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ELECTRON DIFFRACTION STUDY OF $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ E. G. MOSHOPOULOU^{a,*}, J. D. THOMPSON^a, Z. FISK^b and J. L. SARRAO^a^aCondensed Matter and Thermal Physics Group, Los Alamos National Laboratory, Los Alamos, NM 87545, USA^bNational High Magnetic Field Laboratory and Florida State University, Tallahassee, FL 32306, USA

Abstract— $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ has been investigated by electron diffraction and high resolution electron microscopy at room temperature. Ordering between Li and Cu cations is nearly perfect within the (**a**, **c**) plane but there is disorder between Cu and Li cations along the **b** axis. The detection of weak reflections which violate the C centering of the *Cmmm* space group (initially proposed [1] for this compound), indicates that the crystal symmetry allows lattice distortions. The evolution of the structure as a function of the temperature may lead to the determination of whether the low energy singlet–triplet excitation, found in NMR/NQR studies, is coupled with lattice distortions. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: C. electron diffraction, D. lattice distortions, crystal symmetry

1. INTRODUCTION

The evolution of the physical and structural properties of La_2CuO_4 with hole doping into Cu–O planes, via Sr^{2+} substitution for La^{3+} , has been studied extensively; however, several aspects of the nature of the doped hole and the loss of Cu's magnetic moment remain poorly understood. Recently, we started to study the effect of doping into the Cu–O plane itself through Li^+ substitution for Cu^{2+} . In $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$, Li and Cu ions form an ordered superlattice in which all Cu ions are surrounded by four in-plane Li ions and thus, isolated CuO_4 clusters are created [1]. Interestingly, when Li^+ is substituted for Cu^{2+} in La_2CuO_4 , which is an antiferromagnetic insulator ($T_N \cong 325$ K), the Néel state is destroyed and Cu's magnetism completely disappears at $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$, which is a diamagnetic insulator [2]. The material formally contained Cu^{3+} and therefore the diamagnetism is unexpected. It appears that the holes brought into the lattice by the Li^+ , couple to form a singlet with the Cu^{2+} spin, reminiscent of the Zhang–Rice singlet picture [3], but here, on an ordered lattice with apparently immobile holes. NMR/NQR studies [4] suggest that the Cu's magnetism disappears because a bound state is formed between Cu–3d electrons and the hole donated by Li^+ . The formation of this bound state (still poorly understood), is eventually consistent with a strong coupling of electronic and structural degrees of freedom and, therefore, may implicate distortions in the underlying crystal lattice. Indeed, theoretical studies [5, 6] addressed this question and found that the Cu–O (apical and in-plane) and Li–O bond lengths are not in agreement with the ones obtained from the initial

structural investigation of the material [1]. Motivated by these results, we have studied thoroughly the crystal structure of this material, by electron and neutron diffraction, to determine the degree of Li/Cu ordering, as well as to search for possible lattice distortions and their evolution as a function of the temperature. This paper reports only the results of our room temperature, electron-diffraction investigation.

2. ELECTRON DIFFRACTION STUDY

The first structural determination of $\text{La}_2\text{Li}_x\text{Cu}_{1-x}\text{O}_4$ was carried out at 5 K by powder neutron diffraction [1]. An ordering between Cu and Li cations was observed for $x \approx 0.5$, which led to a supercell symmetry *Cmmm*. Because powder neutron diffraction can only partially detect order/disorder effects, this study could not determine accurately the type of eventual disorder between Cu/Li; in addition, it did not investigate the degree of ordering between the Li and Cu ions at room temperature.

The aim of our electron-diffraction experiments was to investigate eventual static and/or dynamic order-disorder and/or superlattice effects in $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and therefore to determine whether in this compound the CuO_2 clusters are confined by four Li neighbors. In other words, the question addressed here is whether the doped hole is confined by the four Li neighbors and therefore whether this material allows (in contrast to the other cuprates) the study of the magnetic behavior of the doped hole in the absence of the confounding contributions of the antiferromagnetically correlated copper moments.

Transmission electron-microscope (TEM) samples were prepared by crushing powder in anhydrous methanol and dispersing it onto 1000-mesh TEM grids. Electron-diffraction patterns and high resolution

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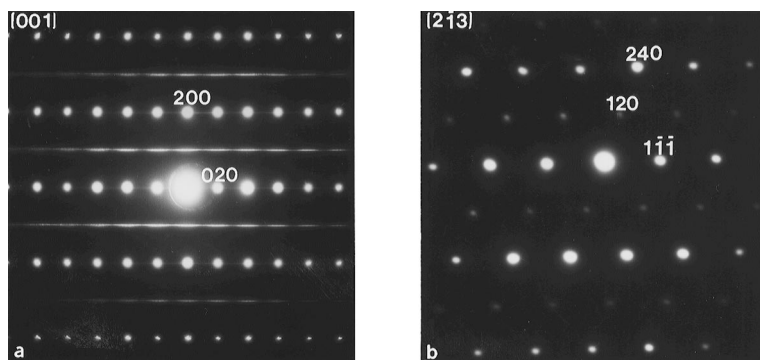


Fig. 1. Selected area diffraction patterns of $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$; (a) $[001]$ zone axis pattern showing the diffuse intensity streaks due to disorder between Li and Cu along the \mathbf{b} axis, and (b): $[2\bar{1}3]$ zone axis pattern exhibiting satellites of type $h+k \neq 2n$.

electron-microscope (HREM) images were taken using a Philips CM30 Electron Microscope operating at 300 W. Besides Bragg reflections, the presence of pronounced diffuse scattering along the $\{010\}$ direction was readily observed. The distribution, intensity and contrast of the Bragg reflections and diffuse intensity were not modified during the observation, so we can exclude the idea that electron-beam irradiation generated any sample damage and associated disorder. The geometry of the diffuse intensity was studied by tilting experiments around \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* directions. An example is given in Fig. 1(a). All diffraction patterns were indexed based on the orthorhombic $Cmmm$ unit cell: $a = 5.267(1) \text{ \AA}$, $b = 13.167(1) \text{ \AA}$ and $c = 5.267(1) \text{ \AA}$.

