Superconductivity in a Spin-Ladder Cuprate

Schön *et al.* (*1*) claimed to have shown that a two-dimensional structure is not needed to support cuprate superconductivity. Based on the references for the structure of the film provided in their article, however, we believe that this conclusion is premature.

In their report on the field-effect-induced modulation of transport properties in thin films of the spin-ladder compound $[CaCu_2O_3]_4$, Schön *et al.* found superconductivity at high-doping levels and argued that the finding bore out the theoretical prediction that holes doped in spin ladders could pair and superconduct. The experimental discovery of superconductivity in a spin ladder would indeed, as Dagotto (*2*) pointed out, constitute a significant result. For that reason, it is essential to determine experimentally that the superconductivity measured as a function of an applied gate voltage in fact originates from a spin-ladder-type structure.

There are two levels of concern when trying to pin the observed field-effect-induced superconductivity to a spin-ladder structure: (i) Because the field effect is an interface phenomenon, the precise condition of the interface represents an obvious concern. In other words, one must ask, What is the chemical (intrinsic doping level) and structural nature of the "active" channel? This information is very hard to establish, but it must be taken into consideration when interpreting the results. (ii) More fundamental is the concern over whether the bulk structure and composition of the $[CaCu_2O_3]_4$ film is indeed that of a spin ladder. It is this basic issue—the verification that the structure and composition of the film contains the necessary arrangement of Cu and O to make a spin ladder—that is the focus of this comment.

The work of Deville Cavellin *et al.* (*3*) regarding the structural and chemical nature of the $[CaCu_2O_3]_4$ film, referenced by Schön *et al.*, did not show an unambiguous analysis of the film's structure. Deville Cavellin *et al.* reported a series of 12 peaks for the film based on x-ray diffraction, and from those data they generated a unit cell. Most of the experimental peaks corresponded to possible reflections from this specified unit cell; however, several experimental peak positions did not match well to any of the reflections determined by the given unit cell, a possible indication that the given unit cell did not represent the best or only fit to the data. Even if the unit cell were the best fit, however, it is a nontrivial jump to claim a spin-ladder arrangement of Cu and O atoms. Such an assertion requires establishing that the individual atoms are properly located within the unit cell, a very challenging step that is of particular significance in the case of the study by Schön *et al.*, because the unit cell that Deville Cavellin *et al.* determined, and on which the Schön *et al.* study rests, does not match that of bulk $CaCu_2O_3$. [$CaCu_2O_3$ is a heavily buckled spin-ladder compound that, because of the buckling, is not strictly a low-dimensional material (*4*)].

To obtain the individual atomic locations within a unit cell via x-ray diffraction requires the collection of numerous peaks and their associated intensity information, neither of which is readily obtainable from a thin film. Therefore, Deville Cavellin *et al.* referenced a high-resolution transmission electron microscopy (HRTEM) study of $SrCu_2O_3$ thin films by Lagües *et al.* (*5*) to claim support for the spin-ladder-type atomic arrangement within their $[CaCu_2O_3]_4$ unit cell. That claim brings up two issues: (i) It would be surprising to find identical thin-film structures between two compounds, $SrCu_2O_3$ and $CaCu_2O_3$, that have large differences in their bulk unit cell size and atom positions. (ii) The HRTEM image shown in the Lagües *et al.* study may be consistent with a spin-ladder arrangement of the Cu-O atoms, but in no way shows that the sample has the correct Cu-O atomic positions to make it a spin ladder compound. This is primarily because the image only shows the *b*-*c* plane, while the Cu-O atom arrangement of interest is in the *a*-*b* plane [see, e.g., figure 3 in (*6*)].

In sum, the referenced papers on the growth and characterization of the $[CaCu_2O_3]_4$ films used by Schön *et al.* provide no unequivocal evidence of a spin-ladder arrangement of the Cu and O atoms in the film studied. Without such evidence, any claim for superconductivity due to doping of a spin ladder is premature.

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Response: Ingle *et al*. raise a very important question—whether the structure of the $[CaCu_2O_3]_4$ thin films in our study (*1*) indeed exhibits a spin-ladder-type structure. To obtain a better fit of the unit cell parameters (Table 1), we have performed extensive additional x-ray diffraction studies (*2*) since our earlier publication (*3*). These investigations have confirmed the isostructural structure of the calcium and strontium phases. We have collected more peaks and performed additional Q-scans. The *a* and *b* (ladder plane) cell parameters found were very close to those obtained for the two-leg ladder Hiroi compounds (*4*) and for the 14-24-41 family (Table 1).

