$$\chi_\mathrm{m} = \frac{N\beta^2 g^2}{3kT}\left\{\frac{546\exp(-27x) + 330\exp(-3x) + 180\exp(17x) + 84\exp(33x)}{13\exp(-27x) + 11\exp(-3x) + 9\exp(17x) + 7\exp(33x)} + \frac{660\exp(-21x) + 360\exp(-x) + 168\exp(15x) + 60\exp(27x)}{22\exp(-21x) + 18\exp(-x) + 14\exp(15x) + 10\exp(27x)} + \frac{540\exp(-15x) + 252\exp(x) + 90\exp(13x) + 18\exp(21x)}{27\exp(-15x) + 21\exp(x) + 15\exp(13x) + 9\exp(21x)} + \frac{336\exp(-9x) + 60\exp(3x) + 24\exp(11x)}{28\exp(-9x) + 20\exp(3x) + 12\exp(11x) + 4\exp(15x)} + \frac{60\exp(-3x) + 12\exp(5x)}{10\exp(-3x) + 6\exp(5x)}\right\} \quad (1)$$

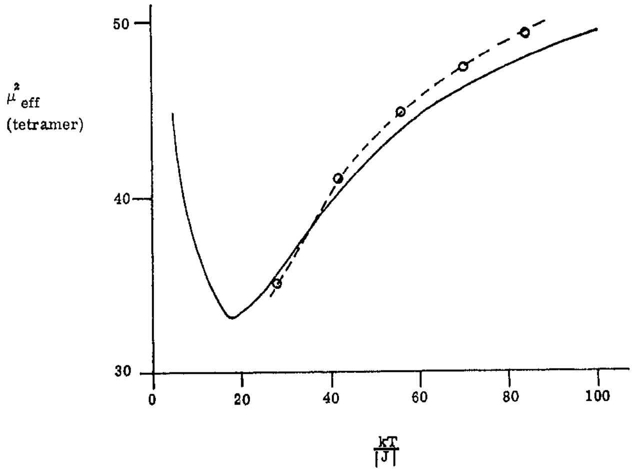

Figure 1.—A comparison of experiment with theory for the trigonal and tetrahedral models: ————, theoretical curve for trigonal model; – – – – –, theoretical curve for tetrahedral model; O, experimental results from ref 1, assuming $J = -3.57k$.

was numerical agreement with a formula due to Van Vleck[2] where the energy levels of the spin system are given by

$$E(S') = \frac{-zJ}{n-1}[S'(S+1) - nS(S+1)]$$

where n is the number of (*equivalent*) atoms in the cluster and z is the number of nearest neighbors for each *equivalent* atom.

Wentworth and Saillant used a number $Z_\mathrm{av} = {}^3/_2$, averaging the number of nearest neighbors for the one central Cr(III) atom ($z = 3$) and the three triangular Cr(III) atoms ($z = 1$). It must be emphasized, however, that the Van Vleck derivation depends on all the atoms in the cluster being exactly equivalent; thus using Z_av over nonequivalent atoms is not correct. This point has also been emphasized by Smart,[3] who shows that the Van Vleck equation is only applicable to three types of clusters: two equivalent atoms (a dimer), three equivalent atoms in an equilateral triangle, or four equivalent atoms arranged in a regular tetrahedron. Although incorrect for the trigonal case, the form of the equation used by Wentworth and Saillant ($Z_\mathrm{av} = {}^3/_2$, $J = -16k$) is in fact the correct expression for the energy levels in a *tetrahedral* [Cr_4] cluster, because (in that case) the product $-zJ$ is $24k$ ($z = 3$, $J = -8k$).

The method of Kambe[4] can be extended to derive the correct expression for the structure proposed by Wentworth and Saillant (eq 1, where $x = -2J/kT$). The agreement between theory and experiment in the trigonal case is much poorer than in the tetrahedral model, as shown in Figure 1. This means that, of the two structures under consideration, the regular tetrahedral arrangement of the four Cr(III) atoms is *more consistent with the magnetic data down to 77°K;* obviously, studies at lower temperatures are needed.

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[2] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter XII.

[3] J. S. Smart in "Magnetism," G. T. Rado and H. Suhl, Ed., Academic Press Inc., New York, N. Y., 1960, Chapter II.

[4] K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).

[5] Contribution No. 3601.

Relations between Lattice Parameter and *x* Value for Some Cubic Tungsten Bronzes[1]

Sir:

Several of the tungsten bronzes (M_xWO_3, where $0 < x < 1$) crystallize in cubic symmetry over part of their composition range. The cubic region is rather extensive ($0.4 < x < 1$) for the sodium tungsten bronzes,[2,3] less extensive for most of the others, and has not been observed for some of them.

