Progress in High Temperature Superconductivity – Vol. 31

Proceedings of the XII Winter Meeting on Low Temperature Physics

SUPERCONDUCTING CERAMICS

Vista Hermosa, Morelos, México 13 – 16 January 1991

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THE IMPORTANCE OF BEING N-TYPE

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ABSTRACT

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* *On sabbatical from the IBM Almaden Research Center, San Jose, California, USA.*

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integrations of dyad products of the group velocity (i.e., dispersion in the energy vs. quasimomentum band structure) over the Fermi surface which in principle could be dominated by small regions of high curvature. This situation is unlikely given the small carrier concentration in high-Tc superconductors relative to most other metals, so that the carriers are very likely confined to band extrema where the effective mass approximation holds and an unambiguous sign can be attached to the carriers. More uncertain is whether band overlap occurs, resulting in electron-hole pockets in which electrons dominate the normal state, yet holes still form the paired state. If, in the p-type compounds, holes reside in O 2p - Cu 3d hybridized valence bands, and, for the n-type case the electrons transport in the Cu 4s conduction band, the most consistent interpretation of core level spectra obtained for each material class [9], then band overlap is improbable given the usual magnitude of the energy gap in transition metal oxides between these two bands. Thus it is prudent to conclude at the present time that charge reciprocity in high temperature superconductors exists and must be accomodated by any theory put forward to describe these materials.

The existence of charge symmetry does not imply structural or chemical symmetry between n- and p-type high-Tc compounds such as found, for example, in covalent semiconductors. Important differences in both crystallographic structure and chemical preparation arise. In Fig. 1 we compare unit cells of the two compounds and the respective doping sites. The principal difference is the coordination of the lanthanide cation with respect to the nearest neighbor oxygen anions. In La_2CuO_4, there is Cu-O plane apical oxygen which in Nd_2CuO_4 moves to its observed position on the unit cell face from its former edge location. Apparently this lack of an apical oxygen is the key structural feature which permits electron delocalization. The host structure choice

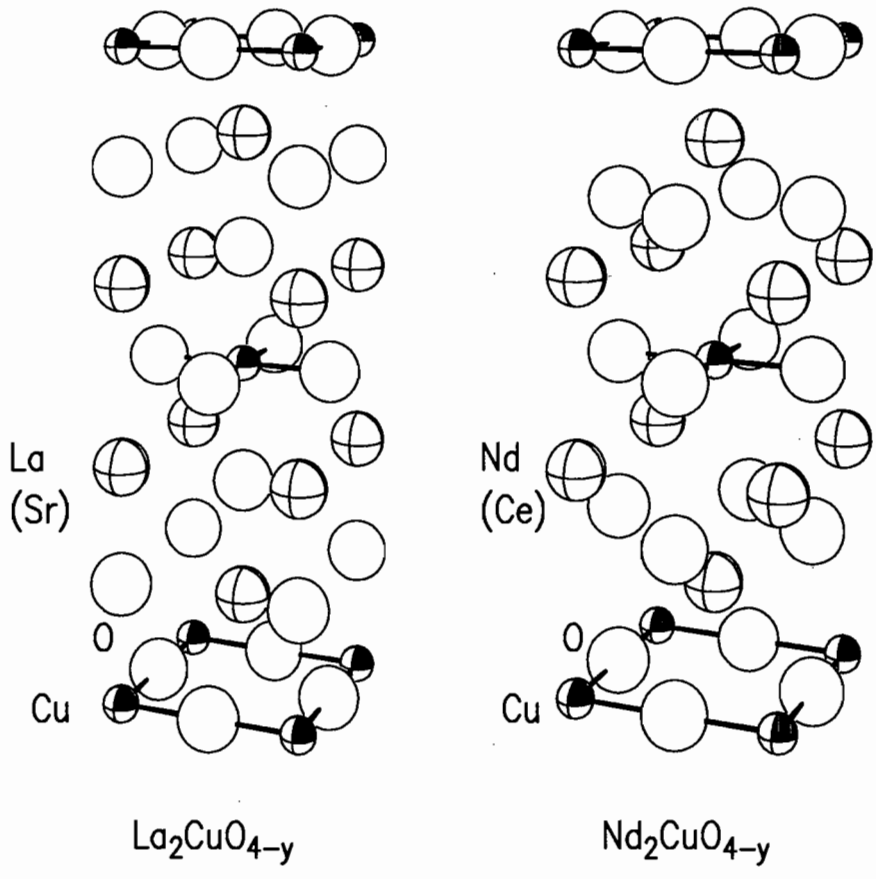

Fig. 1. Unit cells of La_2CuO_{4-y} and Nd_2CuO_{4-y}. Note the absence of apical oxygens in the latter structure.

