discussion.[11] It is peculiar that the Meissner effect is so low in these materials. Magnetic flux penetrating the sample does not get expelled upon cooling through $T_c$. The absolute value of $M$ for the Meissner effect in the single crystal cooled in a field of 14 Oe with $H$ parallel to the $c$ axis is $M = -0.44$ G and $M = -0.05$ G for $H$ perpendicular to the $c$ axis. This is about the same magnitude as the polycrystalline $B$ samples where $M = -0.33$ G if we take into consideration that the Meissner effect could be an average of the single-crystal directions.

## COMPARISON

The comparison of the single crystal in the $c$ axis direction with sample $B$ indicates that the low value of the Meissner effect is a basic property of the crystal and limits the magnitude found in the polycrystalline sample. In addition, it is suggested that the majority of magnetic flux that remains in the samples during cooling through $T_c$ is not frozen in but is decoupled from the sample. Specifically at an applied field of 10 kOe the Meissner effect leads to a value of $M = -0.08 \times 10^{-3}$ emu for the single crystal parallel to the $c$ axis. The diamagnetic shielding is $M = -0.201\times10^{-1}$ emu larger by a factor of 300. Possibly the single crystal has both frozen flux and a Meissner contribution which nearly cancel. More likely the single crystal is in a mixed or intermediate state with normal regions through which the magnetic flux can pass.

The values found for the initial critical field ($H_{c1}$, see Table I) seem to be the same for the three polycrystalline samples and are close to the value found for $H_{c1}$ perpendicular to the $c$ axis of the crystal. Based on the single-crystal values of $H_{c1}$ in different directions a simplistic argument can be made that the polycrystalline $H_{c1}$ should be an average value of $H_{c1}\approx 540$ Oe which is calculated from the cube root of the single-crystal values using 4000 for the $c$ direction and 200 Oe for the other two directions perpendicular to the $c$ axis. A similar average for the $H_{c1}$ values corrected for demagnetization also gives reasonable agreement.

At the present time we have no information on the $H_{c2}$ for these samples. High-field measurements on polycrystalline samples by Orlando *et al.*[12] give values of $H_{c2} \approx 1.5\times10^{6}$ Oe. Probably for single crystals along the $c$ axis $H_{c2}$ is greater than $1.6\times10^{6}$ Oe. Worthington, Gallagher, and Dinger[13] find for $H_{c2}$ parallel to the $c$ axis a value of 23 kOe/deg from measurements just below $T_c$. This is in reasonable agreement with values reported by Iye, Tanegai, Takeya, and Takei.[14]

It was previously mentioned that the $Cu^{2+}$ $3d$ band might have an itinerant antiferromagnetic character as described by Lidiard[9] for chromium metal. The weak temperature dependence of susceptibility and resistivity found in Cr is of the same form noted here in Fig. 5 (sample $B$) and Fig. 6 for $YBa_2Cu_3O_7$. Just how the electron-phonon interaction would be enhanced by an antiferromagnetic itinerant $d$ band remains for theoretical discussion[10,15] but possibly a magnetic mechanism is needed. It also seems possible that neutron diffraction should be able to identify an itinerant band although localized moments could be small and difficult to identify.

As a final remark we note that the current densities vary by a factor of about 6 between the polycrystalline samples and the weakest single-crystal direction. It is suspected that either the low density or grain boundary effects are important in limiting $J_C$ in some manner.

## SUMMARY

The polycrystalline materials and the single crystal have values $H_{c1}$ and Meissner effect which are compatible when the measured values of the crystal are averaged. On the other hand, the current carrying capacity of the polycrystalline materials is much lower than expected from using average values of the single crystal. The magnetic susceptibility above $T_c$ of the polycrystalline samples suggest a highly delocalized magnetic moment for the $Cu^{2+}$.

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