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Comment on the cluster model of alkali-metal tungsten bronzes

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In a recent paper Webman, Jortner, and Cohen proposed that the alkali metal M tungsten bronzes comprise a two-phase system composed of regions of metallic $M\mathrm{WO}_3$, surrounded by insulating WO_3. In this comment we point out that thermodynamic measurements on $\mathrm{Na}_x\mathrm{WO}_3$ and $\mathrm{H}_x\mathrm{WO}_3$ are inconsistent with this model and that these bronzes should be thought of as nonstoichiometric but homogeneous compounds with no tendency to form a two-phase system.

The physical properties of the tungsten bronzes have been studied for over a century.[1] They are particularly interesting because they can be produced with a wide range of electron densities to form insulators or metals. Some are superconducting. Recently, they have been considered for a promising new optical display device.[2] Their general chemical formula is $M_x\mathrm{WO}_3$. Here M is an alkali metal or hydrogen, and the composition parameter x varies between 0 and 1. They are generally thought of as nonstoichiometric, but homogeneous compounds, with no tendency to form a two-phase system. This model, however, has been challenged by Webman, Jortner, and Cohen[3] (WJC), who propose that the bronzes are actually two-phase compounds in which the metal ions associate in clusters forming the phase $M\mathrm{WO}_3$. Therefore, as x increases, the volume occupied by the $M\mathrm{WO}_3$ phase grows at the expense of the WO_3 phase. In support of their model, WJC analyzed some of the published transport data on the bronzes. The good agreement between their transport theory, based on percolation theory, and experiment was taken as evidence for their cluster model of the bronzes. We believe that the agreement between theory and experiment was coincidental, and furthermore that their model is not consistent with some of the recent transport data.[4,5]

The most serious objection to the cluster or two-phase model of the bronzes is that its basic premise is at variance with experimental determinations of the chemical potential of sodium in $\mathrm{Na}_x\mathrm{WO}_3$,[6] and of hydrogen,[7] in $\mathrm{H}_x\mathrm{WO}_3$. As theoretical support of their model, WJC calculated some of the x-dependent terms in the free energy of $\mathrm{Na}_x\mathrm{WO}_3$ and found them to *decrease* with increasing x; thus concluding that a high-x phase was most stable. However, the expression[7] for the free energy of $\mathrm{Na}_x\mathrm{WO}_3$ that fits the experimental measurement of the chemical potential[6] shows that the free energy *increases* with increasing x. Further supporting evidence for the two-phase model is the NMR measurement of Fromhold and Narath,[8] who interpreted their results in terms of clustering in $\mathrm{Na}_x\mathrm{WO}_3$. However, their measurements have been questioned recently by Tunstall.[9]

In this note, we show how the chemical potential of Na and H in $\mathrm{Na}_x\mathrm{WO}_3$ and $\mathrm{H}_x\mathrm{WO}_3$ is obtained from electrochemical investigations of these bronzes.[6,7] Using a theoretical expression for the free energy of the bronze, we then show that clustering is unlikely.

The free energy is obtained from measurements of the emf $\mathcal{E}$ of an electrochemical cell[10] in which $M_x\mathrm{WO}_3$ is made one of the electrodes. The cell is expressed schematically as

$$\text{Cu-reference-electrolyte-}M_x\mathrm{WO}_3\text{-Cu}, \qquad (1)$$

where the Cu phases refer to copper wires connected to the standard reference electrode and the $M_x\mathrm{WO}_3$ electrode. The electrolyte contains the metal ion. The emf of this cell is given by the fundamental relation[11] $\mathcal{E}=-\Delta F/\mathfrak{F}$, where $\mathfrak{F}$ is the Faraday and ΔF is the free energy of transfer of one equivalent of metal from the electrolyte to the solid tungsten bronze at composition $M_x\mathrm{WO}_3$. Apart from constant terms independent of the composition parameter x, ΔF is determined by μ_M, the chemical potential of the metal in the solid phase $M_x\mathrm{WO}_3$, i.e., $\mathcal{E}=-\mu_M/\mathfrak{F}$. The chemical potential is related to the free energy F_m of the bronze by $\mu_M=\partial F_M/\partial x$.

