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High-temperature large diamagnetism in ball-milled $Sr_{0.6}Ca_{0.4}CuO_2$

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The observation of a large effective diamagnetic susceptibility of -3.4×10^{-6} emu g^{-1} Oe^{-1} up to temperatures above 1000 K in highly deformed ball-milled $Sr_{0.6}Ca_{0.4}CuO_2$ is reported. These samples do not exhibit superconductivity at low temperature. This anomalously strong diamagnetism increases with milling time and reaches a maximum value after 500 h of milling. A model is proposed in which excess holes, introduced during milling, have wave functions that are extended over the CuO_2 planes of the crystallites, resulting in large values of the diamagnetic susceptibility. [S0163-1829(97)08134-4]

Diamagnetism is a ubiquitous property of matter that consists in the partial screening of an external magnetic field by the electrons of the material. For most nonmetallic systems, the electron orbits, which are involved in the screening, are of the order of the atomic dimensions resulting in values of the magnetic susceptibility χ_m around -10^{-7} emu g^{-1} Oe^{-1}. Bismuth, which has the largest known diamagnetism of this kind, has a χ_m of -1.35×10^{-6} emu g^{-1} Oe^{-1}.[1] Perfect screening (implying a negative magnetic susceptibility of absolute value $\chi=-1/4\pi$ in cgs units, of the order of $\chi_m=-10^{-2}$ emu g^{-1} Oe^{-1}, referred to unit mass) is obtained in superconductors when electron pairs are unconstrained to react to external fields. The fact that perfect diamagnetism is inherent to any superconducting state has led to a surge of interest in the measurements of diamagnetic susceptibility and, in fact, states of large diamagnetism have often been targeted as ‘‘precursors’’ of superconductivity.[2]

In this paper, we report magnetic behavior induced by ball milling in $Sr_{0.6}Ca_{0.4}CuO_2$: the onset of a large ($\chi_m=-3.4\times10^{-6}$ emu g^{-1} Oe^{-1}) diamagnetism, much higher than that of bismuth, which persists up to 1000 K, whereas no superconductivity can be detected down to 4 K. A few observations of giant diamagnetism in *metastable* phases have been noted earlier: One such phase, induced by applying high pressure, was reported in 1978 by Chu *et al.* and Brandt *et al.*[3] for ClCu and, since then, a few other cases have also been disclosed. Chu *et al.* claimed that all the results related to ClCu could be explained by assuming a superconductive Cu-CuCl interface originated by the disproportion of $2CuCl\rightarrow2Cu+CuCl_2$. The high-$T_c$ superconductivity might be related to the exciton mechanism, as suggested by Allender *et al.*[4] Brown and Homan[5] found an almost perfect flux exclusion in CdS at 77 K, after pressure quenching of the samples. To account for such giant diamagnetism, they invoked either a superconductive state or a different high-temperature collective quantum state. Ogushi *et al.*[6] found large diamagnetism in magnetron sputtered La-Sr-Nb-O films measured up to 320 K. More recently, Hagberg *et al.*[7] measured large diamagnetic susceptibility on superconductive Bi(Pb)-Ca-Sc-Cu-O at temperatures well above the critical point of superconductivity. They inter-

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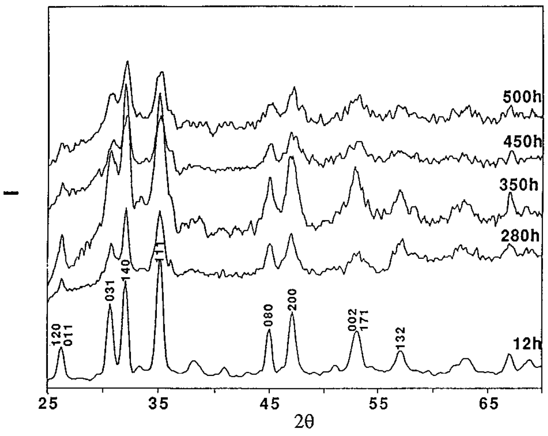