possessing this feature for potential n-type superconductivity has been largely restricted to the Nd_2CuO_4 class, inasmuch as all other Cu-O planar perovskite structures have at least one apically coordinated plane and appear p-type, with any accompanying non-apical planes "dead" with regard to transport; e. g., the middle Cu-O layer in the 2223 structure. As has been pointed out [10], the single exception was the "infinite layer" compound $Ca_{0.86}Sr_{0.14}CuO_2$, which was discovered by Siegrist [11] and coworkers in mid-1988. Recently, two structural isomorphs, $Sr_{0.86}(Nd,Pr)_{0.14}CuO_2$, were synthesized by Smith, et al., [12] and both were found to have superconducting transitions near 40K. By unit cell charge count, the substitution of trivalent Nd or Pr should result in excess negative charge and thus an n-type normal state. However, it was found by the authors of ref. [12] that their preliminary measurements of the Hall constant were positive, a finding they speculate is due to minority phases in their samples. If subsequent research reveals $R_H < 0$, especially near the transition temperature, as additional confirmation of charge counting, then the discovery of n-type superconductivity at 40K is an important advance in at least two aspects. Firstly, unlike the Nd_2CuO_4-based systems, the "infinite layer" compounds do not require direct reduction processing. On the contrary, both the precursor compounds and the final phase are obtained via high pressure oxygen processing. However, when more is known about the microstructure, it may turn out that oxygen vacancies indeed exist. Secondly, and most critically, the discovery of this new high-Tc material demonstrates that transition temperatures as high as those obtained in Sr-doped La_2CuO_4 can be reached in systems without apical oxygens, thus proving that the existence of this ion is not a necessary condition for truly high temperature superconductivity.

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several years the high-Tc discoveries, contained a table of Seebeck coefficients for the isoelectronic series Ln_2CuO_4, where Ln was La or a trivalent rare earth ion. All, except La_2CuO_4, were negative in sign at room temperature. It was thus natural to attempt substituting a tetravalent cation on the lanthanide position in one of these latter compounds. This step was taken by Tokura and co-workers [4] in late 1988 when they synthesized Ce-doped Nd_2CuO_4. However, metallic conductivity, and hence superconductivity, was not obtained until a further crucial step was taken...it was necessary to anneal the samples in a reducing atmosphere and then quench to room temperature. It was also found that Th-doping worked and that Sm_2CuO_4 and Pr_2CuO_4 also provided a suitable host system. Charge counting assuming normal ionic state values resulted in net negative charge per unit cell, which was upheld by temperature dependent measurements of the Hall constant [5] and thermoelectric power [6], both revealing a negative sign down to the onset of superconductivity. Other early experiments [7] indicated that the signs of both these effects went positive before the superconducting state was reached, thus suggesting that these new materials were hole superconductors as well, but it is now nearly certain that this behavior was caused by inhomogeneous doping due to the slow diffusion of the tetravalent species in the host material in the case of ceramics [8], or, non-uniform distribution of oxygen vacancies in the case of single crystals.

The consistently negative sign of the thermopower and Hall constant, supported by the expected excess negative charge from the ionic states involved, are compelling, although not conclusive, arguments for electron pairing in the superconducting state. There is always the possiblity, albeit small, that multiband effects and pathological Fermi surface topology could complicate this straightforward interpretation. Both of these carrier-sign-sensitive measurements in metals involve complex

integrations of dyad products of the group velocity (i.e., dispersion in the energy vs. quasimomentum band structure) over the Fermi surface which in principle could be dominated by small regions of high curvature. This situation is unlikely given the small carrier concentration in high-Tc superconductors relative to most other metals, so that the carriers are very likely confined to band extrema where the effective mass approximation holds and an unambiguous sign can be attached to the carriers. More uncertain is whether band overlap occurs, resulting in electron-hole pockets in which electrons dominate the normal state, yet holes still form the paired state. If, in the p-type compounds, holes reside in O 2p - Cu 3d hybridized valence bands, and, for the n-type case the electrons transport in the Cu 4s conduction band, the most consistent interpretation of core level spectra obtained for each material class [9], then band overlap is improbable given the usual magnitude of the energy gap in transition metal oxides between these two bands. Thus it is prudent to conclude at the present time that charge reciprocity in high temperature superconductors exists and must be accomodated by any theory put forward to describe these materials.