A metal atom introduced into WO_3 becomes dissociated with the electron going to a W^{6+} ion, reducing it to W^{5+}. The metal ion may be free to wander through the lattice or bound to the O^{2-} ion. This makes several contributions to the free energy of $M_x\mathrm{WO}_3$.[7] The first contribution to F is independent of x. It is F_0, the free energy of formation of one mole of pure WO_3. The second term is linear in x. It arises from the reduction of x moles of W^{6+} ions to W^{5+}, the changes in the interactions of the tungsten ions with their neighboring oxygens when some have been reduced, and perhaps the bonding of the metal ions to the oxygens. Next comes a term quadratic in x. This term results from interactions between pairs of those centers which are created upon introduction of the metal; W^{5+}-W^{5+}, M^+-M^+, and the interaction between the metal ion and the W^{5+}. These latter interactions are those that can lead to clustering if their net effect is attractive. On the other hand, if they are repulsive there can be no clustering. We shall neglect terms of higher power in x because the contributions from many-center interactions are probably quite small. This is supported by the good agreement between theory and experiment for x as large as 1.

The final term of interest is that which arises from the entropy of distributing the x moles of metal in one mole of WO_3. The ideal entropy of this process is

$$S = nk \ln\{N!/(xN)![(1-x)N]!\}, \tag{2}$$

where N is Avogadro's number. The factor n can have the value of either 1 or 2. If the electron and the metal ion do not have close spatial correlation, then $n=2$. If, on the other hand, the W^{5+} center and the metal ion are associated (as close neighbors), then $n=1$. Using Stirling's approximation, the ideal free energy of distribution F_d is obtained from Eq. (2) as

$$F_d = nRT[x \ln x + (1-x)\ln(1-x)]. \tag{3}$$

This entropy term will always oppose clustering.

Combining all of the above terms, the molar free energy of M_xWO_3 can be written

$$F = F_0 + Ax + Bx^2 + F_d, \tag{4}$$

where A and B are (as yet undetermined) constants. The chemical potential of M in M_xWO_3 is obtained from Eq. (4) by partial differentiation with respect to x:

$$\mu_M = A + 2B + nRT \ln[x/(1-x)]. \tag{5}$$

This equation is used in the general expression for $\mathcal{E}$ to obtain the cell emf as a function of x. This expression for cell emf was fitted to the published cell data to obtain the constant B in Eq. (4). It is not possible to determine the constant A from an emf measurement. However, this term is irrelevant to clustering which is governed solely by the sign and magnitude of B.[12]

The emf measurements[7] were made over a range of x from 0 to 0.5 on amorphous films of H_xWO_3. Equation (5) for μ_M gave excellent agreement with experiment. The constant B was found to be +0.27 eV. The best fit to the data was obtained with $n=2$. The fact that $n=2$ is strong evidence that the W^{5+} center and the proton do not have close spatial correlation. Applying the same expression to emf measurements made on single crystal Na_xWO_3 by Ramanarayanan and Worrell,[6] we find that $B=+0.67$ eV.

It is clear from the above that clustering is unlikely because, for both bronzes, B is positive. We cannot speculate at this point whether B would be positive for other bronzes.

Another property of amorphous H_xWO_3 is at variance with the cluster model. Electron conductivity σ measurements were made on amorphous H_xWO_3 over a wide range of x.[5] At high x ($x>0.3$) H_xWO_3 is metallic. At low x, however, it behaves like an amorphous semiconductor with $\ln\sigma \propto -T^{1/4}$, which is characteristic of variable range hopping. It seems unlikely that the WJC model would predict the same temperature dependence as the variable-range hopping model. A closer analogy to the cluster model would be the granular cermets[13] which are composed of metal grains imbedded in an insulator. For this system a $\ln\sigma \propto -T^{1/2}$ dependence has been observed.

In conclusion then, there is not good evidence for the cluster model of WJC. In fact, the best test of clustering, the x dependence of the free energy of the alkali metal in the bronze, shows that clustering is unlikely in Na_xWO_3 and H_xWO_3.

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system composed of y moles of MWO_3 and $1-y$ moles of WO_3 and the single-phase system of one mole of M_xWO_3 is $\Delta F = y(1-y)B - 2\,\mathrm{RT}[y\ln y + (1-y)\ln(1-y)]$. For a fixed B, this difference is largest for $y=\frac{1}{2}$. For clustering to be possible, $\Delta F < 0$ and therefore $B < -4RT\ln 2$.

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