K. Alex Müller

Winterthurerstrasse 57, Zürich 8057,
irmamf@bluewin.ch

The Impact of ESR (EPR) on the Understanding of the Cuprates and their Superconductivity*

The impact of nuclear magnetic resonance (NMR) to understanding the classical superconductors was substantial. At the phase transition temperature T_c a peak in the relaxation time of nuclei was observed by Hebel and Slichter in Al, and it could be understood later within the Bardeen-Cooper-Schrieffer (BCS) theory as resulting from the special phase coherence of quasiparticles at the transition [1]. The Slichter peak supported early the BCS theory. After the discovery of the superconductivity in copper oxides NMR was readily detected for the ^{63}Cu and ^{65}Cu nuclei, however no Hebel-Slichter peak was reported to date. This indicated that the superconductivity in these compounds might have a quite different origin. The observed NMR, NQR, their quadrupolar splittings, their relaxation times and intensities were analyzed mainly in terms of a single electronic band following the then popular resonating-valence-bond (RVB) and t-J models. Despite the fact that the Cu^{2+} ion carries an electronic spin as is evidenced by the antiferromagnetism (AFM) of the undoped materials, they remained ESR-silent. This behavior remained unsolved, despite the theoretical efforts of such great spirits as Orbach, Anderson, Chacraverty and others. It became understood by the second EPR experiment to be described below.

Before the above advance an ESR line was discovered by J. Sichelschmidt during his thesis in Bruno Elschner's group in Darmstadt. This center with $S = 1/2$ and axial symmetry along the c-axis of LSCO, in which it was observed, had specific properties of the axial g-values shown in Fig. 1: as a function of temperature they cross near 40 K. It was Boris Kochelaev from the Kazan State University who used a three-spin model for an analytical description [2]: it consists of two Cu^{2+} spins of spin $S = 1/2$ each antiparallel to each other and to the rest of the lattice, plus a hole mainly located on the neighbor oxygens, also with spin $S = 1/2$. The center is stable because the oxygens move out of equilibrium as indicated in an exaggerated way in the upper panel of Fig. 1. Two conformations are possible and there occurs tunneling between them, thus there is a splitting between the energy levels. The two local distortions of the oxygens shown are those of the lifting of the doubly degenerate d(x^2–y^2) orbitals of the Cu^{2+}, the so-called Jahn-Teller (JT) effect.

From the three-spin center there is but one important step to the intersite bipolaron state as introduced by Mihailovic and Kabanov [3]. It occurs by adding a second hole on oxygen orbitals with the antiparalled spin to the first as shown in Fig. 2. The total spin is therefore $S = 0$, thus overcoming the difficulty to move in the AFM lattice which a single polaron with spin has. Bipolarons as such had been proposed earlier by a number of theoreticians but only the intersite Jahn-Teller bipolaron whose model is depicted in Fig. 2 is the true elementary quasiparticle occuring in the copper oxides. A large number of properties of the cuprates can be understood with it: for instance, a quasigap below $T^* > T_c$ occurs due to the formation of the JT bipolarons below T^* upon cooling entering the pseudogap phase. By further lowering the temperature the bipolarons become phase-coherent and T_c. is reached.

The above description appears to belong to a homogeneous system. From the second EPR experiment to be presented hereafter this is not the case even at very low doping: below 6% no superconductivity is present. The EPR experiments were conducted in $La_{1-x}Sr_xCuO_4$, in which a small percentage of Cu^{2+} ions were substituted for Mn^{2+} ions as probes. The EPR spectrum in the latter was monitored as a function of temperature. Two EPR lines were detected: a broad line whose intensity is reduced on cooling and a narrow one which increased substantially. The broad line was shown to result from Mn^{2+} ions coupled magnetically to the AFM lattice. From the analysis the relaxation time of the AFM Cu^{2+} ions could be deduced. It was shown that the microwave energy absorbed by the Mn^{2+} is not directly flowing to the lattice but to the AFM Cu^{2+} ions. In NMR it is the well-known bottleneck effect. From this observation it was inferred that this Cu^{2+} relaxation time is so fast, i.e., the EPR lines of the Cu^{2+} are so broad, that it cannot be detected, thus solving the years-long quest for the "EPR-silent" cuprates [4].

