Coexistence of bulk superconducting and antiferromagnetic order in the spin-ladder system $Sr_2Ca_{12}Cu_{24}O_{41}$

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Combined ac-susceptibility and ac-calorimetry measurements under hydrostatic pressure on new single crystals of the spin-ladder system $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x=12$) in good hydrostatic conditions allow us to unambiguously establish the phase diagram. We show that bulk superconductivity and antiferromagnetic order coexist over a wide pressure range, which is quite rare in strongly correlated systems where the same electrons participate in superconductivity and magnetic order. We suggest that this is possible by the special microscopic structure of this material, containing ladders and chains, with a weak coupling between the two.

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I. INTRODUCTION

It has long been recognized that antiferromagnetism and superconductivity are not antagonistic phenomena[1] but should be able to cohabitate peacefully. In an antiferromagnet, the modulation period of the moments is typically the interatomic distance whereas the superconducting coherence length, i.e., the size of the cooper pair, is usually several tens or hundreds of this distance. The average field felt by the cooper pair is thus zero. In conventional systems, the Fermi sea and the local moments are decoupled. The magnetic energy is therefore rather robust and the coexistence of superconductivity and antiferromagnetism is the general trend. Good examples are found in the Chevrel phases and especially in the family of the borocarbides, where the interplay of rare-earth magnetism with superconductivity is complex, though the general result is that they are still competing phenomena.[2] In strongly correlated electron systems, it is likely that the same carriers will carry the magnetic moment and participate in the Cooper pairing. Magnetism and superconductivity are therefore intimately linked, and it is now known that they can actually be cooperative effects, for example, spin fluctuations are suspected to be the main pairing mechanism in the superconducting state found close to magnetic quantum critical points in heavy-fermion systems.[3] However, this does not necessarily favor coexistence of the two phases which can still be mutually excluding. Indeed, in most of these systems, superconductivity appears only on the border of magnetism and, for example, in the heavy-fermion superconductor $CeRhIn_5$ where quite large regions of coexistence have been reported from resistivity measurements, calorimetry,[4] and NMR (Ref. 5) studies have shown that the range of this apparent coexistence is in fact extremely limited, and only homogeneous in a narrow (0.3 GPa) window around the pressure where the two ordering temperatures cross. Quite surprisingly, there are relatively few cases of strongly correlated systems where clear evidence of homogeneous coexistence of bulk superconductivity and antiferromagnetism is found. In the high-T_C cuprates, the best example is probably $HgBa_2Ca_4Cu_5O_y$ though it is not completely clear if both phenomena coexist on a microscopic scale.[6] Another interesting case is found in organic superconductors. One can find both examples of probable homogeneous coexistence, due to superconductivity and magnetism being carried by distinct subsystems,[7] and of microscopically heterogeneous coexistence, allowed by the fact that the transition with pressure between antiferromagnetism and superconductivity is first order.[8,9] Other systems where the interplay of magnetism and superconductivity exists include the new iron-pnictide superconductors.[10] In this study, we show that, contrary to most of these cases where the general trend is that superconductivity only arises on the border of magnetism, in the case of the spin-ladder system $Sr_{14-x}Ca_xCu_{24}O_{41}$, there is an extremely wide pressure range where bulk antiferromagnetism and superconductivity are found, implying a much more peaceful cohabitation between the two types of order than we have been led to expect.

Although superconductivity in the ladder system $Sr_{14-x}Ca_xCu_{24}O_{41}$ was discovered over 10 years ago,[11] the interplay between the antiferromagnetic (AF) order and superconductivity in this system has been largely ignored. $Sr_{14-x}Ca_xCu_{24}O_{41}$ presents a complex structure consisting of a stacking of planes of Cu_2O_3 ladders and planes of CuO_2 chains. For high levels of Ca doping, superconductivity can be induced by the application of pressure of about 3–4 GPa.[12] The upper critical field presents a very large anisotropy, and strongly exceeds the Pauli paramagnetic limit,[13,14] which suggests that superconducting order parameter is unconventional[15] but the superconducting mechanism is so far not established. Two main scenarios are generally put forward. Dagotto *et al.*[16,17] proposed a model involving the energy gain by pairing holes due to the formation of singlets on the ladder rungs. Another scenario proposes a key role of a change in dimensionality. It is suspected that the application of pressure might increase the interladder coupling sufficiently to recover a two-dimensional (2D) situation analogous to the high-T_C cuprates. In either case it is likely that superconductivity occurs within the ladder plane, and that the mechanism somehow involves the magnetic interactions. Several years ago we showed that the magnetic order persists at high pressure,[18] where superconductivity occurs, and that two transition signatures could be seen in the specific heat implying that there is a coexistence, either homogeneous or heterogeneous, of the two states. In our previous study, it was not possible to identify which state corresponded to each transition. In this new study, we use a recently developed

