ELECTRONIC STRUCTURE STUDIES OF HIGH-T<sub>c</sub> PEROVSKITES AND RELATED MATERIALS*


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INTRODUCTION

In recent months the positron annihilation technique has assumed a useful role in the elucidation of the physics of the new high-critical temperature superconductors.1,2 Unfortunately, electronic structure interpretations of ACPAR measurements have been somewhat controversial.3,4 Elsewhere, we have successfully modeled the anisotropy in the ACPAR data for La$_2$CuO$_4$ using a LCAO-MO model and a localized-ion scheme within the IPM.3 We shall briefly review those results below and offer a justification for our method and its limitations. Its relative success suggests the need for positron annihilation investigations of related systems and the need for careful interpretations of the results. We present here preliminary results from such a study of NiO.

Wachs et al. recently performed 2D-ACPAR experiments upon nearly defect-free crystals of La$_2$CuO$_4$.3 The data showed: i) no discernible structure at the Brillouin zone boundaries and highly isotropic angular correlation spectra for various crystalline orientations, much as was reported for 1D-ACPAR studies for other oxides such as NiO5; and ii) well-defined residual anisotropies in the positron-electron annihilation two-photon momentum distribution (TPMD) angular correlation curves along various directions.

Interpretation of the results of Ref. 3 was guided by the following experimental results. Photoemission, charge transport, magnetization and EELS measurements pointed out details of the electronic structure that could not be explained by the band-theoretical calculations of Mattheis, Freeman, and others.6 In particular, these results show La$_2$CuO$_4$ to be insulating, antiferromagnetic and sharing many other properties of a highly correlated electron system. Thus Wachs et al. started from the viewpoint where valence electrons are assumed to be correlated so strongly that they preferably form localized states rather than itinerant Bloch states.

2D-ACPAP STUDIES OF La$_2$CuO$_4$

The localized-cluster LCAO-MO model adopted in Ref. 3 is a reasonable scheme in this approximation, as it starts from an ionic picture and allows covalency overlap to take place between the Cu and oxygen atoms comprising a constituent copper-oxygen octahedron of this system. The positronic wavefunction used here is derived from a simple localized-ion model8 but reproduces the essential details of more sophisticated calculations.1,3,7 Finally, the TPMD results obtained from this scheme are qualitatively similar and compare favorably to the experimental results. They suggest that an appropriate analysis of the electronic structure might begin with states of a localized character.

We have recently added an additional element to our analysis by applying the formalism of Lock, Crisp, and West8 (LCW) in an attempt to recover the two-dimensional electron-momentum density (EMD) for selected geometries of the measurements of Ref. 3. Figure 1 shows an isodensity contour plot of the approximate 2D-EMD for La$_2$CuO$_4$. The data are taken from Ref. 3; the integration axis is [001] and the Brillouin zone of the twinned, face-centered orthorhombic crystal sample has been referred to the bct lattice, with a = 3.8011, c = 13.149 Angstroms. The
minimum value is 98\% of the maximum, which is close to the constant contribution expected from filled bands\cite{9}. We believe positronic wavefunction effects are responsible for the 2\% variation. Thus, our original statement (Ref. 3) that our La$_2$CuO$_4$ ACPAR data shows no obvious indications of a Fermi surface and itinerant Bloch states is confirmed.

We have studied a related system, NiO, to gain additional insight. Transition-metal monoxides such as NiO are similar to some of the high-\text{T}_c\text{ perovskites}, in that they are antiferromagnetic (Mott-Hubbard) insulators in which the implanted positron preferentially samples similar chemical constituents. Furthermore, it is reasonable to view systems such as these as lattices of nearly localized ions\cite{1,3,5}, with small charge-density deformations due to covalency and crystal-field effects (as in the case of NiO; see Ref. 9).

**2D-ACPAR STUDIES OF NiO**

The NiO specimen used for these measurements was grown at Argonne National Laboratory. Prior to the measurement, the crystal was cut into two identically oriented sections and polished to remove surface defects. Positron lifetime measurements showed a single bulk lifetime of 149\pm 1\ ps between 4 and 285 K.

The two NiO sections were oriented in approximate registry (\pm 1°) and "sandwiched" about a \textsuperscript{22}Na source. The sample-source assembly was cooled to 13K during the course of these experiments. About 41 million counts were collected for each of two momentum integration directions along the <100> and <110> fcc crystalline axes using a square 256x256 matrix with a bin width of 0.208 mrad (-10\% counts peak channel). We estimate the momentum resolution of our apparatus (including the effects of positron wave function thermal broadening) to be about 0.5 x 10^{-3} me.

We obtain the same qualitative results for the NiO as described for La$_2$CuO$_4$ above and in Ref. 3. There is no obvious evidence of a Fermi surface or itinerant Bloch states in the data. Small anisotropies (-10\%) in the substantially "core-like" 2D-ACPAR distribution can be readily modeled using the LCAO-MO model and localized-ion scheme of Refs. 3 and 5. The theory and experiment are in favorable, qualitative agreement. For example, we compare the experimental (theoretical) residual anisotropies in Fig. 2 (top) for the NiO <110> integration direction.

We have also applied LCW to the data of Fig. 2 and to data taken for the <100> crystalline integration direction (not shown). The results are shown in Fig. 3. Again, the maximum-to-minimum variation is

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**Figure 1.** Isodensity contour plot of an approximate 2D-EHD for La$_2$CuO$_4$. The integration axis is [001]. The crystalline axes have been referred to the body-centered tetragonal lattice. The plot is of one projected Brillouin zone in the basal plane. Maximum-to-minimum variation is -2\%, and values below the average have been highlighted.

**Figure 2.** Experimental (top) and theoretical (bottom) plots of the residual anisotropy surfaces for NiO ACPAR data, computed by subtracting annular radial-averaged reference values from the original 2D-distributions. Points outside the outermost annuli have been set to zero. The integration axis is <110>. The values of $p_x$, $p_y$ range between ±26.1 mrad.
about 2% of the average EMD. These results are consistent with the known insulating behavior and calculated band structures for NiO (see, for example, Ref. 9). Since there is no known Fermi surface for this system, we believe the residual differences are significant, but probably due to positron wavefunction effects.

CONCLUSIONS

We have performed 2D-ACPAR measurements on La$_2$CuO$_4$ and NiO. Both of these systems share common physical properties. The ACPAR results also show a suggestive similarity. Firstly and significantly, the ACPAR distributions are very isotropic, with small anisotropic deviations on the order of 10% of the total counts. It is not possible to clearly discern a Fermi surface in either set of data, nor is it possible to identify any features with the symmetry and periodicity of the crystalline reciprocal lattices.

On the other hand, attempts to model both systems by starting with a localized ionic picture and allowing covalency overlap to take place among the atoms comprising an isolated metal atom-oxygen octahedral cluster have proven successful. This result suggests that it might be appropriate for analyses of the electronic structure for high-$T_c$ perovskites to begin with the ansatz of localized electronic states. This approach has worked very well for the transition-metal monoxides.

Finally, application of the LCW formalism to data from both systems yields a result very close to filled-band behavior. We believe the deviations from the latter are significant, but that they originate from positronic wavefunction mixing of the electronic states and not from a Fermi surface. More detailed investigations of the positronic wavefunction in systems such as these is required to clarify this point. In the meantime, the qualitative similarities between our LCW results for NiO and La$_2$CuO$_4$ suggest that one should take care in the application of the LCW formalism and the interpretation of the results for these materials.

REFERENCES

4) Tanigawa, S., et al., unpublished.