FIG. 1. X-ray-diffraction patterns as a function of the milling time. The peaks are identified as corresponding to $SrCuO_2$.

preted this observation in terms of a superconducting material of higher T_c distributed in separated domains and thus not giving rise to zero resistivity. It is worth stressing that, in practically all of these observations, large diamagnetism was connected with a high-temperature superconducting state. Albeit, in our samples, the susceptibility remains large and negative at temperatures as high as about 1000 K, making any explanation based on the existence of superconductive domains very questionable. We propose instead a simple explanation based on the traditional model of diamagnetism but allowing for large-size orbits that are related to the nanostructures originated by the ball-milling process. This is yet another example of peculiar physical phenomena in connection with nanostructures, the detailed description of which is still the subject of much controversy.[8] It is possible that the proposed mechanism might be extended to other systems with intriguing large diamagnetism.

Stoichiometric amounts of $SrCO_3$, $CaCO_3$, and CuO were fired at 900 °C for 4 days to get $Sr_{0.6}Ca_{0.4}CuO_2$. The resulting samples were submitted to mechanical milling on a Fritsch vibrating mill according to the following procedure.[9] Five grams of the starting material was ball milled in a stainless-steel vibrating vial with a 5-cm-diam steel ball. The system was put under a vacuum of 10^{-5} torr and then operated under an oxygen pressure of 1.5 bars. The process was periodically stopped to separate a small amount of sample to determine the structural and magnetic evolution of the material.

Powder x-ray-diffraction patterns were performed on a Siemens D-5000 diffractometer with a graphite monochromator and using Cu K_α radiation. The crystallite average size was deduced from the width of x-ray-diffraction maxima by applying the classical Scherrer equation. The hysteresis loops were obtained using a LDJ 9500 vibrating sample magnetometer. The electrical resistance ρ was measured by means of the standard four-probe method carried out on powdered samples pressed under $150\,\mathrm{kg\,cm^{-2}}$. The exact value of the resistivity was obtained by the Van der Pauw procedure.[10]

Figure 1 shows the powder x-ray-diffraction patterns showing the structural evolution of the material as a function of the milling time. All reflections can be indexed on the basis of the $SrCuO_2$ structural type. A progressive broadening of the diffraction maxima is observed, showing that the crystallinity decreases as the milling time increases up to 500 h, where only broad reflections are observed. The crystallite size corresponding to such a sample, as deduced by a simple Scherrer analysis from the width of both (111) and (200) reflections, is estimated to be around 150 Å. Therefore, we can regard the resulting structure as nanocrystalline. Parallel resistivity measurements indicate an increase of ρ from 2.1×10^{-6} Ω m after 12 h of milling to 0.1×10^{-2} Ω m after 350 h of milling, up to the final value 1.1×10^{-2} Ω m observed after 500 h of milling. This seems to be consistent with the decrease of crystallite size as measured by x-rays.

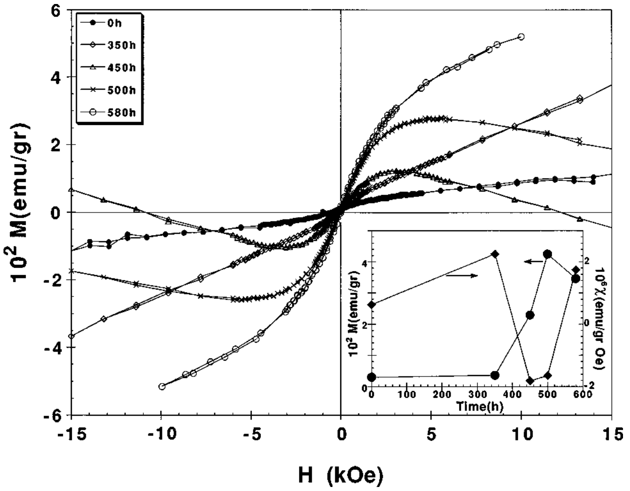

FIG. 2. Room-temperature magnetization curves for different milling times. The inset shows the room-temperature saturation magnetization of the ferromagnetic impurities and the high-field susceptibility of the sample as a function of the milling time.