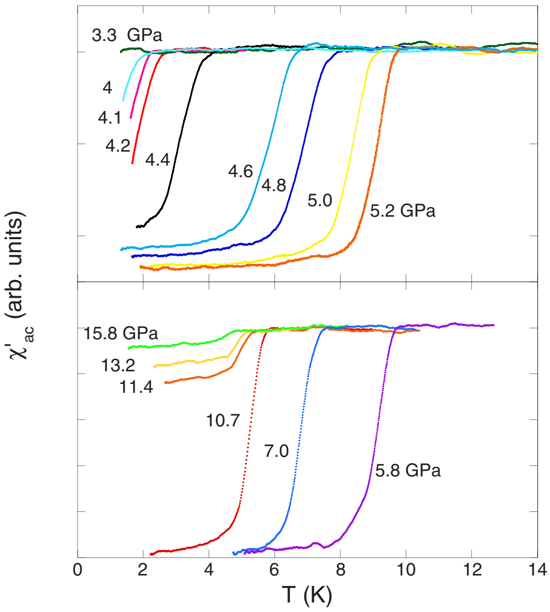

FIG. 1. (Color online) ac susceptibility curves for the superconducting transitions at selected low pressures (top) and high pressures (bottom). The decrease in the height of the transition above 10 GPa is due to damage to the pick-up coil (see text).

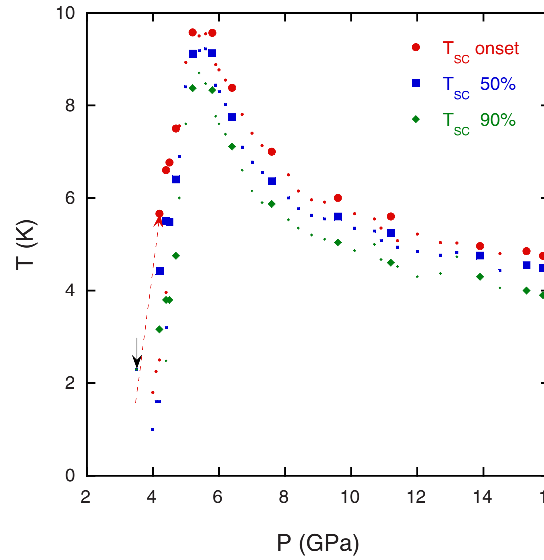

FIG. 2. (Color online) Superconducting phase diagram from ac susceptibility. The large points are measured on initial increasing of pressure. Small points have been measured after a higher pressure has been obtained and then released. The arrow indicates the lowest temperature achieved at 3.5 GPa where no trace of superconductivity was found.

high-pressure ac-susceptibility technique, combined with ac calorimetry to reexamine this "cold case." The addition of ac susceptibility for the detection of the screening by the superconducting state allows us to clearly identify the two states, and we show that there is strong evidence for bulk coexistence over a wide pressure range.

