Z. Phys. B - Condensed Matter 86, 319-324 (1992)

Condensed
Zeitschrift für Physik B Matter

Original contributions

Percolative phase separation in $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$

R.K. Kremer[1], **E. Sigmund**[2], **V. Hizhnyakov**[2,*], **F. Hentsch**[3], **A. Simon**[1], **K.A. Müller**[4], **and M. Mehring**[3]

[1] Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, W-7000 Stuttgart 80, Federal Republic of Germany
[2] Universität Stuttgart, Institut für Theoretische Physik, Teil III, Pfaffenwaldring 57, W-7000 Stuttgart 80, Federal Republic of Germany
[3] Universität Stuttgart, 2. Physikalisches Institut, Pfaffenwaldring 57, W-7000 Stuttgart 80, Federal Republic of Germany
[4] IBM Research Division, Zürich Research Laboratory, CH-8803 Rüschlikon, Switzerland

Received September 9, 1991

We report on the formation of conducting phases in slightly doped La_2CuO_4 samples by the existence of a percolative phase separation. Phase separation can be quenched by rapid cooling and can be restored by the application of a 3 T magnetic field. Magnetically polarizable quasiparticles are shown to be formed by hole doping which fuse to form percolative conducting and below 37 K superconducting phases.

1. Introduction

La_2CuO_4 is the parent compound for the layered copper oxide systems which become superconducting around 40 K. Superconductivity is achieved by either doping with Ba or Sr into the La-sites [1] or by introducing an excess of oxygen viz. raising the oxygen stoichiometry above the level required for formal charge compensation and forming compounds $La_2CuO_{4+\delta}$ with δ up to ≈ 0.05 [2], [3], [4]. Surprisingly, only little variation of the transition temperature T_c with the actual oxygen content is found. Oxygen doping, e.g. by high-pressure oxygen annealing [5], like cation doping, has a strong influence on the magnetic properties. Already small doping concentrations destroy the antiferromagnetic ordering of the Cu moments.

It is experimentally now well established by neutron scattering measurements on powders [6], and single crystals [7], anisotropic electronic transport and magnetic susceptibility [8], ^{139}La NMR [9] that in $La_2CuO_{4+\delta}$ on cooling below room temperature a phase separation occurs which generates domains of essentially stoichiometric insulating La_2CuO_4 and domains of conducting and superconducting areas, the latter showing onset of superconductivity at about 40 K. Jorgensen et al. [6] observe a reversible phase separation below 320 K, Chaillout et al. [7] report the onset of the phase separation at about 280 K, and completion below about 230 K for a sample with $\delta \approx 0.032$. A number of other authors have delt with the phase separation problem, too [10].

The pertinent question in all these scenarios is, however, *(i)* is the phase separation diffusion controlled, *(ii)* is there a characteristic temperature for the onset of phase separation. This motivated us to perform field dependent magnetization measurements on both, oxygen enriched and Sr doped La_2CuO_4 samples under various conditions. The conclusions drawn from the experimental results are in agreement with the model of percolative conducting and superconducting phase formation proposed theoretically before [11].

2. Experimental

$La_2CuO_{4+\delta}$ powder samples were prepared from the oxides by the standard procedure [12]. In the following we refer to it as the 'as-prepared' sample. Part of the 'as-prepared' sample was outgassed in high vacuum 10^{-5} mbar at temperatures given below. $La_{2-x}Sr_xCuO_{4+\delta}$ was synthesized from CuO, La_2O_3 and $SrCO_3$ at 1050° followed by an oxygen annealing at 700 °C. The powder samples were filled into thin walled Suprasil quartz containers and immersed in fast drying lacquer to prevent preferred orientation of the grains. The magnetizations of the quartz sample holders were measured in separate runs and subtracted.

The temperature dependence of magnetizations were measured with a S.H.E. VTS SQUID susceptometer. Special attention was paid to the thermal history of the samples. 'Fast zero-field cooling' ('zfc quenching') of the samples was achieved by rapidly lowering the sample within less than 30 s into the cryostat which was held at the temperature T_s. This procedure allowed quenching rates of the order of 10 K s^{-1}. At the temperature, T_s, a magnetic field of about 90 G was applied and subsequently the temperature was lowered and magnetizations were determined. Magnetization data were taken after

* *Permanent address:* Institute of Physics, Estonian Academy of Sciences, Riia 142, Tartu, Estonia

equilibrating the sample to the desired (lower) temperatures for about 900 s and averaging ten independent magnetization readings. Full acquisition of one data point typically was accomplished after 1500 s. The field dependence of the magnetizations were determined with a MPMS Quantum design magnetometer.