Figure 2 illustrates the room-temperature magnetization curves after milling the samples for selected times t_m. For intermediate values of t_m (around 350 h), the sample still exhibits an overall paramagnetic behavior as evidenced by the positive high-field susceptibility, while an additional, seemingly ferromagnetic, contribution is detected in the range of low applied field. For longer milling times, the following trends are observed: (i) the effective high-field susceptibility evolves from positive to negative values and finally regains a positive value for the longest milling time of 580 h and (ii) the ferromagnetic contribution increases with milling time. The milling time dependence of high-field susceptibility, denoting the effective paramagnetic or diamagnetic character, is depicted in the inset of Fig. 2, as well as that of the saturation magnetization of the ferromagnetic contribution. The diamagnetism disappears in samples kept in air for one month after milling, but remains practically unchanged during the first two weeks.

The temperature dependence of the magnetic behavior up to 1000 K was also analyzed. Figure 3(a) shows the temperature dependence of the magnetization measurements corresponding to the sample milled for 500 h for which the largest room-temperature effective diamagnetic susceptibility (-3.4×10^{-6} emu g^{-1} Oe^{-1}) was observed. Figure 3(b) shows the temperature dependence of the high-field susceptibility along with the saturation magnetization of the ferromagnetic component. It can be seen that the maximum effective diamagnetic susceptibility is obtained at the highest measuring temperature. It should be remarked that the mag-

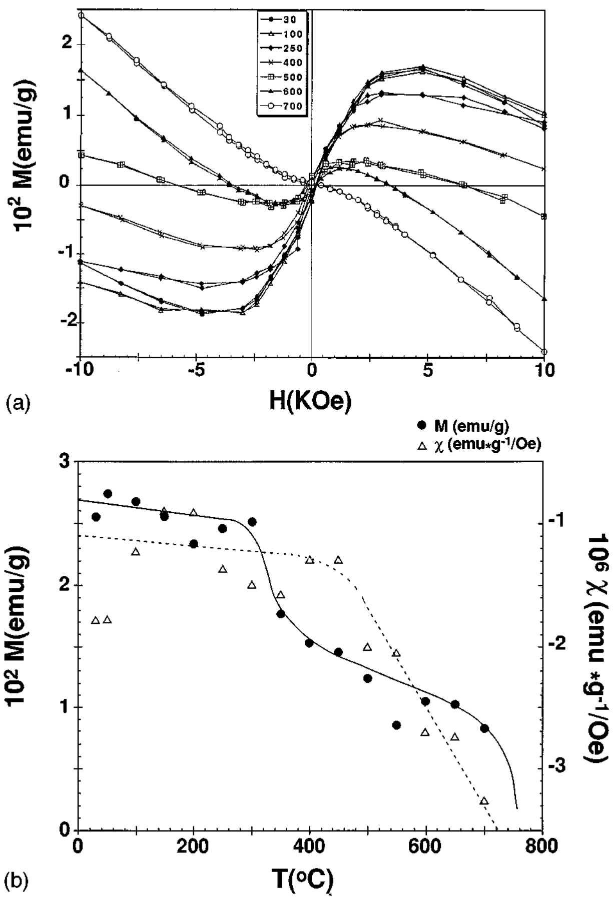

FIG. 3. (a) Temperature dependence of the magnetization curve for the sample ball milled for 500 h. Notice that at the highest temperatures an overall diamagnetic behavior is observed in all the range of applied fields. (b) Temperature dependence of the saturation magnetization of the ferromagnetic impurity and the high-field suceptibility of the sample milled for 500 h. Two Curie temperatures may be observed.

netization curves shown in Figs. 2 and 3 correspond to samples that do not exhibit superconductivity at low temperature.