The monocrystal studied by Kiryukhin *et al*. (*5*) presents a smaller *b* value than all the previous compounds (to our knowledge, no transport or other physical properties were reported on this compound). In addition, the Kiryukhin *et al*. $CaCu_2O_3$ phase referenced by Ingle *et al*. presents surprisingly different in-plane parameters compared with the in-plane Ca-14-24-41 ladder parameters: The *a* parameter (corresponding to the *c/7* parameter in the 14/24/41 compounds) is larger, whereas the *b* parameter (corresponding to the *a* parameter in the 14/24/41 compounds) is smaller. Moreover, the stacking *c* parameter is larger than for $SrCu_2O_3$. Such a discrepancy between standard two-leg ladder compounds and the $CaCu_2O_3$ compound referenced by Ingle *et al*. does not appear for our $(Sr,Ca)Cu_2O_3$ thin films; on the contrary, the different cell parameters follow the regular relation, with the Sr/Ca substitution, as in the Hiroi $SrCu_2O_3$ bulk compound and $(Sr,Ca)_{14}Cu_{24}O_{41}$ standard compounds. Therefore, we believe that our results reflect the 2-leg ladder structure.

Moreover, HRTEM images in the *b-c* plane were also obtained for Ca samples; they proved very similar to those obtained for the Sr phase, but they do not exhibit the same quality, possibly because of the lower stability of the Ca phase and a higher sensitivity to the electron beam. HRTEM images in the *a-b* plane would be extremely difficult to perform on epitaxial films, because the substrate, which plays an important role for the stability and the structure of the films, would have to be removed. HRTEM images with a [310] orientation performed on Sr samples clearly revealed spin-ladder arrangement and depicted the evident dimerization of the ladder planes, with a shift along *a* between two dimers. Finally, we have carried out polarized extended x-ray absorption fine structure (EXAFS) measurements at Cu and Sr thresholds to obtain better unit cell parameters; these results are also consistent with a ladder structure. We continue to conduct additional measurements to further refine the structure.

In sum, we have observed clear evidence of a spin-ladder arrangement in these molecular beam epitaxy (MBE)-grown $[CaCu_2O_3]_4$ thin films.

Table 1. Comparison of the crystallographic parameters for different two-leg ladder compounds. Parameters of MBE phases studied in (*1*) are compared with those of other two-leg spin-ladder compounds. Note that *a*, *b*, and *c/7* parameters in 14/24/41 notation correspond to *b*, *c*, and *a* parameters, respectively, for other phases. F, film; P, powder; C, crystal; Ref., reference that reported the parameters.

Composition	Parameters (nm)					Form	Ref.	Space group
	b ("rungs")	*c*	Distance between Cu planes		*a* ("legs")			
MBE phase								
$[SrCu_2O_3]_4$ on $SrTiO_3$	1.152	1.343	0.336		0.395	F	(*2*)	
$[CaCu_2O_3]_4$ on MgO	1.125	1.242	0.311		0.389	F	(*2*)	
$[CaCu_2O_3]_4$ on $SrTiO_3$	1.125	1.242	0.311		0.388	F	(*2*)	
Hiroi phase								
$SrCu_2O_3$	1.157	0.350	0.350		0.3934	P	(*4*)	Cmmm
$SrCu_2O_3$	1.155	0.349	0.349		0.3929	P	(*6*)	
Kiryukhin phase								
$CaCu_2O_3$	0.995	0.346	0.346		0.408	C	(*5*)	Pmmn
14/24/41 compounds	*a*	*b*	Distance between Cu planes	*c*	*c/7*	Form	Ref.	Space group
$Sr_{14}Cu_{24}O_{41}$	1.147			2.7551	0.394	C	(*7*)	
$Sr_{14}Cu_{24}O_{41}$	1.147	1.337	0.334	2.7501	0.393	P	(*8*)	Pcc2
$Sr_{11}Ca_3Cu_{24}O_{41}$	1.143			2.7487	0.393	C	(*7*)	
$Sr_8Ca_6Cu_{24}O_{41}$	1.138	1.293	0.323	2.7455	0.392	N	(*8*)	Cccm
$Sr_{2,5}Ca_{11,5}Cu_{24}O_{41}$	1.135			2.728	0.390	C	(*9*)	
$Sr_{0,4}Ca_{13,6}Cu_{24}O_{41}$	1.126	1.243	0.311	2.733	0.390	P	(*10*)	F222, Fmm2, Fmmm
$Ca_{14}Cu_{24}O_{41}$	1.125	1.237	0.309	2.7265	0.390	F	(*11*)	

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