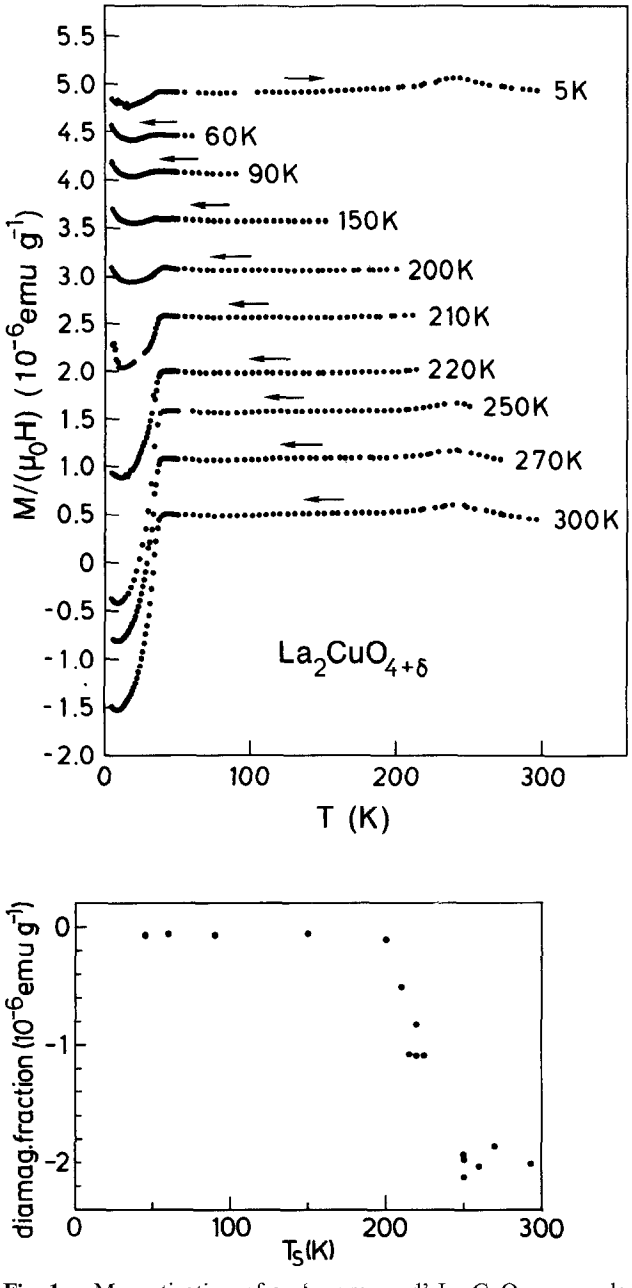

Fig. 1. a Magnetization of an 'as-prepared' $La_2CuO_{4+\delta}$ sample as a function of the temperature. The starting temperatures T_s to which the sample was quenched from room temperature are indicated. The uppermost curve was obtained after quenching the sample to 5 K and slowly heating to room temperature. Beginning from the lowest data set each curve was shifted upwards by a value of 5×10^{-7} emu g^{-1} compared to the preceding one. The measuring field was 90 G, arrows indicate the direction of temperature change during the measurement. **b** Dependence of the Meissner signal of $La_2CuO_{4+\delta}$ on the starting temperature T_s

3. Results

Temperature dependence

The essential results of the magnetization measurements are summarized in Fig. 1a. Below 37 K, the 'as-prepared' sample of $La_2CuO_{4+\delta}$ exhibits a sharp transition from the paramagnetic to a diamagnetic magnetization apparently indicating the presence of superconductivity in our sample giving rise to the Meissner type flux expulsion. The fractional volume of the superconductivity in our sample is estimated from the maximal diamagnetic fraction in the magnetization, -2×10^{-6} emu g^{-1}, and amounts to about 200 ppm. Maxima in the magnetization curves at around 240 K indicate the onset of long-range antiferromagnetic ordering characterized by the Néel temperature T_N.