The large value of the negative linear susceptibility observed at the highest measuring temperatures is certainly a most striking result and it is worth discussing the credibility of these values. First, let us deal with impurities. Assuming that the main ferromagnetic impurities with higher Curie temperature are composed of pure Fe [which is likely, as suggested by the temperature dependence of the ferromagnetic magnetization, Fig. 3(b)], the fractional mass of Fe should be about 10^{-4} for the sample milled for 500 h. From compositional inductively coupled plasma (ICP) analysis it was observed that the relative Fe content increases with milling time from an initial value of 7.4×10^{-5} up to 1.2×10^{-4} after 500 h of milling, which is in very good agreement with the value that is derived from the temperature dependence of the low-field saturation of the magnetization curves. The data shown in Fig. 3(b) suggest the presence of a second ferromagnetic phase, with lower Curie temperature. This phase could be ascribed to either nickel impurities detected by ICP analysis or to a ferromagnetic behavior characteristic of some alkaline-earth cuprates as reported by Burrows *et al.*[11] In fact, the existence of two Curie temperatures suggests that one cannot exclude that the magnetic moments of Cu are aligned in a parallel arrangement, even above room temperature.[12] None of these impurities, however, can contribute to a negative susceptibility. On the contrary, the absolute value for the negative susceptibility in Fig. 3(b) should be understood as a minimum limit for the absolute value of the diamagnetic susceptibility as the effective values of the susceptibility result from a balance between paramagnetic or ferromagnetic (positive) and diamagnetic (negative) contributions. We can then conclude that impurities cannot be responsible of our observed giant diamagnetism.

It is intriguing that the large diamagnetic component appears to be stable at 1000 K, whereas it decays at room temperature in a time scale of weeks. The answer must be sought in chemical reactions taking place during the lengthy *air exposure* at room temperature, which is known[13] to drastically affect the diamagnetic response, whereas the measurements at 1000 K are carried out in vacuum. This seems also to be the case of earlier observations of large diamagnetism, which relaxes with time to negligible values, at a rate that depends on the ambient atmosphere.[7]

We have to conclude that giant diamagnetism is an intrinsic effect of ball-milled $Sr_{0.6}Ca_{0.4}CuO_2$. As stated above, our measurements at 1000 K make it very unlikely that the observed large diamagnetism is related to the presence of superconducting domains. On the other hand, they strongly suggest that large diamagnetism is directly related to metastable or unstable nanocrystalline configurations.

According to the classical picture, the only diamagnetic contribution that can be present in such a nonmetallic material arises from localized atomic electrons. However, as discussed above, those currents are about two order of magnitude lower than observed. Also, if inner electrons control the effect, it would be difficult to explain why the giant diamagnetic component disappears under air exposure. Therefore, a mechanism involving unlocalized electrons seems much more promising. As is well known, the strength of diamagnetism is large when the wave function of the carriers is extended and almost unperturbed by the magnetic field. We propose that the shielding currents, giving rise to the diamagnetic response, are caused by the excess of holes or electrons created immediately after milling, flowing through well-localized and extended orbits, the latter located primarily at the surface of the nanocrystals. The whole process is reminiscent of the well-known case of large-orbit diamagnetism in some organics molecules.[14] An unstable excess of holes may originate as a consequence of an excess of oxygen and/or an excess of broken bonds during the milling process. They can, after some relaxation time or chemical reaction, recombine and disappear. It must be emphasized that the large orbits that we are proposing do not result in an increased macroscopic conductivity as the latter is most probably controlled by the high resistivity of the connective regions between grains. From our x-ray data, it is clear that the longer the milling time, the larger the ratio of connective to nanocrystalline volumes and therefore the observed increase in resistivity is not unexpected.

The above model is consistent with our present understanding of these materials. Cupric oxide superconductors are known to contain two-dimensional CuO_2 sheets made of corner-sharing CuO_4 squares. These are intergrown with counter layers having different compositions and structures. At ambient pressure, $SrCuO_2$ has an orthorhombic structure,[15,16] which can be described in terms of Cu atoms in planar square coordination, connected via edge sharing, giving rise to the formation of $[CuO_2]$ double chains. Such a structure is maintained in the solid solution $Sr_{1-x}Ca_xCuO_2$ for $0<x<0.6$. A mechanism similar to the one that we have proposed for the formation of holes has been reported recently[17] by Zhou *et al.* for $YBa_2Cu_1O_x$. Those authors claim that, under high pressure, holes appear at the CuO_2 planes, through electron transfer to the Cu(l)-O double chains.

