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

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In their comment on our paper [Galstyan *et al.*, Phys. Rev. B **76**, 014501 (2007)], Blackstead *et al.* argued that multiphase $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$ material possesses two distinct superconducting phases and attributed the low-temperature one (~30 K) to the Cu-doped double-perovskite Sr_2YRuO_6 structure. In this Comment, we show that the superconductivity in $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$ is apparently attributed to $YSr_2Cu_3O_{7-\delta}$ or $YSr_2Cu_{3-x}Ru_xO_{7-\delta}$ phases formed at high temperature during the sintering process. A similar situation may occur with low Cu doping, but further detailed work will certainly be helpful to clarify the physics in Sr_2YRuO_6 with relatively low Cu concentration.

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The comment by Blackstead *et al.*[1] argued in favor of their proposed model, in which superconducting (SC) condensation occurs in the SrO planes of the Cu-doped double-perovskite Sr_2YRuO_6 system but is against our experimental results and interpretation[2] that trace SC in samples with a nominal composition of $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$ originates from the inclusions of $YSr_2Cu_3O_{7-\delta}$ (YSCO) or $YSr_2Cu_{3-x}Ru_xO_{7-\delta}$ phases formed in partially melted grains. We stand by our observations regarding $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$, i.e., the samples with high Cu concentration. The data clearly show that the high processing temperature is essential for the observation of SC in Y-Sr-Cu-O. Multiple Cu-containing phases are consequentially observed under such conditions. Samples prepared at temperatures below or close to the melting transition are found to have the same crystal structure but are nonsuperconducting, as was also shown in the publications from other groups.[3,4] Such phase segregation through melting points is generally expected and is supported by the Y-Sr-Cu-O phase diagram. Regarding the $Sr_2Y(Ru_{1-x}Cu_x)O_{6-\delta}$ with $x \leq 0.2$, which is not the focus of our previous paper, the results reported are rather divergent. The absence of any SC signature was noticed by Felner[3] and others. Two groups,[4–6] on the other hand, have reported trace superconductivity with $T_{C,\text{onset}} \sim 60$ and 49 K, respectively, for samples with x down to 0.1. While a firm conclusion apparently has not been reached and some steps such as sample exchange are certainly helpful, it is difficult to understand why the highest volume fraction is still far below 10% after a decade of intensive efforts. Either impurity phases, which often escape the detection of x-ray diffraction (XRD), or special lattice defects or strain should play roles, in our opinion. It should therefore be noted that the range of SC transitions observed for both the Cu-doped Sr_2YRuO_6 and the doped $YSr_2Cu_{3-x}M_xO_{7-\delta}$ (M=transition metals) is actually very broad, from ~65 to 0 K, and can be easily understood as the result of the Cu inhomogeneity or local lattice distortions. It is also well recognized that a few percent of impurities are often within the instrumentation resolution of XRD or neutron diffraction (ND) methods, as shown in our work and in good agreement with Blackstead *et al.*[7] and other publications.[3–5] To totally exclude the formation of the secondary phases merely based on XRD or ND is unjustified in our opinion. The appearance of impurity phases (i.e., the apparent solubility limit) strongly depends on local stoichiometry rather than on the nominal composition. It is a common problem that imperfect grinding or mixing during synthesis may lead to much higher local doping levels.

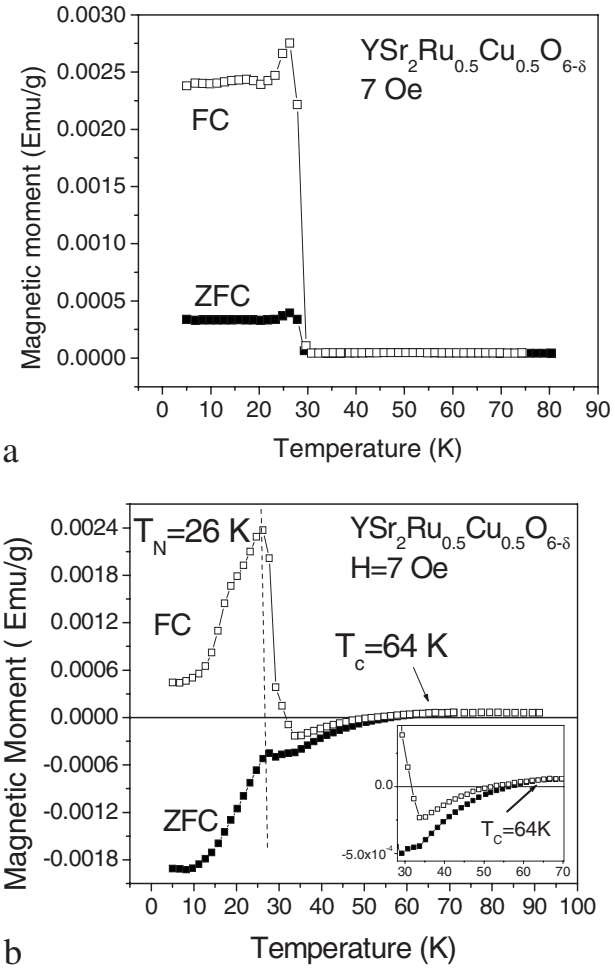

FIG. 1. ZFC and FC magnetization curves for $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$ synthesized (a) at 1290 and (b) at 1360 °C, respectively. Inset: ZFC and FC magnetization curves between 30 and 80 K.