The diamagnetic fraction in the magnetization strongly depends on the temperature T_s to which the sample was rapidly quenched. Slow cooling began at the 'starting' temperature T_s from whereon magnetization data were acquired during slow cooling temperature scans. Note that a sudden decrease of the diamagnetic fraction by about one and a half orders of magnitude occurs at values of T_s in the range of 200–250 K (Fig. 1b).

Surprisingly, the zfc sample quenched to 5 K (Fig. 1a, uppermost curve) shows a very small diamagnetic fraction only. This is in contrast to the usual behaviour of bulk high-T_c superconductors where flux expulsion after zfc ('shielding') yields a much higher diamagnetic signal than for fc (field cooled) samples ('Meissner effect'). If, however, zero field cooling was performed *slowly* with the same temperature interval step sequence, including equilibration, as before the diagmagnetic shielding signal became maximal (Fig. 2). This observation clearly demonstrates that the superconducting fraction of the sample strongly depends on the thermal treatment.

In addition we have performed zfc and fc temperature scans, both by slowly cooling down with the temperature interval step sequence as before. The fc diamagnetic frac-

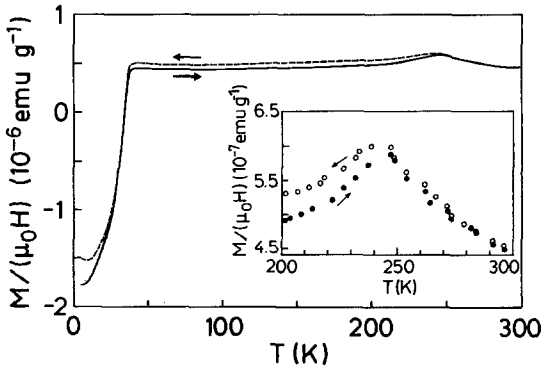

Fig. 2. Magnetization of the $La_2CuO_{4+\delta}$ sample as a function of the temperature. Arrows indicate the direction of the temperature variation. The zfc magnetization curve was measured after the sample had been cooled slowly from room temperature to 5 K by using the same temperature interval step sequence, including equilibration, as in the subsequent heating (or cooling) cycles and with application of a measuring field of 90 G

tion was observed to be only slightly smaller than the zfc diamagnetic signal, again in contrast to what is observed usually in bulk high-T_c superconductors. However, a small difference in the fc and zfc magnetizations is observed above T_c up to room temperature, a feature which became even more pronounced in the Sr doped samples to be discussed below.

A similar dependence of the diamagnetic Meissner signal of a $La_2CuO_{4+\delta}$ sample on the temperature T_s was reported before by Yoshizaki et al. [14] which was interpreted as anomalous enhancement of the superconducting fractional volume due to field cooling of the sample. This interpretation is not confirmed by our results. In particular, the authors obtained less diamagnetic shielding after zero-field cooling to 5 K and subsequent data acquisition while raising the temperature. Our results, however, clearly show that by slow zf cooling the formation of superconductivity is favoured and the diamagnetic fraction of the sample can be enlarged. Since no details about cooling conditions were given by Yoshizaki et al., we assume that their zfc curve corresponds to our zf quenched measurement (uppermost curve in Fig. 1a).

For the 'as-prepared' $La_2CuO_{4+\delta}$ sample the appearance of superconductivity is intimately related to the presence of excess oxygen in the sample. We observed that the Meissner signal completely vanishes after the sample has been vacuum annealed at 500 °C for 12 h. Simultaneously, the paramagnetic background magnetization at high temperatures is considerably reduced and the high temperature magnetization maximum indicating antiferromagnetic long-rang ordering shifted from 240(5) K, for the as-prepared sample, to 291(5) K for the vacuum annealed sample (Fig. 3). The latter effect is well known and has been taken as evidence for a strong reduction of excess oxygen for the outgassed sample [15].

Since we have no direct determination of the excess oxygen content δ of the as-prepared sample an estimate of δ was attempted by using the T_N vs δ relationship proposed by Saylor et al. [15]. Taking the maximum temperature $T_{max} = 240(5)$ K as the onset of long-range ordering viz. as the Néel temperature, Fig. 1 in [15] suggest $\delta = 0.017(2)$ for our sample. According to this relation the excess oxygen content δ of the 500 °C vacuum annealed sample is less than 0.007.

