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High Tc Superconductors: The Scaling of Tc with the Number of Bound Holes Associated With Charge Transfer Neutralizing the Multivalence Cations

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ABSTRACT

It is observed that for the known high-Tc Cu-, Tl-, and Bi-based superconductors, Tc scales consistently with the number of bound holes per unit cell which arise from charge transfer excitations of frequency $\sim 3X10^{13}$ that neutralize the multivalence cations into diamagnetic states. The resulting holes are established on the oxygens. Extrapolation of this empirical fit in the up-temperature direction suggests a Tc of about 220-230K at a value of 25 holes/unit cell (approximately the maximum that can be materials-engineered into a high-Tc K_2MnF_4 or triple Perovskite structure). In the down-temperature direction the extrapolation gives a Tc of about 25K for a normal metal of zero holes. These extrapolations are in accord with experimental data suggesting maximum Tc in the vicinity of 235K for the Y-Ba-Cu-O system as well as the known maximum temperature of 23K for low-Tc materials shown by Nb_3Ge. The approach is also consistent with the experimental findings that only multivalence ions which are diamagnetic in their atomic state (Cu, Tl, Bi, Pb, Sb) associate with high-Tc compounds.

(1) THE DIFFERENCE IN SCALING PARAMETERS FOR HIGH- AND LOW- Tc

(A) Low-Tc

Since conventional low-Tc superconductors are known to be governed by the strong-coupled electron-phonon mechanism, and since we believe that such coupling cannot fully explain the properties and mechanism of high-Tc superconductors[1,2], we search for a scaling parameter related to vibration of atoms and to low-Tc that does not scale in a similar manner for high-Tc.

In Fig 1A we plot Tc versus density (ρ) for conventional low-Tc superconductors. These show a peaking Tc at densities of 6-9 gm/cm^3 for materials with positive magnetic susceptibility at room temperature and at about 11-14 gm/cm^3 for materials with negative magnetic susceptibility (circled in Fig 1A). In the inset to Fig. 1A the plot of Tc vs weight is given. The peaking of Tc with density can be understood in terms of the dependency of the frequency term (in the Debye temperature relationship) with density. Plotting Tc vs atomic weight for the A15 superconductors (Nb_3X or V_3X) shows a generally decreasing trend with atomic weight.

The critical field above which magnetic flux can no longer be excluded from the interior of a superconductor is given by $H_c=H_o(1-(T/Tc)^2)$ In Fig. 1B, H_o is shown vs the number of missing electrons that would fill the partially-filled subshells for the superconducting elements. There is a general dependence of H_o on this number. The exceptions Ti, Th, Zr, and Pa (not plotted) have a d^2 state in their outershell configuration which presumably adds another unique factor. Hg being the other exception has vastly differing electronic properties than the other metals. The fit in Fig. 1B suggested searching for related scaling in high-Tc.

(B) HIGH-Tc SUPERCONDUCTING SCALING

A rather clearcut general increase of Tc with molecular weight is shown for all of the known high-Tc superconducting oxides except for $Bi_2Sr_2Cu_1O_6$ and possibly $Ba(PbBi)O_3$ (which may be largely phonon-induced superconductors). This mass or weight dependence is very different from that in low-Tc superconductors given in Fig. 1A, suggesting a very different role of the mass parameter in the two types of superconductors. In the high-Tc materials, the mass dependence seems related to the added complexity of the two (or three) different types of polyhedral building blocks and more extensive layering in substances having a greater number of ions per unit cell.