The narrow line has a Lorentzian shape. Its width is independent of the Sr^{2+} doping (up to 6%) and shows no oxygen isotope effect. It was assigned to Mn^{2+} ions sited in metallic-type clusters or stripes, the latter being dynamic, i.e. deforming and moving in the lattice in an intrinsic way. The intensity of this line grows exponentially upon cooling. The activation

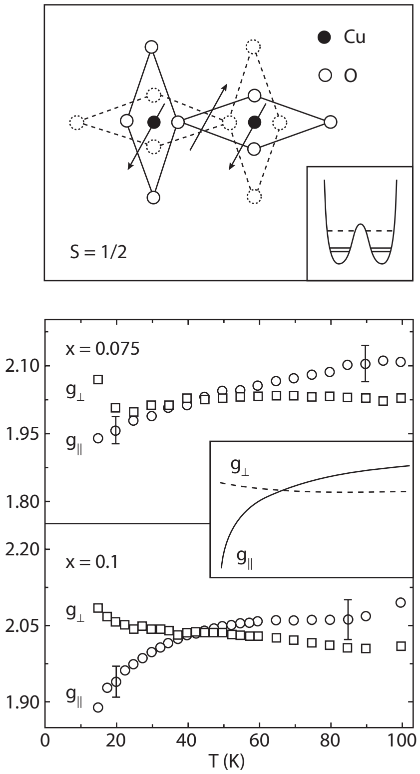

Fig. 1. Upper panel: Three-spin magnetic polaron which is regarded as the EPR-active center in the CuO$_2$ plane. The Jahn-Teller distorted polaron has two degenerate configurations as indicated by the dashed lines. The inset shows the corresponding double-well potential with the excited vibronic states (dashed lines) and the ground state split by tunneling (solid lines). Lower panel: Temperature dependence of the ***g***-factors for two different doping concentrations. The inset shows the results obtained from model calculations based on the three-spin polaron (3SP) of the upper panel [2].

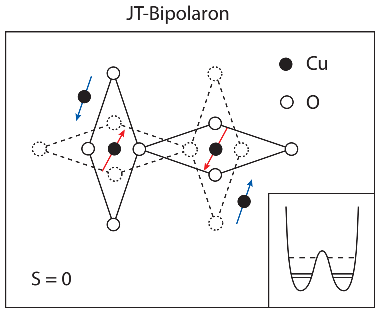

Fig. 2. Schematic representation of the bipolaron [3].

energy DE is independent of the doping and is 460 ± 40 K (Fig. 3). It was concluded that this energy is the one necessary to form the intersite JT bipolaron (Fig. 2) These bipolarons cluster to form metallic aggregates. Their size is limited because they repel each other due to the Coulomb interaction, as impressing simulations of the group of Mihailovic in Ljubliana has demonstrated [1]. With these experimentally obtained parameters the onset of superconductivity at 6% Sr^{2+} doping and the maximum of T_c near 15% were obtained in agreement with the experimental findings [5].

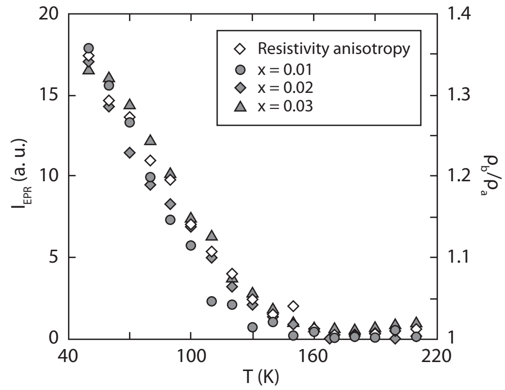

Fig. 3. Temperature dependence of the narrow EPR line intensities in La$_{2-x}$Sr$_x$Cu$_{0.98}$Mn$_{0.02}$O$_4$ [4] and the resistivity anisotropic ratio in La$_{1.97}$Sr$_{0.03}$CuO$_4$ [8].