In the oxygen rich 'as-prepared' sample the results in Fig. 1 clearly prove that the phase separation leading to superconducting domains is critically affected by the thermal treatment of the sample. Superconductivity, for example, can almost completely be suppressed by rapid temperature quenching of the sample. Slow cooling (some hours, as provided in the slow cooling procedures), on the other hand, supports the formation of the superconducting domains. Related observations have been reported recently for $YBa_2Cu_3O_{7-\delta}$ by Veal et al. [16]. They have detected a rise of the superconducting transition temperature by as much as 15 K after room-temperature annealing of quenched oxygen-deficient samples of $YBa_2Cu_3O_{7-\delta}$ for several days. We note that in the $La_2CuO_{4+\delta}$ as well as in the $YBa_2Cu_3O_{6.5}$ compounds annealing effects appear in a similar temperature range.

Field dependence

The formation of superconducting phases in $La_2CuO_{4+\delta}$ not only depends on the thermal treatment of the sample but can also be initiated by application of sizeable magnetic fields. This is demonstrated in Fig. 4. After quenching the sample from room temperature to 220 K the sample was exposed to a ± 3 Tesla magnetic field for a duration of 5 h. Then the field was turned off and a measuring field of 90 G was applied. Magnetizations were recorded during slow fc runs. For reference the sample was again quenched to and held at 220 K in zero field for 5 h. The sign of the field in Fig. 4 refers to the direction of the measuring field. If the large polarization field and the measuring field are parallel (+) the high temperature paramagnetic magnetization is enhanced and if both are antiparallel (−) a significant reduction of the paramagnetic signal is observed. The superconducting (diamag-

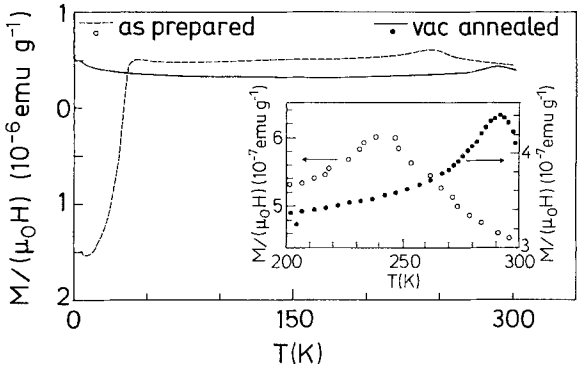

Fig. 3. fc magnetizations as a function of temperature of the 'as-prepared' $La_2CuO_{4+\delta}$ sample and after it was outgassed in high vacuum at 500 °C for 12 h. The insert shows the section around the Néel temperatures on an enlarged scale

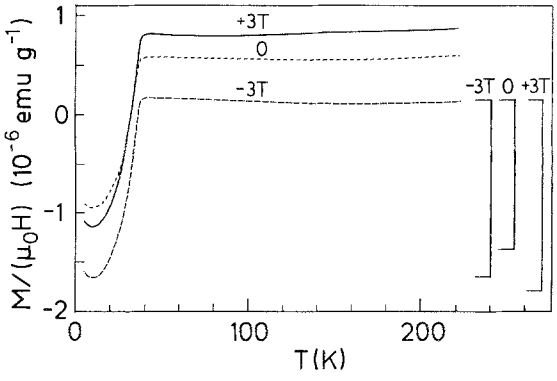

Fig. 4. fc magnetizations as a function of temperature of the 'as-prepared' $La_2CuO_{4+\delta}$ sample and after quenching the sample from temperature to 220 K and applying a magnetic field of ± 3 Tesla for 5 h. The sign refers to the direction of the measuring field. The reference (indicated by 0) was held at 220 K for 5 h in zero field. The length of the bars gives the maximal diamagnetic fraction obtained with the indicated polarization field