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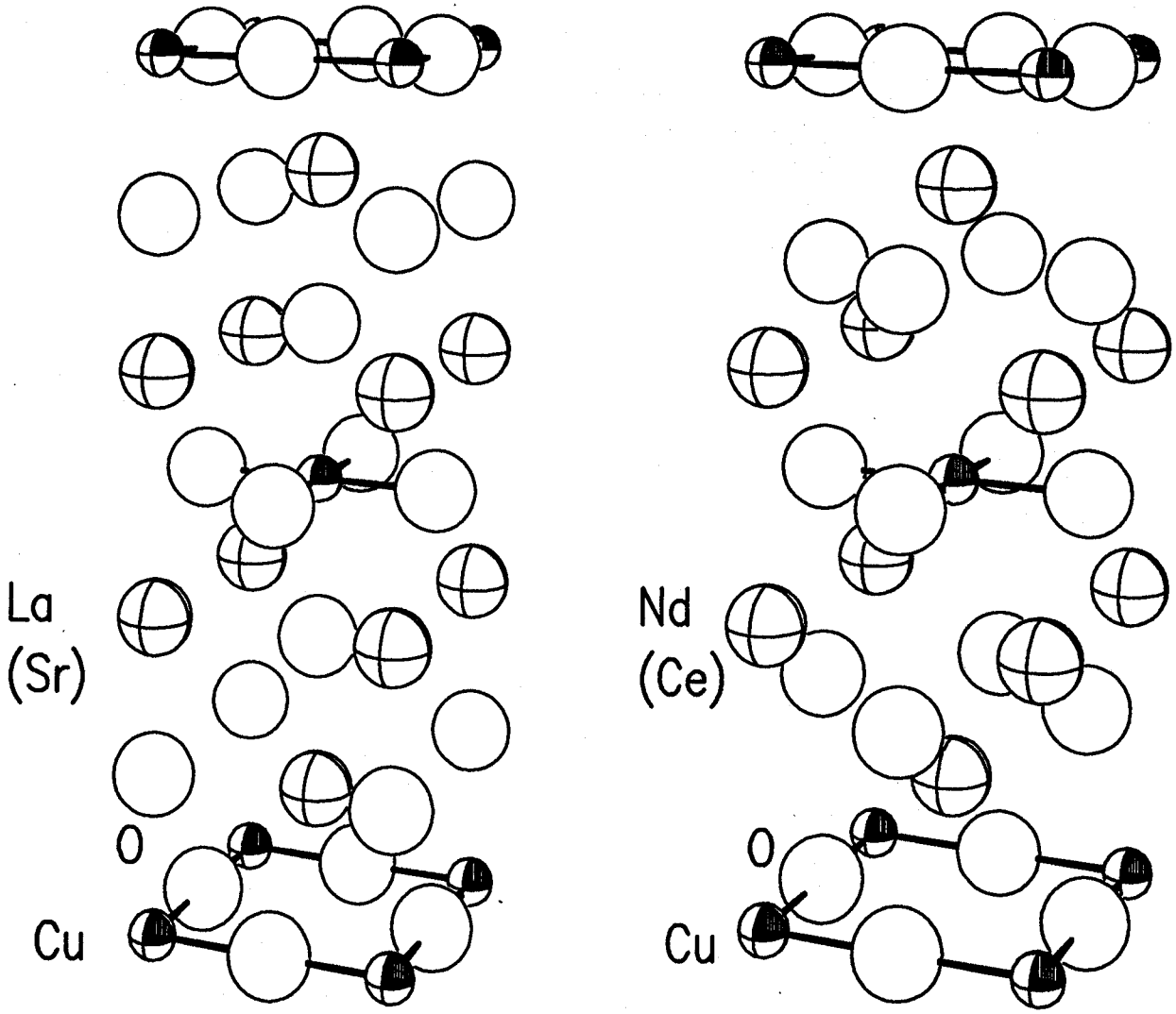

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