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Calculated surface properties of La_2CuO_4 : implications for high- T_c behaviour

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Abstract. Calculations are reported of the structure, dynamics and stoichiometry of the surfaces of tetragonal La_2CuO_4 with implications for the surface and inter-granular conductivity and flux pinning.

1. Introduction

The composition, structure and dynamics of the surfaces of high- T_c materials play a distinctive role in controlling the surface conductivity, inter-granular weak links and possibly the magnetic flux pinning. In common with what is found for most ceramic materials, experimental surface data for these materials at the atomic level are difficult to obtain and hence sparse. As a result, they remain poorly understood. However, recent atomistic simulations of the normal-state bulk properties and defect chemistry of these materials [1, 2] have proved sufficiently encouraging to prompt corresponding studies of the surfaces. Accordingly, this paper presents preliminary results for tetragonal La_2CuO_4 . Included in this report are the surface structures, energies, phonon densities of states and stoichiometries.

2. Theoretical methods

The theoretical methods used here are essentially those used in recent studies of bulk properties [1, 2]. The calculations are formulated within the framework of an ionic model and are based on two-body electron gas potentials [3] which embrace the Dick–Overhauser shell approach to ionic polarisation [4]. The essential feature of the lattice simulations is the relaxation of the atomic positions and ionic polarisation in the vicinity of the surface to the point at which there is zero force on each of these atoms. Thus the surface structures reported here correspond to *fully relaxed* atomic positions, defect energies calculated with respect to fully relaxed defective and non-defective surfaces and surface-excess phonon densities of states obtained from the lattice dynamics of fully relaxed semi-infinite slabs consisting of 20 layers of ions.

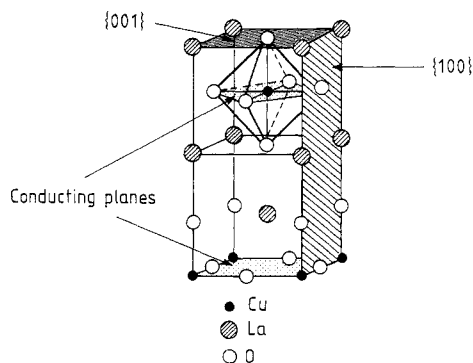


Figure 1. The $\{001\}$ and $\{100\}$ surfaces and conducting planes in La_2CuO_4 .

Table 1. Calculated surface energies and dipole and residual bulk potentials for La_2CuO_4 .

| Surface | Energy (J m^{-2}) | | Surface dipole (au) | Bulk potential (V) |
|-------------------------------------|------------------------------|---------|---------------------|--------------------|
| | Unrelaxed | Relaxed | | |
| $\{001\}$ La_2CuO_4 | 1.7 | 1.3 | -0.001 | -0.2 |
| $\{100\}$ La_2CuO_4 | 4.6 | 1.3 | 0.006 | 1.0 |

3. Results

The two lowest-index surfaces of tetragonal La_2CuO_4 are the $\{001\}$ and $\{100\}$: they are shown in figure 1. The $\{001\}$ surface is essentially LaO , whereas the $\{100\}$ surface consists of the full molecular unit La_2CuO_4 . The corresponding surfaces in the orthorhombic phase are $\{001\}$ and $\{110\}$, with near identical structures. The calculated energies are given in table 1. In the absence of surface relaxation the $\{001\}$ surface would dominate the crystal morphology to the exclusion of the necessary surfaces for inter-granular conductivity. However, extensive relaxation of the $\{100\}$ surface, unlike that of the $\{001\}$ surface, leads to approximately equi-energetic surfaces and with this important implications for the superconductivity of polycrystalline material. The presence of the $\{100\}$ surface also influences the residual bulk potential due to the surface dipole and consequently the bulk electronic energy levels and space-charge characteristics. Details of the $\{100\}$ surface relaxation are shown in figure 2. The principal features are atomic displacements of up to 0.4 \AA perpendicular to the surface and 0.2 \AA within the surface planes and also displacements of up to 0.06 \AA six layers into the bulk. Thus the extent of the $\{100\}$ surface relaxation into the bulk is comparable to the coherence length in the superconducting a -plane ($\approx 15 \text{ \AA}$) and hence a possible source of flux pinning in La_2CuO_4 . Atomic displacements at the $\{001\}$ surface are calculated to be at least an order of magnitude less than those at the $\{100\}$ surface.