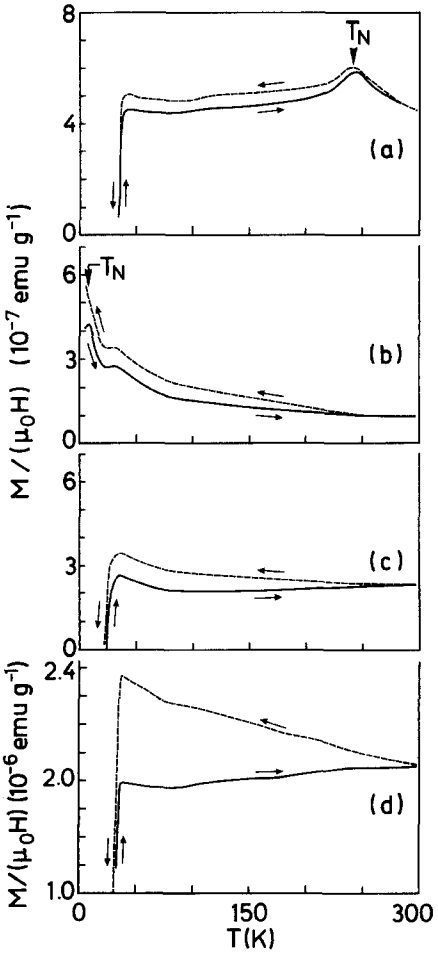

Fig. 5. fc and zfc magnetizations of the 'as-prepared' $La_2CuO_{4+\delta}$ sample **a** and moderately Sr doped samples $La_{2-x}Sr_xCuO_4$ (**b**: $x=0.02$; **c**: $x=0.04$; **d**: $x=0.06$) as a function of the temperature. Arrows indicate the direction of the temperature variation. The zfc magnetization curve was measured after the sample had been cooled slowly from room temperature to 5 K by using the same temperature interval step sequence, including equilibration, as in the subsequent heating (or cooling) cycles and with applied magnetic field. The Néel temperatures T_N for the 'as-prepared' sample and for $La_{1.98}Sr_{0.02}CuO_4$ are indicated. Note: The zero of ordinate for $La_{1.94}Sr_{0.06}CuO_4$ has been suppressed

netic) fraction of the sample exposed to the polarization field is about 20% larger than that of the reference sample when no polarizing field is applied. This observation is independent of the direction of the polarization field with respect to the measuring field. Performing the same polarizing field procedure at a holding temperature of 180 K does not change the diamagnetic fraction, whereas, a remnant paramagnetic polarization is obtained like before.

Finally, we turn to the results obtained for the Sr doped samples (Fig. 5). As can be seen from Figs. 5b–5d the diamagnetic fraction increases with higher Sr contents. The most obvious feature is the distinct separation between the fc and the zfc magnetization both for the 'as-prepared' $La_2CuO_{4+\delta}$ and the Sr doped samples in the same temperature range. It is important to note that this temperature range is well above any of the Néel temperatures in the Sr doped samples. This rules out any argument relating the observed phenomena to spin canting or other antiferromagnetic ordering mechanisms [17]. The magnitude of the fc-zfc separation hints at a strong correlation between the amount of holes induced by the doping and the observed magnetic polarization. We find that the 'as-prepared' $La_2CuO_{4+\delta}$ sample shows quantitatively similar behaviour as the $La_{1.98}Sr_{0.02}CuO_4$ sample.

4. Discussion

The measurements presented in this article clearly prove that in the investigated samples diffusion processes of magnetic quasiparticles take place which can be influenced either by thermal treatment (fast and slow cooling) or by magnetic field. Under slow cooling conditions the diffusion process occurs in all the samples in the temperature range from around 300 K down to about 200 K. It can very effectively be suppressed by a fast cooling (quenching) procedure. The result of the diffusion is the appearance of a diamagnetic signal below T_c caused by the formation of a conducting and below T_c superconducting phase. The diamagnetic signal and the corresponding superconducting phase is larger the more complete the diffusion process was, i.e. the longer the system was kept at a temperature between 200 and 250 K. At higher temperatures thermal fluctuations destroy the conducting phase.

Our current understanding of the observed phenomena is as follows. Magnetic quasiparticles are formed by the interaction of the added holes with the antiferromagnetic background. These magnetic quasiparticles can partially combine by a diffusion controlled process into a conducting and below T_c superconducting phase which gives rise to the observed diamagnetic signal. This conducting phase is of fractal nature and forms a metallic percolative network. Not all the quasiparticles, however, combine into this phase but rather coexist with single magnetic quasiparticles which give rise to the observed paramagnetic behaviour. The equilibrium between these two subsystems can be shifted by thermal treatment of the samples. With increasing temperature thermal fluctuations gradually destroy the conducting (superconducting) phase and breaking it up into magnetic quasiparticles. This can best be seen in Fig. 2, 5c and 5d where, when starting at low temperatures (5 K), a monotonic increase in the paramagnetic signal (lower curves) is observed. Application of a weak magnetic field (e.g. the measuring field of a few hundred Gauss) during the cooling procedure seems to increase the paramagnetic signal with a corresponding decrease of the superconducting phase as seen in the low temperature part of Fig. 2 (dashed line). In contrast to this increase the application of a strong magnetic field (e.g. ± 3 T) enlarges the superconducting phase as seen in Fig. 4. There the sample was quenched to 220 K in order to suppress the diffusion of the quasiparticles. Then, by applying a strong magnetic field (3 T) a polarization of the magnetic quasiparticles is observed and in addition an increase of the superconducting (diamagnetic) phase. The magnetic field obviously supports the formation of the superconducting phase by increasing the diffusion constant of the quasi-

