# Comment on "Origin of the superconductivity in the Y-Sr-Ru-O and Y-Sr-Cu-O systems"

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Galstyan *et al.* [Phys. Rev. B **76**, 014501 (2007)] asserted that superconductivity reported for $Sr_2YRu_{1-u}Cu_uO_6$ is due to inclusions of $YSr_2Cu_3O_7$. We have synthesized samples of this magnetic material ($u=0.10$) which exhibit diamagnetism exceeding that possible even if all of the available dopant Cu were present in $YSr_2Cu_3O_7$. Our materials were studied with neutron diffraction, scanning electron microscopy, energy dispersive x-ray analysis, and SQUID magnetometry. We found no evidence for inclusions of $YSr_2Cu_3O_7$. Despite their claim, this is in agreement with a primary finding of Galstyan *et al.* that granular $YSr_2Cu_3O_7$ is present only in material doped with Cu at 250% of the known Cu solubility limit. The lack of superconductivity at low Cu doping in their material is likely due to their failure to follow published synthesis procedures. It is concluded that the findings of Galstyan *et al.* actually support our contention that properly synthesized $Sr_2YRu_{1-u}Cu_uO_6$ is a single phase material which exhibits high temperature superconductivity.

In a recent paper,[1] it was argued that the observed superconductivity[2–4] in $Sr_2YRu_{1-u}Cu_uO_6$ (Sr-O6) was due to inclusions of $YSr_2Cu_3O_{7-\delta}$ (YSCO). The YSCO purportedly formed as a consequence of pressure provided by partial melting of surrounding grains. The micrograph offered (Fig. 5 of Ref. [1]) in support of this proposal appears to have a void adjacent to the grain identified as being YSCO. The superconducting onset transition temperature (64K) observed was associated with YSCO. However, examination of Fig. 3a of Ref. [1] reveals *two* diamagnetic transitions: the first, a weak transition, occurs at ~64 K, while a second larger transition occurs at ~30 K, simultaneously (or very nearly so) with the magnetic ordering of the $YRuO_4$ layers in the Sr-O6. The transition at ~30 K is typical of the previously reported superconducting transition temperature[3] for the Sr-O6. The transition at ~64 K is reasonably attributed to the small concentration of YSCO reported by Galstyan, and represents less than 1% of the ideal Meissner fraction. Since there are no reports of multiple superconducting transitions in YSCO, it is appropriate to conclude that two distinct superconducting phases are present in their complex, multiphase sample. Despite the high (attempted) substitution of Ru by Cu (50%) in this sample, well above the solubility limit[2] of Cu in Sr-O6, the apparent Meissner fraction is much smaller than our measured value for a sample containing only 10% Cu. Galstyan *et al.*[1] also showed that any YSCO appears in a granular phase. Thus, it is very unlikely that the onset of ferromagnetic order in the $YRuO_4$ planes could enhance the superconductivity of the (distant) granular YSCO. It is therefore not possible that resistive zeros, reported[3] for $Sr_2YRu_{1-u}Cu_uO_6$, could be attributed to this impurity, since collecting *all* of the Cu into the impurity phase could yield a maximum concentration of 3.33% YSCO (for $u=0.10$ in $Sr_2YRu_{1-u}Cu_uO_6$), well below the $3d$ percolation limit of ~17% required for a granular phase. Based on our experience, the preparation procedures reported by Galstyan *et al.*[1] would not be expected to produce quality superconducting O6; we are successful only by guarding against Ru loss with well conditioned[5] furnace tubes and careful control of calcin-

ing and sintering times, temperatures, and atmosphere. This is little different from the control of oxygen required for successful preparation of YBCO and even more so for the ruthenocuprate O8 and O10 phases. However, it is no surprise that the Cu-rich phases could emerge from Galstyan's procedures since the Cu concentration (50%) was well above the reported Cu solubility limit[2] (~20%) in the Sr-O6 phases. With lower (~10%) doping, Galstyan *et al.*[1] found that the Cu was fully incorporated in the Sr-O6 phase, thereby associating the observation of superconductivity[6] to the Sr-O6 phase and not to the purported impurity. In Fig. 1, magnetization data from a 10% doped $Sr_2YRuO_6$ sample are presented. It is to be noted that (1) the diamagnetism exceeds
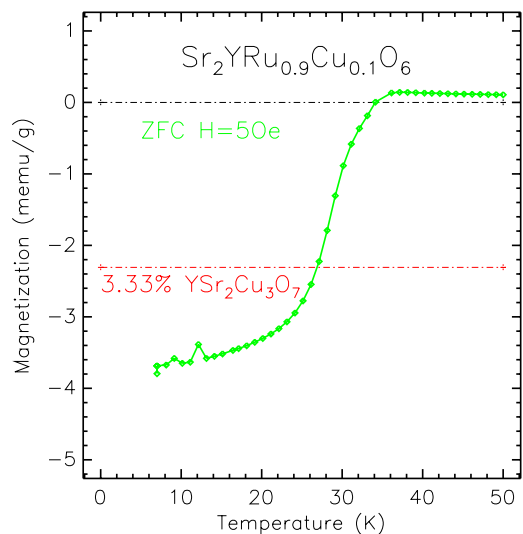