Furthermore, the formation energy of 460 K lies within that between 100 and 700 K of ab initio calculations by Kochelaev and Safina at the Kazan State University [6]. This span is due to the not sufficiently known electronic correlation energy present in the bipolaron. The independence of E_p on the Sr^{2+} doping up to 6% follows the theoretical paper of Alexandrov, Kabanov and Mott, in which this formation energy was predicted to behave in this way [7]. Ando [8] measured the anisotropy of the magnetoresistance in monodomain LSCO as a function of temperature. He found an exponential increase upon cooling, and as Fig. 3 shows, the increase is the same as the intensity increase of the narrow Mn^{2+} EPR line. Ando concluded from his macroscopic measurements that they resulted from the anisotropy of the stripes present. From the agreement of the macroscopic magnetoresistance and microscopic EPR enhancement the clustering of the bipolarons to stripes follows.

The impact of the two EPR experiments described above on understanding the microscopic origin of the superconductivity in the copper oxides in terms of the intersite JT bipolaronic quasiparticles has been remarkable: The first experiment on the three-spin polaron [9] was leading in a direct way to the bipolarons present in the cuprates, and the EPR of the Mn^{2+} as a probe on the presence of metallic clusters or stripes with the aggregation of these bipolarons at concentrations of hole doping so low that no superconductivity sets in yet. Only at larger concentrations the density of metallic entities gets sufficiently large that phase coherence occurs by tunneling through near insulating AFM regions. At all concentrations an intrinsic heterogeneity is present overlooked by many theories. Finally, it should be noted that this important advance was achieved by the experimental results at the universities of Darmstadt and Zürich on the one side and the deep theoretical insight of Boris Kochelaev at the Kazan State University explaining them on the other side. One might as well compare the advance of these but two experiments with the very large number of NMR results published, which were for a long time interpreted in terms of single band theories, and even more so regarding the expensive work in photoemission. In the latter dispersions of energies versus wavelength are measured. This is valuable in presence of large correlation lengths present as in classical superconductors. However in the doped cuprates with the bipolarons as quasi precursors of the Cooper pairs present, the coherence lengths are on the order of a lattice distance and a description in terms of local deformations and time is more appropriate, as is usually used in EPR.

References

* This article is a slightly up to date extract from a Viewpoint by K. A. Müller, J. Phys. Cond. Matter 19, 251002 (2007)

1. M. Tinkham, Introduction to Superconductivity (McGraw-Hill, New York, 1975) chapt. 2, subsect. 9, p. 55.
2. B. J. Kochelaev, J. Sichelschmidt, B. Elschner, W. Lemor, and A. Loidl, Phys. Rev. Lett. 79, 4274 (1997)
3. V. V. Kabanov and D. Mihailovic, J. Supercond. 13, 959 (2000); D. Mihailovic and V. V. Kabanov, Phys. Rev B 63, 054505 (2001)
4. A. Shengelaya, M. Brun, B. J. Kochelaev, A. Safina, K. Conder, and K. A. Müller, Phys. Rev. Lett. 93, 017001 (2004)
5. D. Mihailivic, V. V. Kabanov, and K. A. Müller, Europhys. Lett. 57, 254 (2002)
6. B. Kochelaev, A. M. Safina, A. S. Shengelaya, K. A. Müller, and K. Conder, Mod. Phys. Lett. B 17, 415 (2003)
7. A. S. Alexandrov, V. V. Kabanov, and N. F. Mott, Phys. Rev. Lett. 77, 4796 (1996)
8. Y. Ando, Kouji Segawa, Seiki Komiya, and A. N. Lavrov, Phys. Rev. Lett. 88, 137005 (2002)
9. The existence of the 3 SP, Fig. 1, was deduced early by V. J. Emery and G. Reiter, Phys. Rev. B 38, 4547 (1988). It has likely a higher energy than the bipolaron, Fig. 2.