Microscopic inhomogeneity in sodium tungsten bronze: A comment

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(Received 17 May 1976)

In a recent paper dealing with the electronic transport properties of the alkali-tungsten bronzes, Webman Jortner, and Cohen have sought to explain many of the observed properties of the tungsten bronzes by assuming strong clustering of the alkali components in the alloys, so that charge transport can be described by a classical percolation theory. This comment points out that many results from experiments in sodium tungsten bronze are inconsistent with this microscopic model.

Webman, Jortner, and Cohen[1] (hereafter referred to as WJC) have analyzed the transport data obtained from experiments in alkali-tungsten bronzes and so have demonstrated that a clustered model of the M component in M_xWO_3, where M is an alkali atom, can produce values of the conductivity σ, and the Hall coefficient R, that are in substantial agreement with experiment over the range of metallic samples $x \sim 0.4$ up to $x = 0.9$. A central hypothesis in new treatment is that of clustering; WJC assume that, for example, in Na_xWO_3 all the sodium ions exist in regions of formula unit $NaWO_3$. These clustered regions, dispersed among the other regions of formula unit WO_3, are assumed to be ~100 Å in diameter.

In our view, however, WJC have not taken into account much of the published experimental data in setting up their model of the microscopic structure of the alkali-tungsten bronzes. Their assumption of large clusters relies very heavily on the results, and supporting analysis, of a 1964 paper[2] by Fromhold and Narath on the nuclear magnetic resonance of ^{23}Na. More recent investigations[3,4] have however called into question both the quality of the samples with which Fromhold and Narath obtained their results and their interpretation of the observed quadrupole effects in the ^{23}Na nuclear resonance spectra. These recent investigations do not support the premises on which WJC have relied in arguing for a particular interpretation of the experimental properties of the bronzes. A further argument against the microscopic inhomogeneity proposed by WJC can be advanced by looking at x-ray results.[5]

Dealing first with our objections resulting from the additional nuclear resonance results not considered by WJC, the recent data[4] illustrates the x^2 dependence for ^{23}Na of $(T_1T)^{-1}$ between $x = 0.35$ and $x = 0.89$, and shows that $(T_1T)^{-1}$ is also proportional to x^2 for ^{183}W over the whole concentration range[7] (where T_1 is the nuclear spin-lattice relaxation time and T the absolute temperature). Within the context of a model for Na_xWO_3 involving randomly dispersed sodium, Ref. 4 also shows that the linear variation with x of the density of states at the Fermi level can be explained as a simple consequence of a particular shape of the tungsten-oxygen $5d$-$2p$ conduction band; the total number of conduction electrons per formula unit in Na_xWO_3 is given by $x = \int_{-\infty}^{E_F} N(E)dE$ at $T = 0$ K, where $N(E)$ is the density of states, so that if $N(E)$ has an exponential variation with energy then $x \propto N(E_F)$. The relations $(T_1T)^{-1} \propto x^2$ and $N(E_F) \propto x$ are consistent with each other if Na_xWO_3 is a homogeneous metal, with the sodium ions randomly dispersed, since for homogeneous metals $(T_1T)^{-1} \propto [N(E_F)]^2$. WJC lay great emphasis on the support given to their model from the lack of dependence of $(T_1T)^{-1}$ on x in the experiments of Fromhold and Narath.[2] Furthermore, clustering accounts[6] at once for the relation $N(E_F)$ proportional to x. It is our contention that the Fromhold and Narath[2] experiments were in error in assessing $(T_1T)^{-1}$ as independent of x (possibly because of poor samples; they admit the presence of very strong paramagnetic impurity relaxation competing with the metallic process in relaxing the sodium spins). Given that $(T_1T)^{-1}$ is really proportional to x^2 over the main part of the concentration range of alloys involved, then the specific heat and susceptibility results, exhibiting $N(E_F)$ proportional to x, reinforce the idea that sodium tungsten bronze is a homogeneous metal with a conduction band having an exponential dependence of its density of states on energy.

Much of the evidence relating to clustering from Fromhold and Narath[2] comes from an analysis of the relative intensities of the two sorts of sodium nuclear resonance signals that are always present in the bronzes, and WJC rely on this as justification for their model. Fromhold and Narath[2] neglect conduction-electron screening explicitly in their treatment; Bonera *et al.*[3] have argued strongly that screening effects should be taken into account in the analysis, and have demonstrated that the inclusion of screening materially affects the

argument about clustering. Furthermore, the present author, by extending the nuclear resonance measurements so that they cover the range $x = 0.22$ to $x = 0.89$, has shown that the results of measurements of the quadrupole interactions in the sodium tungsten bronzes are more naturally explained as being generated by the presence of two sorts of sodium sites, one having cubic symmetry and the other having some lower symmetry. Neutron-diffraction data supports the idea of their being some noncubic sodium sites in the low-temperature phase.[8]

Weinberger[9] has recently reported an investigation of the tungsten nuclear resonance in Na_xWO_3, in samples with x down to 0.22. The tungsten line is broad but unstructured throughout the compositional range investigated; there is no evidence for the two types of tungsten sites such as would exist if the microscopic inhomogeneity hypothesis of WJC were correct.

Turning now to the x-ray data,[4,5] the results of powder spectra over the range $x = 0.22$ to $x = 0.89$ show a cubic arrangement with a lattice constant given by

$$a = 3.7845 + 0.0820x \text{ Å}.$$

A fully metallic region should then exhibit a lattice constant of 3.866 Å and a sodium-free region a lattice constant of 3.7845 Å. In a sample containing clusters of metallic regions, of a size 50 to 100 Å in diameter, within sodium-free regions, a doublet spectra should be observed. In fact, fairly narrow singlet x-ray lines are observed over the whole range of x.

In conclusion, sodium tungsten bronze almost certainly does not show the microscopic inhomogeneity described by WJC. The nuclear resonance work, measuring both $(T_1T)^{-1}$ in quadrupolar effects, on which WJC have relied in modeling the bronzes, has not been supported by subsequent nuclear resonance studies. The standard x-ray formula on which compositional determinations in the bronzes are based does not seem compatible with the postulated structure in WJC.

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