If, as Bardeen [5] has suggested, it is likely that phonons are involved to some extent in pairing in high- T_c materials, the lattice dynamics of the appropriate surfaces could play a significant role in controlling both surface and inter-granular conductivity. Figure 3 shows the surface-excess phonon density of states for the $\{001\}$ surface of La_2CuO_4 compared with that for the bulk. Two points in particular emerge. The first is the presence of strong surface modes at $\approx 15, 40, 46$ and 53 meV ; the second, and perhaps

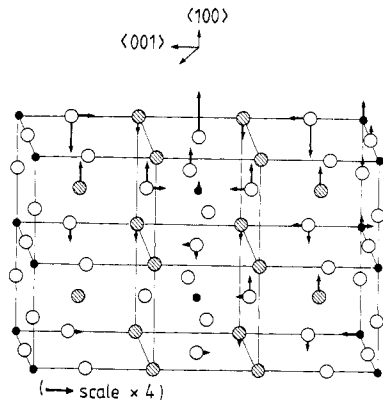


Figure 2. The calculated relaxed structure of the $\{100\}$ surface of La_2CuO_4 .

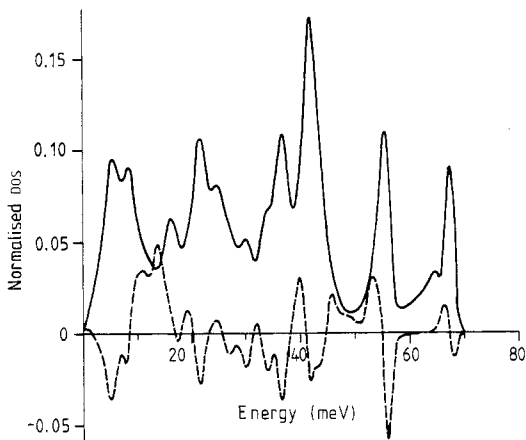


Figure 3. The calculated bulk (—) and $\{001\}$ surface-excess (---) phonon densities of states of La_2CuO_4 .

more significant, is the diminution in intensity of the bulk mode at ≈ 10 meV which corresponds to the symmetric in-plane breathing mode of four oxygen atoms in the CuO_2 plane. There is both experimental [6] and theoretical [7] evidence for electron-phonon coupling in high- T_c materials via this mode in the bulk, which suggests a decrease in coupling by this mechanism at the surface. Further theoretical evidence, not reported here in detail, indicates that a similar decrease in the intensity of the 10 meV mode occurs at the $\{100\}$ surface. Surface defect calculations find (small-polaron) Cu holes (Cu^{3+}) to be more stable at the $\{001\}$ surface than in the bulk by ≈ 0.5 eV and O holes (O^-) more stable by ≈ 1.0 eV. The oxidation and impurity doping characteristics of this surface are calculated to be similar to that of the bulk, with La vacancies and holes as the majority defects, O vacancies unstable with respect to holes and Sr and Ba substitution of the La sublattice with decreased solution energies, which suggests surface enrichment at high temperatures. The defect characteristics of the $\{100\}$ surface are predicted to be quite different with Cu holes less stable and O holes more stable than in the bulk and O vacancies stable with respect to holes. Furthermore, preliminary results suggest that Cu substitution by Sr is favoured, rather than La substitution as in the bulk. Thus the ($\{001\}$) surface conductivity of La_2CuO_4 is predicted to be largely unaffected by the point defect structure whereas the ($\{100\}$) inter-granular conductivity is predicted to be severely limited by the oxidation and impurity substitution characteristics.

4. Conclusions

The principal conclusions of this preliminary report are as follows. Firstly, extensive lattice relaxation occurs at the {100} surface of La_2CuO_4 , unlike the case for the {001} surface which is close to the bulk termination. This leads to surfaces of approximately equal energy and from this the appropriate morphology for both surface and inter-granular conductivity. Secondly, the calculated surface-excess phonon densities suggest a decrease in electron-phonon coupling at both surfaces with consequent effects on the surface and inter-granular superconductivity. Finally, the magnitude of the atomic displacements and the defect characteristics of the {100} surface suggest that they might be the principal causes of weak links in La_2CuO_4 and possibly responsible for flux pinning at free surfaces and grain boundaries.

References

- [1] Allan N L and Mackrodt W C 1988 *Phil. Mag.* A **58** 555
- [2] Allan N L, Lawton J M and Mackrodt W C 1989 *Phil. Mag.* B **59** 191
- [3] Mackrodt W C and Stewart R F 1979 *J. Phys. C: Solid State Phys.* **12** 431
- [4] Dick B G and Overhauser A W 1958 *Phys. Rev.* **112** 90
- [5] Bardeen J 1988 *Mater. Res. Soc. Symp. Proc.* **99** 27
- [6] Ramirez A P, Batlogg B, Aeppli G, Cava R J, Reitman E, Goldman A and Shirane G 1987 *Phys. Rev. B* **35** 8833
- [7] Weber W 1987 *Phys. Rev. Lett.* **58** 1371