A linear relation

$$a_0\ (\text{Å}) = 0.0819x + 3.7846 \qquad (1)$$

between the x value and the lattice parameter, a_0, of the sodium bronzes in the cubic region was first observed by Brown and Banks.[4]

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[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2228.

[2] G. Hägg, *Nature*, **135**, 874 (1935); *Z. Physik. Chem.* (Leipzig), **B29**, 192 (1935).

[3] W. F. deJong, *Z. Krist.*, **81**, 314 (1932).

[4] B. W. Brown and E. Banks, *J. Am. Chem. Soc.*, **76**, 963 (1954).

The use of thermal neutron activation analysis for sodium by Reuland and Voigt[5] coupled with lattice parameter determinations by Shanks gave an equation

$$a_0\ (\text{Å}) = 0.818x + 3.7850 \qquad (2)$$

in excellent agreement with eq 1.

Among the other tungsten bronzes which crystallize in cubic symmetry for certain values of x are those of lithium,[4,6,7] the rare earths,[8] and uranium.[9] During the course of an investigation on properties of these compounds, lattice parameter data for the cubic tungsten bronzes of gadolinium and uranium were determined from Debye–Scherrer powder photographs and their x values were determined by activation analysis.[10,11] Graphs of a_0 *vs.* x are shown in Figure 1, together with data on the cubic bronzes of lithium and sodium.[5] The composition of the lithium bronzes was obtained with the method of Straumanis and Hsu.[12]

It can be seen that, for the tungsten bronzes of sodium, gadolinium, and uranium, the lattice expands as the x value is increased. This is due to removal of positive charge from the tungsten as the metal ion is added, giving it a formal charge approaching +5 rather than +6 and resulting in an expansion of the lattice. In the case of lithium the lattice of the Li_xWO_3 contracts appreciably as x increases because of the small size of the lithium ions. In this case the removal of charge from the tungsten is not sufficient to balance the charge effect of the small lithium ions.

As is the case for the sodium bronzes, the relation between the lattice parameters and x values for the other cubic tungsten bronzes appears to be a linear one, although the range over which this structure exists is much more limited in these cases. However, lines drawn visually through these points and extrapolated to $x = 0$ yield a common intercept, in spite of large differences in the slopes of the lines. The value of this intercept is essentially that previously observed for the sodium tungsten bronze, 3.785 Å, as shown most dramatically in the case of the extrapolation for the lithium bronzes. This intercept corresponds to the parameter of a theoretical cubic WO_3 lattice. No such structure is known to exist for WO_3.

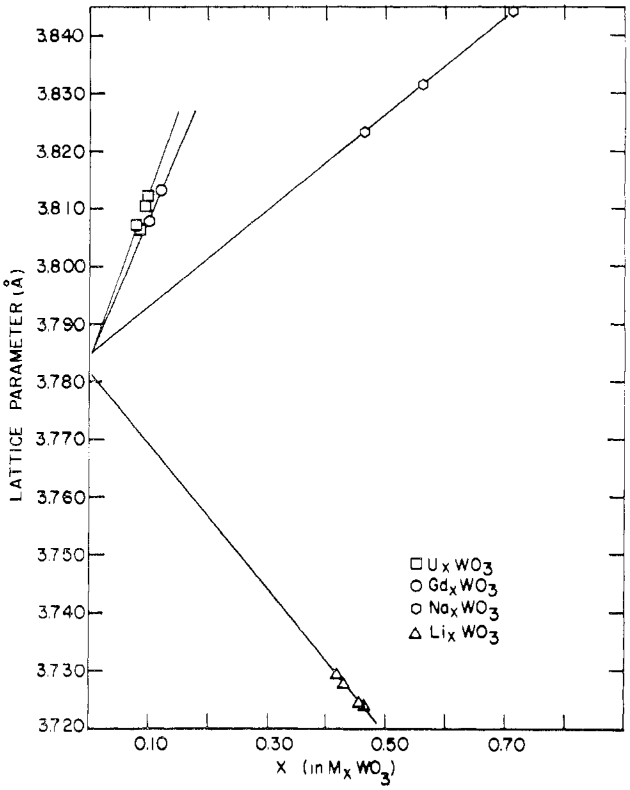

Figure 1.—Lattice parameter *vs.* x value for M_xWO_3. Slopes of lines: U, 0.278; Gd, 0.230; Na, 0.0818; Li, −0.134.

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