The presence of diffuse intensity in the diffraction patterns, strictly confined to a geometric locus, indicates that there is, besides the Bragg reflections, diffuse intensity confined in a surface in the reciprocal space; the intersections of this surface with the reciprocal planes results in the observed diffuse intensity contours in the diffraction patterns. It has been shown [7] that this particular distribution of the scattering intensity, i.e. Bragg + modulated diffuse intensity, stems from diffraction by a structure, periodic in average, but subject to the following conditions: substitutional disorder between two atoms of different charges is allowed; this disorder is restricted on the Bravais lattice and; the local order is perfect. The existence of short-range order and the requirement that electrical neutrality of the crystal should be satisfied locally imply that the structure consists of identical atom clusters having the macroscopic composition of the crystal. The theory of invariant clusters [7] allows us to determine the type of disorder in the cluster from the distribution of the diffuse intensity in reciprocal space and vice versa. This theory is basically summarized in the following two equations:

$$\sum_k \omega_k \exp(2i\pi \mathbf{g} \cdot \mathbf{r}_k) = 0,$$

which is the equation of the surface of the diffuse

intensity in reciprocal space, and:

$$\sum_k \omega_k \bar{\sigma} = 0,$$

which gives the equation of the occupation operators in the cluster (ordering relation).

In the above equations, each atom, k , forming the cluster is defined by a vector $\mathbf{r}_k = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$, whose origin is related to the cluster; $\mathbf{g} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is the reciprocal space vector, where h , k and l can take continuous values; ω_k is the Fourier coefficient; and $\bar{\sigma}_k$ is the operator of the occupation of site k .

For the case of $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$, the invariant cluster chosen is shown in Fig. 2. We assume the following model of disorder: Cu and Li are perfectly ordered in the (\mathbf{a}, \mathbf{c}) plane, but out of plane, the site A $(0, 0, 0)$ is occupied by either Cu or Li. The sublattice (Cu, Li) in this cluster is determined by the vectors: $(0, 0, 0)$; $(\pm \mathbf{a}/2, \mathbf{b}/2, 0)$; $(0, \pm \mathbf{b}/2, \mathbf{c}/2)$; $(0, \pm \mathbf{b}/2, -\mathbf{c}/2)$; $(\pm \mathbf{a}/2, -\mathbf{b}/2, 0)$. By applying this model in conjunction with the two

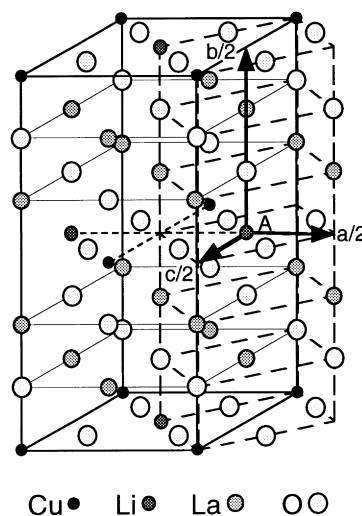


Fig. 2. Schematic of the crystal structure of $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ and of the invariant cluster (broken lines) having the macroscopic composition of the crystal.

equations given above, we deduce the equation of the surface of diffuse intensity in reciprocal space:

$$\cos\pi h \cos\pi k + \cos\pi l = 0$$

The calculated intersections of this surface with the reciprocal planes are in very good agreement with the experimental diffraction patterns. This observation means that in $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$, the Cu and Li ions form an ordered sublattice in the (**a**, **c**) plane, but they are disordered along the **b** axis. To distinguish between static and dynamic disorder, HREM images were taken with the central beam and the first shell of basic spots, also including diffuse streaks. These images only reproduce the type of disorder determined by the diffraction patterns and they do not reproduce the average of the atom columns. This observation implies that the nature of disorder is static.

Indexation of other selected area diffraction patterns show weak reflections with $h + k \neq 2n$; these reflections are expected to be extinct in the *Cmmm* space group. An example is given in Fig. 1(b). These extra peaks cannot be due to multiple diffraction, because no vector combination of those allowed by the C-centering reflections, $h + k = 2n$, can lead to reflections with $h + k \neq 2n$. Also, these extra reflections cannot be explained as intersections of the diffuse intensity streaks with the reciprocal planes to which they belong. Additionally, attempts to attribute these extra peaks to the presence of twin boundaries in the grains were unsuccessful. The observation of these reflections suggest that the actual space group symmetry of the material is lower and it may allow lattice distortions.

3. CONCLUSION

This study of the $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$, through the reconstruction of reciprocal space from the electron-diffraction patterns, have revealed two new structural features. First, the ordering between Li–Cu within the (**a**, **c**) planes is nearly perfect but there is only weak correlation between successive (**a**, **c**) planes. Second, the crystal structure (based on main and superlattice reflections) has lower than *Cmmm* symmetry; this lower symmetry eventually allows distortions which could not been identified within the *Cmmm* description. The detailed determination of these distortions and their evolution as a function of the temperature will be given elsewhere.

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