particles. This interpretation agrees also with the magnetoresistance data where for the case of $La_2CuO_{4+\delta}$ a remarkable increase in the conductivity for $T > 120$ K and an applied field $\geqq 3$ T was found [13]. These temperatures and field values coincide with ours. Since the conductivity is of diffusive character and therefore proportional to the diffusion constant according to the Einstein relation we arrive at the conclusion that both, the phase separation as well as the conduction process are due to the diffusion of magnetic quasiparticles.

Let us now discuss in more detail the Sr doped samples. In the $La_{2-x}Sr_xCuO_4$ system the holes created by Sr doping form magnetic quasiparticles which can diffuse. Diffusion of the Sr counterion at the relevant temperatures is negligibly small. Because of the Coulomb binding energy between counterion and quasiparticle, the diffusion process is limited and affords a certain activation energy. Only small conducting microphases can therefore be formed in the low doping regime. Since Sr is randomly distributed (and not diffusing) a considerable dispersion of size and distribution of physical properties of these microphases results. The experimental evidence for this dispersion can be seen e.g. in Fig. 5c in the temperature range 25–35 K. The transition region around T_c is smeared out, no sharp transition is observed. These observations depend also strongly on the sample treatment as can be seen by comparing the slow zfc and fc curves. It is also observed that the diffusion process can be very effectively suppressed by fast cooling demonstrating that the mobility of the quasiparticles is largely reduced.

In the low doping regime the microphases are distributed in the sample and do not suppress bulk antiferromagnetic order. For higher doping microphase clusters grow and start to become connected destroying long-range antiferromagnetic order [18]. In this higher doping regime where no long-range antiferromagnetic order exists anymore, nonhomogeneous large *fractal* or *percolative* clusters of conducting (superconducting) phases are formed. A clustering or percolation of this type, however, can only take place when the subunit i.e. the magnetic quasiparticle has a considerable size (several lattice units). In such a diffusion controlled clustering process there is no critical phase transition temperature, but merely a temperature region where the conducting phase (delocalized holes) coexists with a noncondensed phase consisting of separated magnetic quasiparticles.

In the case of excess oxygen doping ($La_2CuO_{4+\delta}$) the same magnetic quasiparticles are formed as with strontium doping. Therefore basically the same features are observed. Again diffusion of the excess oxygen at the temperatures discussed here is too low to play any essential role. However, the binding energy of these quasiparticles to the counterions seems to be much smaller than in the strontium doped case. This follows from the very sharp drop of the magnetization below T_c in the $La_2CuO_{4+\delta}$ sample (Fig. 5a) compared with the much smoother decrease in the Sr doped samples (Fig. 5b and 5c) although the total amount of holes is even larger in the Sr doped samples. This can only be understood on the basis that larger and more homogeneous conducting (superconducting) phases are formed in the oxygen doped case. In order to allow for this the diffusion process has to be more effective.

There have been observations that hydrogen diffusion plays a certain role in $La_2CuO_{4+\delta}$ [19] at the temperatures discussed here. Currently there is not clear evidence that the diffusion of the magnetic quasiparticles is influenced in any way by this hydrogen. Further investigations have to clarify this point.

The results presented above are in good agreement with the model proposed earlier [11] in order to explain the doping mechanisms in high-T_c superconductivity in the cuprate systems. There it was shown that by hole doping of the antiferromagnetically ordered systems small ferromagnetic clusters with a size of 10 to 20 parallel Cu spins are created. This process is favoured since the loss of exchange energy due to magnetic disorder is exceeded by the gain due to lowering of the kinetic energy. These clusters are rather large and heavy and are expected to have low mobility. At higher hole conentrations the clusters start to form large fractal or percolative clusters. Within this percolation picture the experimentally obtained magnetic and conductive phase diagrams can be understood very naturally by assuming a single cluster size which comprises 10 to 15 Cu spins [18, 20].