In Fig. 2 we plot Tc versus the total number of bound holes (P(b)) per unit cell associated with the ionization of the multivalence cations and associated with charge transfer from the oxygens.[3] We define the number of bound holes associated with a charge transfer excitation as the number of resulting holes on the oxygens when a multivalence cation is transiently ($3X10^{13}$ times per sec) neutralized by the excitation. Thus for $Y_1Ba_2Cu_3O_{7-}$ which for charge neutrality can be written as $Y^{3+}{}_1Cu^{3+}{}_1Ba^{2+}{}_2Cu^{2+}{}_2O_{7-}$ we illustrate how a maximum of seven bound holes are created: the charge transfer $Cu^{3+} + O^{2-} + O^{2-}$ yields $Cu^0 + O^0 + O^-$ thus creating three bound holes on oxygens; the charge transfer $Cu^{2+} + O^{2-}$ yields $Cu^0 + O^0$ creating two holes on oxygens. Since there are 2 Cu^{2+} and only 1 Cu^{3+} we sum 2(2)+3=7. The apical oxygen (O(4)) in the CuO_5 pyramidal building block is believed to be the optimal candidate ion as the charge transfer agent. There is then, by this empirical method of calculating P(b), found to be a linear correlation for the high-Tc superconductors in Tc vs P(b) as shown in Fig. 2. The correlation is described by the least-square best fit as Tc=7.9 P(b) + 27.2. For P(b)=0, characteristic of low-Tc superconductors, the fit in Fig 2 gives Tc=27.2K which is approximately the maximum Tc for electron-phonon induced superconductivity (experimentally 23K). On the other hand a theoretical superconducting high-Tc lattice involving the highest valence states of the functioning ions such as Bi^{5+} and Sb^{5+}, and having the 2223X form, could achieve a maximum of about 25 holes/unit cell which according to Fig 2 would lead to a Tc of about 225K. According to Ref 4, this is the maximum Tc for superconductivity derived from an excitonic mechanism, such a mechanism necessarily requiring the existence of bound holes. Since $SrTiO_3$, $Ba(PbBi)O_3$, and $Bi_2Sr_2Cu_1O_6$ do not fit the straight line representation in Fig 2, we suspect that superconductivity in those materials is governed largely by electron-phonon coupling rather than by bound holes or exciton. The value of P(b) =7 for $Y_1Ba_2Cu_3O_7$ implies a maximum allowable carrier concentration in the normal state of about $10^{22}cm^{-3}$. In our previous work (5) we show that near Tc the actual positive carrier concentration is 10^{21} to $10^{22}cm^{-3}$.

Recently the compound $Y_5Ba_6Cu_{11}O_y$ has been synthesized and shown under oxygen overpressure to have a transition to zero electrical resistance at 235-265K (Ref. 6). For charge balance with this stoichiometry, and considering a K_2MnF_4 type structure, the value of P(b) would be expected to be 25-27 leading to a Tc in Fig. 2 of about 235K. Presently this phase seems to be of a filamentary or interfacial nature and has not been formed in high enough yield to derive conclusions regarding Meissner exclusion, however, the correlation with the empirical fit indeed exists.

References

1. J. Bednorz and K. Mueller, Z Phys. B64, 189 (1986).
2. C. W. Chu, P. Hor, R. Meng, L. Gao, Z. Hueng and Y. Wang, Phys. Rev. Lett. 58(4), 405, and 58(9), 908 (1987).
3. G. C. Vezzoli, M.F. Chen, F. Craver, W. Stanley, M. Shoga, A. Safari, T. Burke, B. Moon and B. Lalevic, Proc. of MRS Boston Meeting Dec 1989.
4. L.V. Keldysh and A. N. Kozlov, JETP Lett 5, 190 (1967), and A. A. Abrikosov, Zh. Eksp. Teor. Fiz Pis'ma Red 27, 37 (1978).
5. G. C. Vezzoli, T. Burke, B. Moon, A. Safari, H. Hundyar, B. Lalevic, R. Bonometti, C. Alexander, C. Rau, and K. Waters, J. Magnetism and Magnetic Materials 79, 146 (1989).
6. J. T. Chen, L-X Qian, L-Q Wang, L. E. Wenger, and E.M. Logothetis, Mod. Phys. Lett B (in press)