II. EXPERIMENTAL DETAILS

The growth and characterization of single crystals of $Sr_2Ca_{12}Cu_{24}O_{41}$ by the traveling solvent float-zone technique has been reported elsewhere.[19] ac-susceptibility and ac-calorimetry measurements were performed under high pressure in a diamond-anvil cell with argon as the hydrostatic pressure-transmitting medium. The pressure could be tuned *in situ* at low temperature using a purpose-built bellows system,[20] and was measured using the ruby fluorescence scale. For the ac susceptibility, a miniature pick-up coil was inserted in the pressure chamber,[21] and an ac field of 1 Oe at 733 Hz was applied. For the ac calorimetry, a Au/AuFe thermocouple was attached to the sample with GE varnish. The sample was heated by a laser, modulated by a mechanical chopper at about 5600 Hz, and guided to the sample by an optical fiber.[22]

III. RESULTS AND DISCUSSION

Typical ac-susceptibility curves are shown in Fig. 1 and the complete superconducting phase diagram from ac-susceptibility measurements is shown in Fig. 2. In this experiment, it was not possible to gradually increase the pressure which tended to increment in jumps of about 1 GPa. The large points are the most reliable being obtained upon an initial increase in pressure. The pressure could then be released and gently reincreased to fill in the gaps (small points). At 3.5 GPa, no trace of superconductivity was found down to 2.3 K, then on increasing the pressure to 4.4 GPa, a complete superconducting transition was obtained. On releasing the pressure, we found an onset of superconductivity at 1.8 K at 4.0 GPa. The superconducting (SC) critical temperature, T_{SC} initially increases rapidly up to about 10 K at 5 GPa. This is followed by a plateau, then a very sharp decrease at 5.8 GPa. T_{SC} then levels off and its pressure dependence is quite weak above 8 GPa. Above 10 GPa, the transition was still visible up to the highest pressure measured (15.8 GPa) but with considerably reduced height. We established with reasonable certainty that this was due to damage to the pick-up coil as the reduced height was maintained when the pressure was released below 10 GPa again. In the ac-calorimetry setup, the signal is a complex function of the sample heat capacity and the thermal link between the sample and its surroundings. Hence, an anomaly in the specific heat will show up in the signal amplitude but also in the phase. In fact, the phase is often a much more sensitive probe. In Fig. 3 (left), we show traces of $1/T_{ac}$ (referred to as the amplitude of the signal) and the signal phase, θ. The AF transition is hardly visible in the amplitude whereas θ shows a clear negative peak at the Néel temperature, T_N. At higher pressures, two weak but clear anomalies are visible, and can be emphasized by the subtraction of a background signal (Fig. 3 right). Contrary to our previous study, we can unambiguously identify the superconducting transition by comparison with the ac-susceptibility data. We find that the peak in the calorimetry data coincides approximately with the 50% point of the susceptibility transition. The second anomaly does not of course provide proof of AF order but as we have followed it from low pressure where AF order has been established, we assume that this is the case. In Fig. 4,

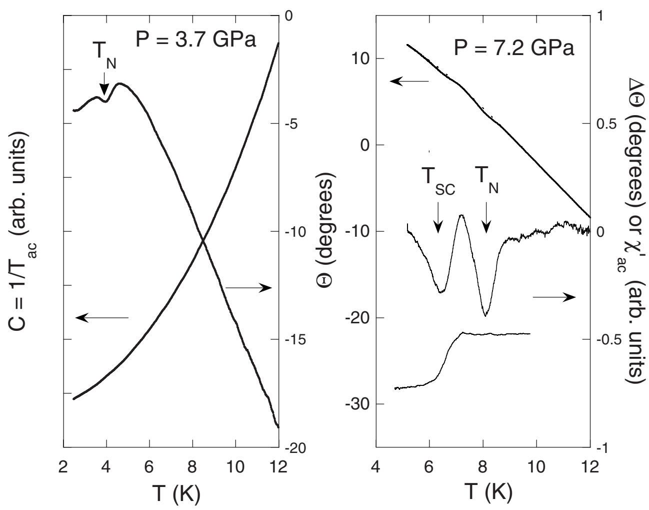

FIG. 3. (Left) Curves of the calculated sample heat capacity and the signal phase from the ac-calorimetry measurement at 3.7 GPa. The antiferromagnetic transition is hardly visible in C but appears as a clear anomaly in the phase. (Right) Phase of the calorimetry signal at 7.2 GPa (top curve). Two anomalies are visible which show up clearly after a background signal (dotted line) has been subtracted as two negative peaks (middle curve). The ac-susceptibility signal at a similar pressure is overlaid (bottom curve), showing that the lower temperature anomaly corresponds approximately to the midpoint of the superconducting transition.