In order to obtain an experimental value for the total spin of the magnetic quasiparticles we have performed magnetic susceptibility measurements versus magnetic field on the $La_{1.98}Sr_{0.02}CuO_4$ sample with a Néel temperature $T_N \approx 7$ K (Fig. 5b) for different temperatures. The sample was chosen because our available magnetic fields were limited to 5 T. Alignment of particles with the expected magnetic moment $\leqq 10\,\mu_B$ can appreciably be achieved at these fields only for temperatures $T_N < T < 50$ K. The temperature must also be higher than T_N otherwise the internal field caused by the long-range magnetic order suppresses spin alignment. The results are presented in Fig. 6. Fitting the experimental field dependences of the susceptibility with a differentiated Brillouin function leads to magnetic moments on the order of $10\,\mu_B$ for the magnetic quasiparticles. By using a g-

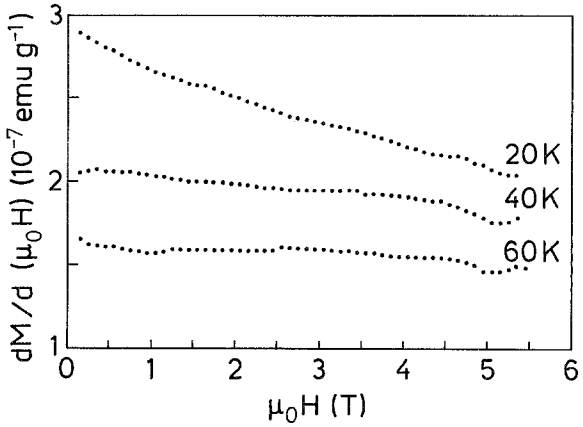

Fig. 6. Susceptibilities dM/dH of $La_{1.98}Sr_{0.02}CuO_4$ as a function of the magnetic field. The indicated temperatures correspond to the final temperature which was reached under zfc from room temperature

value of 2.2 and taking into account a reduction factor of 0.63 due to quantum fluctuations we estimate the size of the magnetic quasiparticles to about 15 copper spins. This result agrees very well with the cluster size estimation ($N=13$ copper spins) obtained from the percolation model [11, 18].

5. Conclusions

Our analysis of temperature and field dependent magnetic measurements establishes the formation of a percolative phase separation in the La_2CuO_4 system. Hole doping of this system creates magnetic quasiparticles (of the order of 15 copper spins) which can form large fractal clusters of high conductivity and which become superconducting below $T_c \approx 40$ K. The formation of this percolative conducting phase is controlled by the diffusion of the magnetic quasiparticles. The diffusion process can be quenched by rapid cooling below 200 K. There is no critical temperature for the phase separation but rather a temperature range (200–300 K) where the separation sets in. A coexistence region occurs where the highly conducting (metallic) phase and noncondensed magnetic quasiparticles compete. The bonding between these two phases is influenced by large magnetic fields (several Tesla) and thermal treatment, basically by influencing the diffusion constant of the magnetic quasiparticles. We believe that these mechanisms apply as well to all other high-T_c superconductors based on cuprate layers.

We thank E. Brücher and M. Gehrke for help with the magnetization measurements. Prof. Reinen (U Marburg) kindly provided the Sr doped samples. The work is supported by the Bundesministerium für Forschung und Technologie and by the Land Baden-Württemberg.