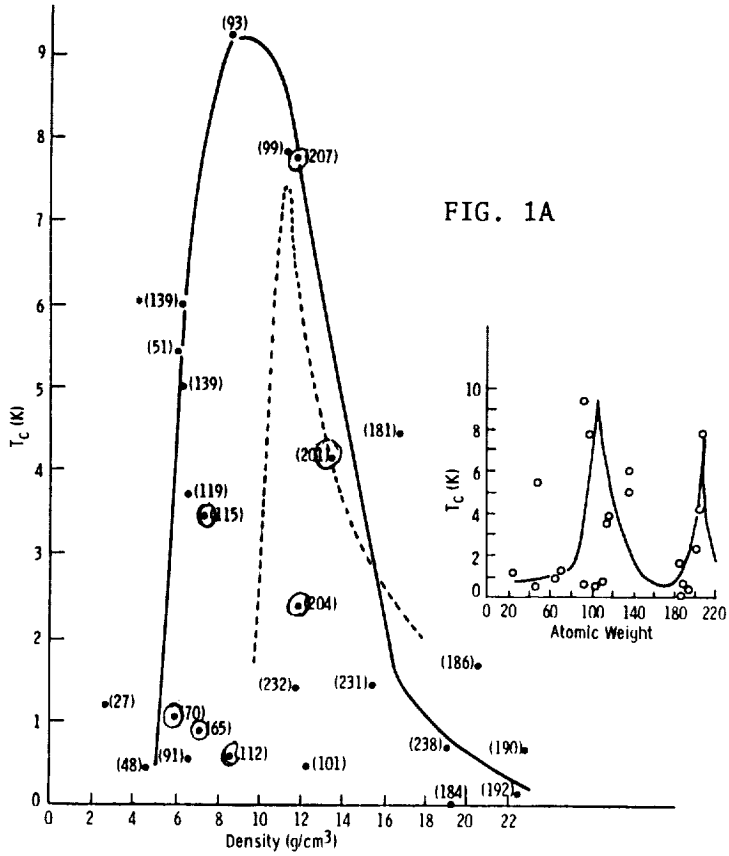


FIG. 1A

FOR CONVENTIONAL LOW-T_c ELEMENTAL SUPERCONDUCTORS VERSUS DENSITY (WEIGHT IS IN PARENTHESES)