FIG. 1. (Color online) Zero-field-cooled magnetization data for Sr-O6 as a function of temperature with an applied field of 5 Oe. These data show a superconducting onset at ~30 K. The red line indicates the maximum possible diamagnetism produced by hypothetical "perfect" $YSr_2Cu_3O_7$. The sample's diamagnetism exceeds this limit.
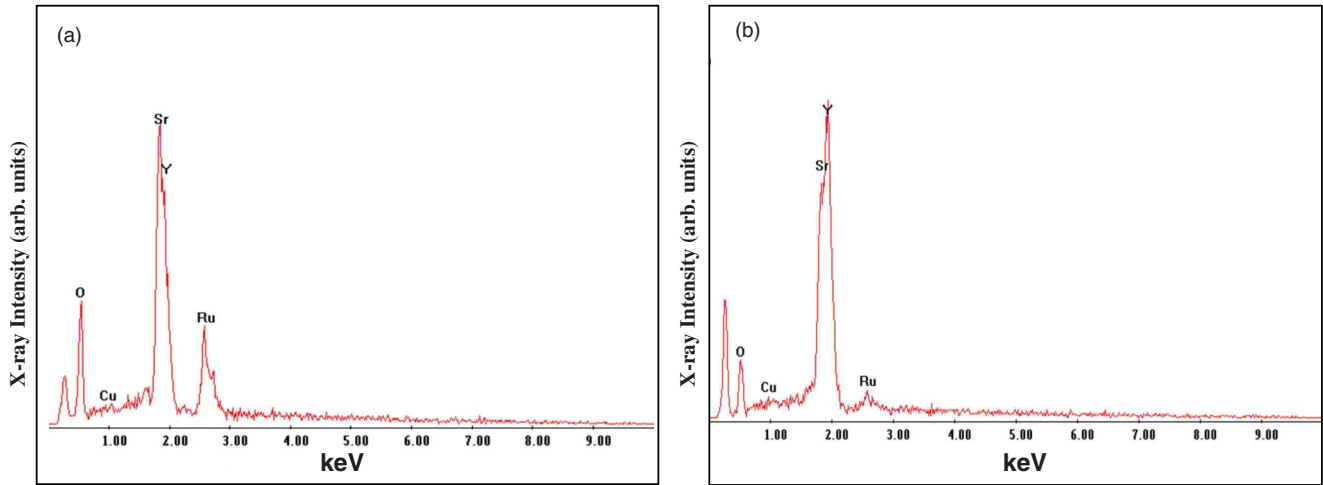
FIG. 2. (Color online) [(a) (left) and (b) (right)] In the left panel, EDX intensities shown indicate a small content of Cu relative to Ru. In the right panel, the beam was focused on secondary material. Here the Ru and Cu intensities are very small, and Y and Sr dominate the data. In no location were grains with a large Cu content appropriate to YSCO found. The EDX peak to the left of oxygen is due to carbon.

that shown by Galstyan *et al.*,[1] *even though these authors used five times as much dopant Cu,* and (2) *The magnetization substantially* ($\sim$165%) exceeds that possible with 100% incorporation of the available Cu into perfect YSCO. We are not aware that YSCO exhibiting 100% flux expulsion has ever been demonstrated. Thus, it seems very unlikely that *our result could be due to an impurity.* The *sharp* diamagnetic transition at $\sim$30 K, shown here, at a temperature anomalously low for YSCO (roughly 1/2 of its characteristic $T_c$), is coincident with the second transition reported by Galstyan *et al.*[1]

Scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDXA) studies were carried out on our Sr-O6 material following the final sintering. The sample selected for examination was cut from the center of the pellet, and the piece was measured by superconducting quantum interference device (SQUID), which yielded the data shown in Fig. 1. The micrographs show no evidence for isolated second phase grains; all sampled grains (2–5 $\mu$m diameter) have similar compositions. However, the EDXA studies show that the bulk grains have a composition distinctly different from inhomogeneous "secondary" phase material. A typical bulk grain as measured using quantitative energy dispersive x-ray spectroscopy (EDS) with ZAF (where "Z" refers to the atomic number, "A" to absorption, and "F" to fluorescence) corrections shows the approximate 2:1:1 ratios of Sr to Y to Ru+Cu, and a Ru/Cu ratio consistent with the nominal value of 9, (considering the large uncertainty on the Cu concentration) see Fig. 2(a). Figure 2(b) shows EDXA data for typical secondary material in which the Ru and Cu concentrations are distinctly reduced relative to the Y and Sr concentrations of the bulk grains. Some other scans show even lower transition-metal concentrations. These data imply that the "secondary" material is substantially depleted in Ru and Cu, relative to the bulk. This is apparently a consequence of transition-metal ion loss due to volatility during the calcining and sintering steps, producing grains of superconducting Sr-O6 coated with relatively thick insulating Y-Sr-O

compounds. This explains the poor resistive transitions in some samples of Sr and Ba-O6, as well as reduced Meissner fractions. EDXA analysis of a large number of randomly chosen grains failed to find any characteristic of YSCO. This is in complete agreement with Galstyan *et al.*[1] in their conclusion that for a low Cu concentration (10%), the sample has a single phase Sr-O6 composition. Thus, while Galstyan *et al.*[1] claim to have disposed of arguments for superconductivity in Sr-O6, careful analysis suggests that their work actually supports it. The absence of superconducting Sr-O6 in Galstayn's "stoichiometric" 10% Cu sample and its presence in the 50% Cu sample are easily understood. The processing parameters of their 10% Cu sample were guaranteed to lead to transition-metal loss, which, we have found, destroys the superconductivity. On the other hand, in their 50% Cu-doped sample, the solid O6 phase, doped with Cu to the solubility limit, can coexist with a Cu-rich melt at the upper processing temperature. The Cu chemical pressure of the melt guarantees that the O6 phase remains relatively vacancy-free on the transition-metal sites.

We have recently shown that incorporation of superconducting GdBa$_2$Cu$_3$O$_7$ (Gd123) into the homolog[7] Ba$_2$GdRuO$_6$ proceeds without producing either granular superconductivity or coating Ba-O6 grains with Gd123. The composite material was sintered at a temperature closely comparable to that appropriate to the Sr-O6 processing. This sintering produces a material in which the Gd123 is dissociated, partially doping the host with Cu, with the formation of additional Cu-doped Gd-O6 material. Ba$_2$GdRu$_{1-u}$Cu$_u$O$_6$ does not superconduct.[8] We have recently reported similar dissociation results[9] with Ba$_2$YRuO$_6$ doped by Y123, which show that Y123 completely decomposes and Cu dopes the Ba-O6 phase, when processed at the sintering temperature required for the formation of superconducting Ba-O6. Thus, it is concluded that (within solubility limits) the O7 phases are not stable in the O6 materials at their high characteristic processing temperatures, and that the observed O6 superconductivity is *not* due to impurity phases.

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[5] Our furnace tubes are used exclusively for one material, with walls coated with $RuO_2$ and $CuO$.

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[7] H. A. Blackstead, M. Kornecki, M. P. Smylie, P. J. McGinn, W. B. Yelon, and Q. Cai, J. Alloys Compd. **466**, 31 (2008).

[8] H. A. Blackstead, J. D. Dow, D. R. Harshman, W. B. Yelon, M. X. Chen, M. K. Wu, D. Y. Chen, F. Z. Chien, and D. B. Pulling, Phys. Rev. B **63**, 214412 (2001); Neutron diffraction carried out on a 15% Cu-doped sample found no identifiable impurities at the 1% level. In addition, the neutron-diffraction patterns for YSCO and $Sr_2YRuO_6$ are distinctly different, with no overlapping peaks at the angles of the most intense reflections.

[9] H. A. Blackstead, W. B. Yelon, M. Kornecki, M. P. Smylie, P. J. McGinn, J. B. Yang, W. J. James, and Q. Cai, J. Appl. Phys. **103**, 033904 (2008).