we show the evolution of the phase signal curves with increasing pressure. The two anomalies merge into one at about 6 GPa, then separate again above 7 GPa as T_N crosses T_{SC}. The AF transition anomaly could be followed up to 9.5 GPa, and the superconducting anomaly was visible up to the

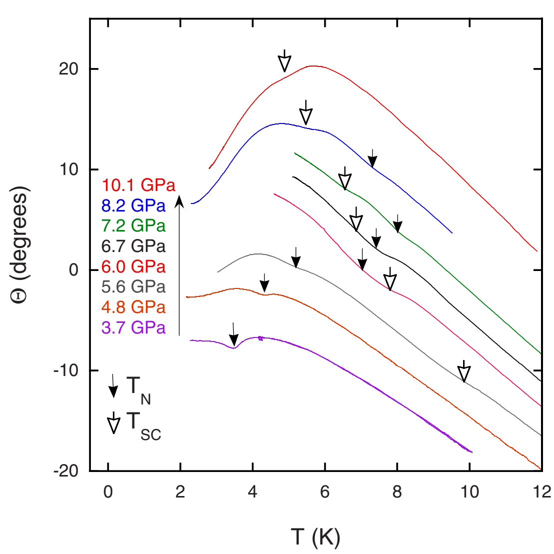

FIG. 4. (Color online) Phase of the ac-calorimetry signal at selected pressures. The transitions are indicated by the full (AF transition) and open (SC transition) arrows. The identification of the SC transition is unambiguous from comparison with the ac-susceptibility data. Between 6 and 7 GPa, a single broad transition is observed as the two transition temperatures cross each other. In this case, the SC arrow is positioned from the ac-susceptibility data.

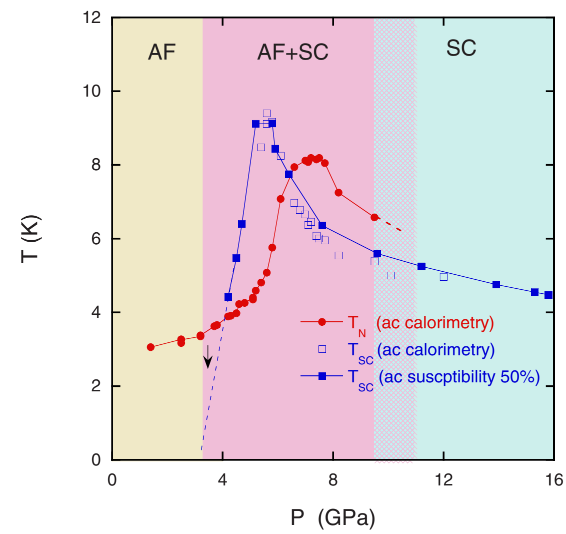

FIG. 5. (Color online) Phase diagram for the antiferromagnetic and superconducting phases combining ac-calorimetry and ac-susceptibility measurements. The criterion for the ac susceptibility is the 50% point.

maximum pressure of 13.4 GPa. The full phase diagram combining both techniques is shown in Fig. 5.

We have now established the superconducting phase diagram up to much higher pressure than in previous studies. Our results are qualitatively similar to the report of Nagata *et al.*,[12] though we find that the optimum pressure range is 5–6 GPa rather than 4 GPa as found previously. This discrepancy may be due to different pressure conditions. In our case, the use of argon as pressure-transmitting medium, and the *in situ* measurement of ruby fluorescence should provide good hydrostaticity and reliable pressure determination. However, we believe that the difference probably comes mainly from the different type of measurement, using ac susceptibility and specific heat instead of resistivity. Indeed, in resistivity measurements, it was shown that if the $R=0$ criterion is used instead of the onset, the optimum is shifted to higher pressure.[12] More importantly, below the optimum pressure, no indication of bulk superconductivity is found. In the ac-calorimetry experiment, the superconducting transition was only seen for pressures higher than 5 GPa whereas recently a sharp decrease in the spin-gap value was found at 3.8 GPa,[23] and previous reports suggested a closing of the gap at about 4 GPa.[24]

