ANOMALOUS MAGNETIC PROPERTIES
OF SOME HIGH-TEMPERATURE
MAGNETIC SUPERCONDUCTORS


Recently, superconductivity up to 98 K was found in the multiphased
Y1.2Ba0.8CuO4+6 compound system.1-3 Later, it was found that the
orthorhombic YBa2Cu3O6+δ phase is responsible for this high-temperature
superconductivity.4,5 Following this line, it has now been demonstrated
that all single-phased LaBa2Cu3O6+δ (L = Y, all rare earths) are
superconductors with the transition temperatures Tc ~90 K. 6-9 The most
striking of all is that Gd2Ba2Cu3O6+δ has a Tc of ~94 K, because Gd3+
ions have been known to depress the superconducting transition temperature
very markedly owing to the fact that Gd3+ has the highest spin (7/2) among
all rare-earth ions. The unusually high Tc's point to the need of a study
of the magnetic properties of some of these magnetic superconductors. We have
found that all our samples exhibit almost perfect diamagnetism. Furthermore,
we have shown that the magnetic moment at low temperature has an additional
structure; it first increases with field until it reaches a maximum around
120 G, then decreases slightly to ~200 G, above which the moment increases
with increasing field with a much smaller slope.

The samples GdBa2Cu3O6+δ(Tc ~ 92 K),6,10 EuBa2Cu3O6+δ(-95 K),6-8
SmBa2Cu3O6+δ(-94 K),7 used in this study were prepared by the method

*Department of Physics, University of Houston, Houston, TX 77004, USA
**Research & Development Division, Lockheed Missiles & Space Company, Inc.,
3251 Hanover St., Palo Alto, CA 94304-1191, USA
described in Ref. 1. The x-ray-diffraction patterns show that all these samples possess only a single phase. An SHE Model 905 SQUID magnetometer of the National Magnet Laboratory (MIT) was used to measure the magnetic moment of these samples from 2 to 300 K in a magnetic field, H, from -2 to -1000 G. All the samples used are thin disks, and, hence, the demagnetization effect is negligible.

Figure 1a shows the inverse of the magnetic susceptibility, 1/\( \chi \), for \( \text{GdBa}_2\text{Cu}_3\text{O}_{6+\delta} \) plotted against temperature \( T \) for \( T > T_C \). The data can be fitted to the Curie-Weiss law, \( \chi = C/(T + \theta) \), with \( C = 7.39 \times 10^{-2} \text{ emu-K} \), and \( \theta = 6 \text{ K} \). The Curie constant, \( C \), is in excellent agreement with the calculated value, assuming that the 5-state \( \text{Gd}^{3+} \) magnetic moments are responsible for the magnetism observed at high temperature. (In this calculation, we have ignored the contribution from the \( \text{Cu}^{2+} \) ions, because the magnetic moment of a \( \text{Cu}^{2+} \) ion (\( S = 1/2 \)) is much smaller than that of a \( \text{Gd}^{3+} \) ion (\( S = 7/2 \)).) Within our experimental accuracy, the temperature-independent term is negligible. The temperature dependence also suggests that \( \text{Gd}^{3+} \) ions interact antiferromagnetically. The measured \( \theta \) value is consistent with the recently determined heat capacity which demonstrates a pronounced magnetic anomaly around \( T_N = 2.22 \text{ K} \) in a single-phase \( \text{GdBa}_2\text{Cu}_3\text{O}_{6+\delta} \) sample. We can thus conclude that superconductivity coexists with antiferromagnetism below \( T_N \).

Figure 1b displays our data for \( \text{EuBa}_2\text{Cu}_3\text{O}_{6+\delta} \) (denoted by triangles). The Mossbauer experiment has shown that the \( \text{Eu} \) ions in \( \text{EuBa}_2\text{Cu}_3\text{O}_{6+\delta} \) are in the trivalent state from 300 K down to 4 K, and, hence, the ion has the nonmagnetic single ground-state. This Mossbauer result suggests that the susceptibility for the \( \text{Eu} \) sample should be much less than that for the \( \text{Gd} \) sample. Our data show that the susceptibility for the \( \text{Eu} \) sample is indeed about a factor of 10 smaller than that for the \( \text{Gd} \) sample.

The \( \text{Eu} \) data also display some temperature dependence, indicating that some of the \( \text{Eu}^{3+} \) excited states are occupied at \( T > 100 \text{ K} \). For \( \text{SmBa}_2\text{Cu}_3\text{O}_{6+\delta} \), as shown in Fig. 1b, the susceptibility is small, as expected, because a \( \text{Sm}^{3+} \) ion has a rather small magnetic moment. The nearly temperature-independent result points out that most of the crystal field-split levels of the ground-state multiplet (\( J = 5/2 \)) are occupied above 100 K.

Figure 2a depicts the temperature dependencies of the diamagnetic susceptibility of \( \text{GdBa}_2\text{Cu}_3\text{O}_{6+\delta} \) measured in several cooling fields. The data (denoted by solid circles) were taken as the sample was cooled in zero field, and, hence, the demagnetization effect is negligible.