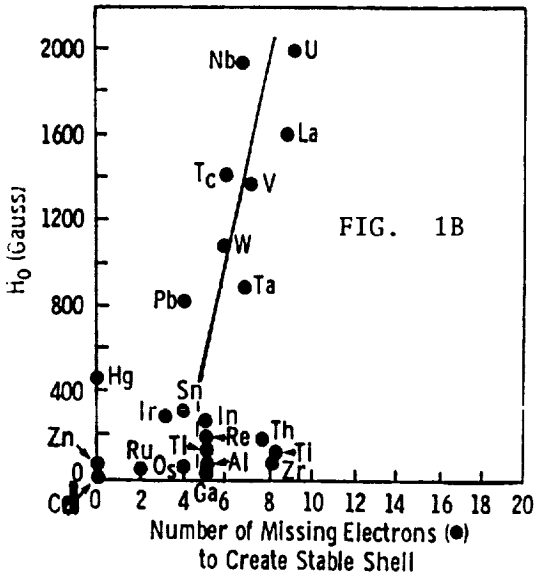
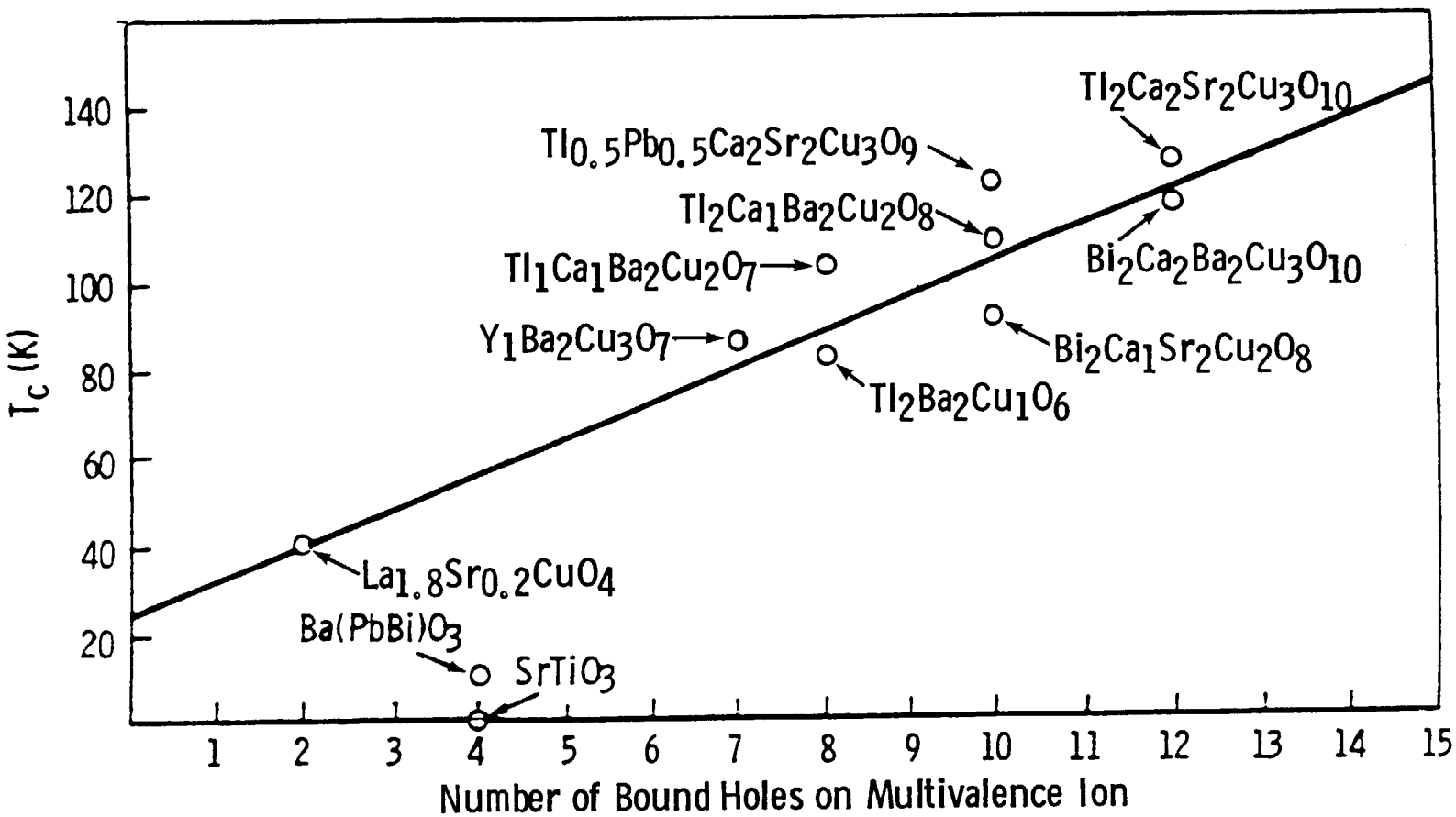


FIG. 1B

H_0 VERSUS NUMBER OF MISSING ELECTRONS TO FORM STABLE SHELL IN LOW-T_c ELEMENTAL SUPERCONDUCTOR



(These holes can be the core of bound excitons on the multivalence cations)

TRANSITION TEMPERATURE FOR HIGH-T_c MATERIALS VERSUS NUMBER OF HOLES DUE TO IONIZATION OF MULTIVALENCE METAL ATOM

FIG. 2