Large Deviations from the Universal Relationship between T_c and Hole Density in Cuprate Superconductors

In a recent Letter [1], Zhang and Sato propose an interesting universal relationship between T_c and hole density in p-type cuprate superconductors. By scaling T_c to the maximal attainable transition temperature ($T_{c,\max}$) in a given family, they show that the plots of τ_c ($\equiv T_c/T_{c,\max}$) fall on the same trapezoidal curve when plotted against hole content ($p_{\rm sh}$). Using selected data from the literature which they considered reliable, they confirmed this relationship for systems with widely different $T_{c,\max}$. This suggests, as the authors have noted, that the variation of T_c within a family depends entirely on the level of hole doping within the CuO_2 planes, while the value of $T_{c,\max}$ also depends on structural features outside these planes. In the data that Zhang and Sato employed, several methods for estimating the total hole density were used, including chemical titration, thermogravimetric analysis, bond-valence sums, and the Hall effect. The coalescence of the plots of τ_c vs $p_{\rm sh}$ on one curve demonstrates that all these methods yield equivalent estimates of hole density.

Our Comment points out that there are certain important exceptions to the universal relationship proposed by Zhang and Sato, even within the 1:2:3 system. One such exception is the 1:2:3 family that we discovered recently [2] $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$, that exists as a single phase in the range $0 \le x \le\sim 0.5$. In this family, Ca^{2+} substitutes on the Y^{3+} site and some La^{3+} substitutes on the Ba^{2+} site. These constitute mutually charge-compensating cosubstitutions whereby Q is fixed throughout, i.e., $Q = 7.25$ independent of x. (Here Q denotes the formal total charge on the noncopper cations, and we have used the structure of $YBa_2Cu_3O_7$ for site notation.) When the oxygen content (y) is maintained constant, the chemically determined hole density ($p_{\rm tot}$) remains constant [e.g., $p_{\rm tot} = \frac{1}{3}(2y - Q - 6) = 0.283$ for $y = 7.05$]. However, T_c varies substantially (more than 20 K) with cation composition x [2]. Irrespective of the method by which the mobile hole density per CuO_2 plane ($p_{\rm sh}$) is estimated, this big variation in T_c corresponds to a vertical line since *both* y and Q remain constant. This line falls roughly in the middle of the trapezoid, unlike the behavior of the other families investigated by Zhang and Sato.

We demonstrate this by superimposing the behavior of our new family on the data of Fig. 1 of Ref. [1]. To this end, a method for estimating $p_{\rm sh}$ is required. Following Tokura *et al.* [3], who found a way of separating between *mobile* holes in the planes and localized electrons in the charge reservoir through examination of the metal-insulator boundary (MIB), we define [2] $p_{\rm sh} \equiv \frac{1}{2}(y - Q + \frac{1}{2})$. This assumes that every hole in excess of $p^*_{\rm tot}$ at the MIB splits into two halves: one on the planes, the other in the charge reservoir. Shafer *et al.* [4] have since confirmed the validity of this approach for other families within the 1:2:3 system. They have shown that, in cases where the Hall number is temperature independent, it compares well with $p_{\rm sh}$. Above $p^*_{\rm tot}$, the same approach implies that each additional oxygen donates *one* mobile hole. This agrees with the thermoelectric power results by Fisher *et al.* [5]. In Fig. 1 we show the behavior of the new family superimposed on the plot of Zhang and Sato. The vertical straight line describing a 21 K variation in T_c at constant $p_{\rm sh}$ (=0.15, i.e., at $y = 7.05$) is in marked disagreement with the universal plot.

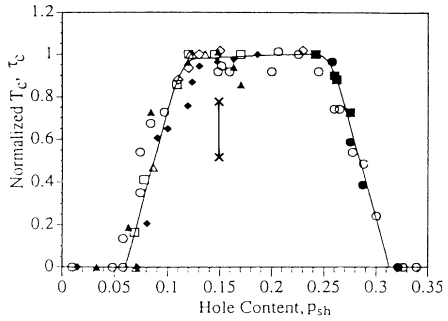

FIG. 1. The universal dependence of τ_c on $p_{\rm sh}$ (Ref. [1]). The vertical line (×) at $p_{\rm sh} = 0.15$ corresponds to the family $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_{7.05}$ with x varying from 0.1 to 0.4.

We note that in families exhibiting the universal behavior, the hole density is varied by direct doping. In the present family, cosubstitution prevents direct doping. We believe that the *mobile* hole density in the planes nevertheless changes due to charge redistribution. Specifically, we suggest that oxygen accumulation in the vicinity of the La that replaces Ba gives rise to internal electron transfer from the CuO_2 planes to the charge reservoir. Deviations from the universal dependence of τ_c on $p_{\rm sh}$ can therefore serve as an indicator for cases where charge redistribution, rather than direct doping, is the important factor controlling T_c.

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Received 22 July 1993
PACS numbers: 74.72.–h, 74.25.–q, 74.62.Dh

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0031-9007/93/71(20)/3392(1)$06.00