With increasing pressure, both T_{SC} and T_N are considerably enhanced. It has been suggested that the increase in T_{SC} is associated with a (small) transfer of holes from the chains to the ladders.[25] Another key ingredient is that the optimum value of T_{SC} is strongly linked to remarkable lattice instability[26] as is often observed for conventional and unconventional superconductors. The strong increase in T_N occurs at about 6 GPa, a slightly higher pressure than the increase in T_{SC} but lower than the 8.5 GPa reported for the lattice anomaly. However, the lattice anomaly was measured at room temperature, and could occur at a lower pressure at low temperature so both the concomitant increase in T_N and decrease in T_{SC} might be driven by changes in the electronic and magnetic correlations, associated or not with the lattice instability. We also show that superconductivity exists at least up to 15.8 GPa whereas previous reports stopped at 8 GPa.[12] In fact, T_{SC} varies surprisingly little with pressure at the highest pressures reached. T_N also varies relatively little at high pressure where we could follow it up to 9.5 GPa.

Understanding the pressure dependence of T_{SC} also needs addressing its interplay with the AF order. Although the simultaneous presence of the two transitions in the specific heat does not completely prove microscopic coexistence of the two phases, it does prove that bulk AF order and superconductivity are both present in the sample. This occurs over a pressure range of at least 6 GPa. This pressure range can be compared with typical pressure scales of the features in the magnetic and superconducting phase diagrams which are on the order of only 2–3 GPa. A heterogeneous coexistence due to a first-order transition over such a pressure range is therefore unlikely. A microscopic coexistence of the two phases with similar ordering temperatures is of particular interest in the context of the unconventional pairing mechanism expected in ladder systems, and we would expect to see some evidence of interplay between them in the pressure dependence of their ordering temperatures. From this phase diagram, the interplay between the two ordered states is not obvious. Nuclear quadrupole resonance/NMR studies[27] concluded that the magnetic spins both on ladders and chains are magnetically ordered, although the ordered moment on the ladders is tiny ($0.02\mu_B$ is reported[27]). On the other hand, AF ordering on the ladder can be understood in the presence of mainly unpaired holes but this would seem to be incompatible with the existence of the spin gap[28] which implies that the spin singlet state still exists, and with superconductivity. It seems likely therefore that, at least when superconductivity occurs, the AF order is confined to the chains. It is therefore tempting to look at the compound as two subsystems, with AF order occurring in the chains, and superconductivity in the ladder planes, and basically no interaction between the two. This however ignores the fact that the one-dimensional or 2D description is an oversimplification, and, even if highly anisotropic, in the end both AF order and superconductivity are three-dimensional phenomena. It is therefore almost certain that some interdependencies must exist between the chains and the ladders as discussed by Vuletic *et al.*[25] We therefore look for signs of interplay between the two states. Actually, the pressure dependences of T_{SC} and T_N are qualitatively similar, both showing a pronounced maximum. This might suggest that they are mutually reinforcing phenomena. Although we cannot discard this scenario, the significant difference in the pressure (about 2 GPa) argues against it. On the other hand, a clear indication can be found at 5.8 GPa where the increase in T_N coincides exactly with the very sharp decrease in T_{SC} suggesting some competition between the two phases. We suggest therefore a picture of superconductivity and antiferromagnetism interfering homogeneously over a large pressure window (4–10 GPa), with the specificity of a microscopic decoupling between the ladders and the chains.

IV. CONCLUSION

Through combined ac-susceptibility and ac-calorimetry measurements under pressure on the spin-ladder system $Sr_2Ca_{12}Cu_{24}O_{41}$, we have unambiguously determined the antiferromagnetic and superconducting phase diagram, shedding light on the coexistence of the two phases in this system. Superconductivity is found to exist up to at least 15 GPa, with an optimum pressure for bulk superconductivity of 5–6 GPa, somewhat higher than previously reported values. Superconductivity and antiferromagnetic order are found to coexist over a large pressure window (4–10 GPa) with evidence for only weak competition between the phases. We suggest therefore a picture of superconductivity and antiferromagnetism interfering homogeneously, with the specificity of a microscopic decoupling between the ladders and the chains. We hope this work will stimulate future theoretical studies of superconductivity in spin-ladder systems to address more explicitly this question.

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