In order to make a simple estimate of the magnitude of the diamagnetic susceptibility let us consider a tube built by pieces of CuO_2 planes, with radius r, which contains a tightly bound hole. Let us call b the amplitude with which the hole jumps from any particular ith atom to any of the immediately adjacent ones in the tube. $(i+1)$th or $(i-1)$th atoms. We assume that the amplitude of hopping is negligible for adjacent atoms along the direction perpendicular to the tube surface. When a magnetic field B parallel to the axis of the tube acts, the amplitude of hopping from the ith atom to the adjacent atoms, along the direction perpendicular to the field splits into two different values: $b\ \exp(qAa/h)$ and $b\ \exp(-qAa/h)$, where a is the interatomic distance and A the vector potential of the applied field. The diamagnetic moment of the tube m_t is given by $-dE/dB$, where E is the total energy of the holes in tight-binding approximation. According to a simple calculation m_t becomes[18]

$$m_t=(Br^2/m_{\mathrm{eff}})q^2\sin(N_h\pi/N), \tag{1}$$

where N_h is the total number of noninteracting holes in the tube formed by N atoms and m_{eff} and q are the effective mass and the electric charge of the hole, respectively. Notice that m_{eff} is given by $h^2/2ba^2$.

The resultant diamagnetic moment per unit volume should be $N_t\langle m_t\rangle$, where N_t is the number of CuO_2 tubes containing holes, per unit volume, and $\langle m_t\rangle$ the ring moment averaged on orientation. The averaging procedure in orientation leads to the introduction of the factor $\frac{2}{3}$ on the right-hand side of Eq. (1). If we consider that N_h takes non-negligible values only near the interfaces, the average radius should be close to that of the nanocrystals and the total number of tubes N_t should be approximately the number of crystallites per unit volume. The diamagnetic susceptibility as derived from Eq. (1) becomes

$$\chi=-(2\pi r^2q^2N_t/3Nm_{\mathrm{eff}})N_{h0}e^{-1/\tau}, \tag{2}$$

where we have included a relaxation time τ to account for the unstable character of N_h under air exposure ($N_h=N_{h0}e^{-t/\tau}$). For the longest milling times, the ratio of the total number of holes N_tN_h to the total number of atoms N_tN per unit volume can be estimated as follows. The atoms available to have a hole are assumed to be those placed over the nanocrystals surface, which for 10-nm-diam particles becomes approximately a 10% of the total number of atoms.[19] The excess number of carriers or holes per unit volume is expected to be of the order of a few percent of the total number of available positions resulting in $N_{h0}/N\sim10^{-3}$. However, the radius of the orbit is of the order of the nanocrystals radii, which are about 75 Å. Hence the term r^2 in Eq. (1) increases almost four orders of magnitude with respect to that of atomic diamagnetic susceptibility. Finally, the small value of m_{eff} may also contribute to enhance χ. According to these considerations, the diamagnetic susceptibility of the surface shielding currents can reasonably reach values one or two orders of magnitude larger than that corresponding to the normal atomic diamagnetic susceptibility, which agrees with the experimental values reported here. The ratio N_{h0}/N is the product of the ratio of surface to volume atoms in the tube (proportional to $1/r$) times the probability of freeing a carrier on a surface atom broken bond. The latter can be expected to increase with milling time before reaching a saturation value. This would explain the maximum that is observed in χ as a function of milling time

In conclusion, we have observed a giant diamagnetism in ball-milled $Si_{0.6}Ca_{0.4}CuO_2$, which persists up to 1000 K. It cannot reasonably be ascribed to the presence of small volume fractions of superconductive phases. A simple model, in which an unstable excess of carriers can flow along well-defined and extended orbits across the nanocrystals, such as those presumably provided by CuO_2 planes, can account for this large diamagnetic component.

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