![Fig. 1](image_url)
field, and the susceptibility was determined by the relation \( \chi = \frac{dM}{dH} \) for \( H \leq 20 \, G \), where \( M \) is the magnetization of the sample. As shown, the diamagnetic susceptibility below \( \sim 65 \, K \) is almost temperature independent and close to that of a perfect diamagnet \( \chi = -1/4\pi \). However, it drops sharply to \(-20\%\) at \( \sim 80 \, K \), above which the decrease is less steep, thus exhibiting a shoulder. This temperature dependence seems to indicate that there are two superconducting transition temperatures, at \( T_{C1} = 75 \, K \) and \( T_{C2} = 93 \, K \). We have also cooled the sample in 10 G from \(-300 \, K \) to the temperature of interest. These data, as denoted by the solid triangles in Fig. 2a, are nearly the same as those for the zero-field-cooled case. In contrast, when the sample is cooled in 300 G, as shown by the solid squares, the susceptibility values \( (M/H) \) are greatly depressed but the presence of a shoulder is still apparent. The depressed susceptibility shows the penetration of the field. The sintered sample is a little porous and the lower critical field, \( H_{C1} \), is smaller than \(-100 \, G \) according to the field dependence of the magnetization as shown in Fig. 3a. Figure 2b shows our results for the single-phase EuBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) sample cooled in 10 G (denoted by solid circles). The temperature dependence is similar to that shown in Fig. 2a for GdBa\(_2\)Cu\(_3\)O\(_{6+\delta}\). In fact, a similar shoulder has also been observed by the ac-susceptibility technique (denoted by solid squares). We have also studied a SmBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) sample. The data again show \(-100\%\) diamagnetism at low temperature, and the temperature dependence of \( \chi \) is similar to those of the two samples discussed above.

The presence of two \( T_{C} \)'s may be accounted for by assuming that there are two phases in the sample. We have ruled out this possibility because the x-ray diffractograms obtained for all the samples used in this study show that there is only one phase. About three decades ago, Suhl et al. considered the s-d overlapping bands and showed that it is possible to have two superconducting transition temperatures when the phonon-mediated s-d interaction is weak.\(^{13}\) Our data shown in Figs. 2a and 2b seem to agree with this theoretical prediction. Nonetheless, it is not clear whether these two transition temperatures arise from the s and d bands in the Cu-O layers or from the two d bands owing to Cu\(^{2+}\), as recently proposed by Lee and Inmm.\(^{14}\) Very recently, from neutron data,\(^{15}\) it has been shown that the middle layer of the three adjacent Cu-O layers\(^{4}\) exhibits 50 percent oxygen deficiency, resulting in one-dimensional conductivity. In this case, Su (Su, W.P., personal communication) has predicted that the middle layer, being one-dimensional, can give rise to a high \( T_{C} \). We may speculate that the two side layers become superconducting at a somewhat lower temperature; and,

---

**Fig. 2** Temperature dependence of the dc diamagnetic susceptibility, \( \chi \), expressed in terms of percentage with respect to perfect diamagnetism for (a) GdBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) cooled in 0, 10 and 300 G, and (b) EuBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) cooled in zero field. The ac result from Ref. 6 is also included.
Fig. 3 Field dependence of the magnetization, $M$, for (a) GdBa$_2$Cu$_3$O$_{6+\delta}$ at various temperatures, and (b) EuBa$_2$Cu$_3$O$_{6+\delta}$ and SmBa$_2$Cu$_3$O$_{6+\delta}$. 

- GdBa$_2$Cu$_3$O$_{6+\delta}$
  - 6 K
  - 15 K
  - 30 K
  - 45 K
  - 60 K
  - 83 K

- EuBa$_2$Cu$_3$O$_{6+\delta}$
- SmBa$_2$Cu$_3$O$_{6+\delta}$
therefore, two kinds of electrons give rise to two superconducting transition temperatures. Instead we may attribute the shoulders to the grain boundaries. Even though all these models could explain our results, more data are necessary in order to compare theory with experiment.

Figure 3a shows the field dependencies of the magnetization, M, of the GdBa$_2$Cu$_3$O$_6$+δ sample observed at various temperatures. The sample was cooled in zero field, and then an external field, H, was applied. At 6 K, M is linear in H for H < 50 G with a slope close to $X = -1/4\pi$; it reaches a maximum at $H \sim 100$ G, above which M decreases somewhat till $H = 200$ G. Then, M again increases linearly with increasing H up to ~1 kG with a slope of only ~1/5 of the initial slope ($=1/4\pi$) for H < 50 G. The data taken at ~2 K exhibit almost the same field dependence. The data seem to suggest that only ~20 percent of the sample volume is superconducting for H > 200 G. As demonstrated in Fig. 3a, the maximum is broadened at higher temperature and eventually disappears for T > 75 K. The figure shows that the field at which the broad peak occurs decreases with increasing temperature. As shown in Fig. 3b, a similar maximum has been observed in EuBa$_2$Cu$_3$O$_6$+δ. Even though a clear maximum is absent for SmBa$_2$Cu$_3$O$_6$+δ, the data as displayed in Fig. 3b suggest the presence of a broadened peak as in the case for GdBa$_2$Cu$_3$O$_6$+δ at T > 75 K.

We may interpret the presence of the maximum in terms of the destruction of the shielding current by the applied field of ~100 G, and the decreases slope above 200 G in terms of the fact that the sample is porous and the grain sizes are comparable with the penetration depth.

In conclusion, in this communication, we have presented our results showing anomalous temperature and field dependencies. We have attempted to interpret these results in terms of the grain boundaries. Further experiments are required in order to understand the anomalous results reported in this letter.

We would like to express our gratitude to D. H. Lee, W. P. Su and C. S. Ting for some stimulating discussions. The work at Lockheed was supported by the Lockheed Independent Research funds and that at Houston by NSF Grant No. DMR 8616537, NASA Grant No. NAGW-977 and NAG8-51 and the Energy Laboratory of the University of Houston. The National Magnet Laboratory is supported by the National Science Foundation.

References

10. Fisk, Z., presented a the APL March Meeting, March 18, 1987 that the Los Alamos group had observed a superconducting onset temperature of Gd$_1.5$Be$_1.5$Cu$_3$O$_x$, exhibiting about 20 percent of perfect diamagnetism at 7 K.