References

1. Bednorz, J.G., Müller, K.A.: Z. Phys. B - Condensed Matter **64**, 189 (1986); Bednorz, J.G., Takashige, M., Müller, K.A.: Europhys. Lett. **3**, 379 (1987)
2. Beille, J., Cabanel, R., Chaillout, C., Chevalier, B., Demazeau, G., Deslandes, F., Etourneau, J., Lejay, P., Michel, C., Provost, J., Raveau, B., Sulpice, A., Tholence, J.L., Tournier, R.: C.R. Acad. Sci. Paris, t. 304, Série II, no. 18 (1987)
3. Grant, P.M., Parkin, S.S.P., Lee, V.Y., Engler, E.M., Ramirez, M.L., Lim, G., Green, R.L.: Phys. Rev. Lett. **58**, 2482 (1987)
4. Green, R.L., Maletta, H., Plaskett, T.S., Bednorz, J.G., Müller, K.A.: Solid State Commun. **63**, 379 (1987)
5. Beille, J., Chevallier, B., Demazeau, G., Deslandes, F., Etourneau, J., Laborde, O., Michel, C., Lejay, P., Provost, J., Reveau, B., Sulpice, A., Tholence, J.L., Tournier, R.: Physica B**146**, 307 (1987)
6. Jorgensen, J.D., Dabrowski, B., Shiyou Pei, Hinks, D.G., Soderholm, L., Morosin, B., Schirber, J.E., Venturini, E.L., Ginley, D.S.: Phys. Rev. B**38**, 11337 (1988)
7. Chaillout, C., Cheong, S.-W., Fisk, Z., Lehmann, M.S., Marezio, M., Morosin, B., Schirber, J.E.: Physica C**158**, 183 (1989); Chaillout, C., Chenavas, J., Cheong, S.-W., Fisk, Z., Marezio, M., Morosin, B., Schirber, J.E.: Physica C**170**, 87 (1990)
8. Hundley, M.F., Thompson, J.D., Cheong, S.-W., Fisk, Z., Schirber, J.E.: Phys. Rev. B**41**, 4062 (1990)
9. Hammel, P.C., Reyes, A.P., Fisk, Z., Takigawa, M., Thompson, J.D., Heffner, R.H., Cheong, S.-W., Schirber, J.E.: Phys. Rev. B**42**, 6781 (1990)
10. Emery, V.J., Kivelson, S.A., Lin, H.Q.: Phys. Rev. Lett. **64**, 475 (1990); Phillips, J.C., Phys. Rev. B**39**, 7356 (1989); Phys. Rev. B**40**, 7348 (1989); Phys. Rev. Lett. **64**, 1605 (1990); Marder, M., Papanicolaou, N., Psaltakis, G.C.: Phys. Rev. B**41**, 6920 (1990); Castellani, C., Grilli, M., Kotliar, G.: Preprint
11. Hizhnyakov, V., Sigmund, E.: Physica C**156**, 655 (1988)
12. Bednorz, J.G., Takashige, M., Müller, K.A.: Mat. Res. Bull. **22**, 819 (1987)
13. Thio, T., Thurston, T.R., Preyer, N.W., Picone, P.J., Kastner, M.A., Jenssen, H.P., Gabbe, D.R., Chen, C.Y., Birgeneau, R.J., Aharony, A.: Phys. Rev. B**38**, 905 (1988)
14. Yoshizaki, R., Sawada, H., Iwazumi, T., Ikeda, H.: Physica C**153–155**, 1495 (1988)
15. Saylor, J., Takacs, L., Hohenemser, C., Budnick, J.I., Chamberland, B.: Phys. Rev. B**40**, 6854 (1989)
16. Veal, B.W., You, H., Paulikas, A.P., Shi, H., Fang, Y., Downey, J.W.: Phys. Rev. B**42**, 447 (1990); Veal, B.W., Paulikas, A.P., You, H., Shi, H., Fang, Y., Downey, J.W.: Phys. Rev. B**42**, 6305 (1990)
17. Thio, T., Chen, C.Y., Freer, B.S., Gabbe, D.R., Jenssen, H.P., Kastner, M.A., Picone, P.J., Preyer, N.W., Birgeneau, R.J.: Phys. Rev. B**41**, 231 (1990)
18. Hizhnyakov, V., Sigmund, E.: Mat. Lett. **9**, 425 (1990); Hizhnyakov, V., Kristoffel, N.N., Sigmund, E.: Physica C**161**, 435 (1989)
19. Rudolf, P., Paulus, W., Schöllhorn, R.: Private communication
20. Sigmund, E., Hizhnyakov, V.: Electronic properties of high-T_c superconductors and related compounds. In: Springer Series in Solid-State Sciences. Vol. 99, p. 366. Berlin, Heidelberg, New York: Springer 1991
21. Gernier, J.-C., Wattiaux, A., Lagueyte, N., Park, J.C., Marquestaut, E., Etourneau, J., Pouchard, M.: Physica C**173**, 139 (1991);
Gernier, J.-C., Wattiaux, A., Doumerc, J.-P., Dordor, P., Fournes, L., Chaminade, J.-P., Pouchard, M.: J. Solid State Chem. **95** (1991)

Note added in proof. After submission of the paper we became aware of the work by Pouchard and co-workers [21] in which it was demonstrated that O^- diffusion is still possible at the relevant temperatures above 220 K.