

Comment on "Missing Valence States, Diamagnetic Insulators, and Superconductors"

The metallic elements with highest T_c (such as Hg and Pb) do not conduct exceedingly well above T_c (but if alkali and coinage metals have any T_c at all, it is very close to 0 K). Varma¹ suggests that compounds (e.g., mixed oxides) of eleven elements reluctant to retain odd values of the Kossel² electron number $K = Z - z$, where z is the oxidation state (usually written with Roman numerals), show propensity to high T_c . Factually, $K = 19$ Ti(III) and V(IV) are more frequent^{3,4} than $K = 20$ Ti(II) and V(III), and niobium forms clusters like $\text{Nb}_6\text{Cl}_{12}^{q+}$ ($q = 2-4$) but rarely monomeric Nb(III). It is the hallmark of the "main-group" elements to have even K (nitrogen presenting the strongest exceptions) and 20 out of the first 101 K values are indeed not yet known.⁴ Among d -group elements, odd K are predominant in Cr(III), Mn(II), and Fe(III), and in the six lanthanides Nd, Sm, Gd, Dy, Er, and Yb; and all such odd K values are known (with marginal doubts about $K = 77$). Mixed oxides containing P, S, As, Se, and Te should favor superconductivity according to Varma.¹

It is an old dream²⁻⁵ to rationalize chemistry (for two-digit⁶ values of Z) by ionization energies I_n of gaseous M^{n+} , and we all agree^{1,3} that strong Madelung potentials, and in most cases also covalent bonding, are needed ingredients. However, when $U_n = I_{n+1} - I_n$ values vary nonmonotonically with n in eight post-transitional¹ elements, it is simply due to crossing a closed shell $4s$, $5p$, or $6s$. The chemical effect that Ga(II), Ge(III), In(II), Sn(III), Sb(IV), Tl(II), Pb(III), and Bi(IV) all disproportionate to adjacent z values can be described by a metaphoric "effective U_n " being negative, but this is the rule rather than the exception in main groups.

Varma¹ notes that $\text{BaPb}_{1-x}\text{BiO}_3$ and $\text{Ba}_y\text{K}_{1-y}\text{BiO}_3$ need values of x or y below a critical limit to go metallic, suggesting symphonic distortions of internuclear distances, which are readily rearranged during electron transport, when the Bi(III) concentration is sufficiently below half of the octahedral sites (and superconducting exactly⁷ at $x = 0.25$ or close⁸ to $y = 0.6$). The high T_c must be connected with the doping by Pb or K; BaBiO_3 is an insulator like MnF_2 and NiO , and cervantite $\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{O}_4$ and $\text{I}^{\text{III}}(\text{I}^{\text{V}}\text{O}_3)_3$ are translucent straw yellow

and diamagnetic. The greater propensity to show fluctuating valence of Bi(V) and Bi(III) may be connected with the larger differences in bond lengths and angles between Sb(V) and Sb(III) than in bismuth compounds.

$3d^8$ Cu(III), $3d^9$ Cu(II), and $3d^{10}$ Cu(I) occurring in a given oxide might have been a good case of almost vanishing U_{eff} (difference between ionization energy and electron affinity on a given site in condensed matter), but in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ there is no evidence⁹ for participation of Cu $3d$ in the loosest bound orbitals at the Fermi level [actually, many nonconducting, or even gaseous, Cu(II), Fe(III), or lanthanide compounds have higher photoelectron¹⁰ ionization energies $I(3d)$ or $I(4f)$ than the highest occupied valence shells]. It seems¹¹ that the superconductivity of copper-containing oxides rather involves "heavy" conduction electrons with $m^*/m \sim 5$ coupled by superexchange to oxygen anions, rationalizing¹¹ the nonmonotonic variation of T_c with the number 1, 2, 3, 4, . . . of Cu-containing layers in Tl-Ca-Ba-Cu and Bi-Ca-Sr-Cu oxides.

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Received 13 June 1989

PACS numbers: 74.10.+v, 74.65.+n

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