The first argument presented by Blackstead *et al.*[1] in their comment presents the two-step-like transition in the zero-field-cooled (ZFC) curve for $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$ as evidence for two distinct SC phases and assigns the low-temperature one (~30 K) to the double-perovskite $Sr_2YRu_{1-x}Cu_xO_{6-\delta}$, which, in our opinion, is inconsistent with our data. Note that Ref. 3 in the comment by Blackstead *et al.*[1] reported the onset of SC at around 45 K. We disagree with the aforementioned argument because (1) in general, any SC phases should be equally detected by the dc ZFC magnetization and the ac susceptibility, since both depend on the supercurrent induced by the external field. The two, however, can be different in magnetic systems where the domain relaxation time makes the difference. It is, therefore, worth noting that the magnetic anomaly deduced from the ZFC term of dc measurements is not shown in the ac plot. The ac susceptibility curve shown in our published work as Fig. 3(b) (Ref. 2) does not display any evidence of a second SC phase at around 30 K or at around 45 K. (2) The field-cooled (FC) magnetization, which significantly rises below 30 K, also contradicts the superconducting-transition interpretation. (3) It should be pointed out that both the antiferromagnetic (AFM) transition of Sr_2YRuO_6 at 26 K and the weak ferromagnetic (WFM) ordering[5,8] at around 30 K have been previously reported. These transitions are also demonstrated by our non-SC sample $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$ synthesized at 1290 °C [Fig. 1(a)]. These can make a smooth T_C distribution look like a two-step transition for the SC $Sr_2YRu_{0.5}Cu_{0.5}O_{6-\delta}$ sample synthesized at 1360 °C, in our opinion [Fig. 1(b)]. The upturn slightly above 26 K further demonstrates that this is likely the case. In addition, it is worth noting that our non-SC $Sr_2YRu_{0.9}Cu_{0.1}O_{6-\delta}$ sample possesses the same magnetic transitions at 26 and 30 K.[2]

The second argument by Blackstead *et al.*[1] was that the diamagnetic response, M_{ZFC}, reached −0.0038 emu/g in one of their $Sr_2YRu_{0.9}Cu_{0.1}O_{6-\delta}$ samples, which is larger than the −0.0023 emu/g upper limit that is expected. It should be cautioned that the shielding effect, M_{ZFC} (as repeatedly demonstrated in multiphase samples), can be well above the true volume fraction if local percolation exists. Our scanning electron microscopy (SEM) data clearly demonstrated that the superconducting YSCO grains actually surround large melt residuals. The low fields used in measuring M_{ZFC}, therefore, are excluded from these parts as well. The assumption in the comment that the M_{ZFC} can be used as flux repulsion is unjustified, in our opinion.

The final argument by Blackstead *et al.*,[1] as mentioned above, was that the absence of SC in our lower (10%) Cu-doped Sr_2YRuO_6 sample was the result of the Ru loss. However, it presents a logical dilemma that if the Ru loss is the root, a larger Cu/Ru ratio should result. In fact, the samples with low concentrations of Cu ($x<0.1$) in $Sr_2YRu_{1-x}Cu_xO_{6-\delta}$ prepared by different groups are not identical. While the arguments of the comments cannot convince us, more effort may still be required to properly synthesize these ruthenocuprates and to clarify the actual physics.

[1] H. A. Blackstead, P. J. McGinn, M. P. Smylie, W. B. Yelon, J. B. Yang, and W. J. James, preceding Comment, Phys. Rev. B **79**, 016501 (2009).
[2] E. Galstyan, Y. Y. Xue, M. Iliev, Y. Sun, and C. W. Chu, Phys. Rev. B **76**, 014501 (2007).
[3] I. Felner, J. Magn. Magn. Mater. **246**, 191 (2002).
[4] M. K. Wu, D. Y. Chen, F. Z. Chien, S. R. Sheen, D. C. Ling, C. Y. Tai, G. Y. Tseng, D. H. Chen, and F. C. Zhang, Z. Phys. B: Condens. Matter **102**, 37 (1996).
[5] D. Y. Chen, F. Z. Chien, D. C. Ling, J. T. Tseng, S. R. Sheen, M. J. Wang, and M. K. Wu, Physica C **282-287**, 73 (1997).
[6] D. R. Harshman, W. J. Kossler, A. J. Greer, D. R. Noakes, C. E. Stronach, E. Koster, M. K. Wu, F. Z. Chien, J. P. Franck, I. Isaac, and J. D. Dow, Phys. Rev. B **67**, 054509 (2003).
[7] 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).
[8] R. P. Singh and C. V. Tomy, Phys. Rev. B **78**, 024432 (2008).