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Low-Temperature Heat Capacity of Some Alkali Metal Tungstates*

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Heat capacity measurements have been made on the two triclinic tungstates, $Li_{0.2}WO_3$ and $Na_{0.33}WO_3$ from 1 to 60 K. In addition to the normal Debye term the data show a large contribution which can be fit to a single Einstein mode associated with the oscillation of the alkali ions in the holes formed by the corner bonding of six WO_6 octahedra. The Einstein characteristic temperatures obtained are 71 ± 2 and 78 ± 2 K for $Li_{0.2}WO_3$ and $Na_{0.33}WO_3$, respectively. The results are compared with those reported earlier for the hexagonal tungsten bronzes.

I. Introduction

Recent measurements of the heat capacity of hexagonal alkali tungsten bronzes (*1*–*3*) have shown the existence of a large, low temperature contribution in excess of the normal Debye-like heat capacity. This additional contribution has been explained as the result of an Einstein-like mode associated with the movement of the alkali atoms within the large six-sided rings or channels formed by the WO_6 octahedra in the *a–b* plane. Bevolo *et al.* (*3*) were able to demonstrate that the magnitude and characteristic temperature of the mode depended on the mass and ionic radius of the alkali atom.

A triclinic sodium tungstate with a stoichiometry near $Na_{0.33}Wo_3$ and with sodium sites similar to the hexagonal bronzes has been reported by Shanks (*4*) and Franzen *et al.* (*5*). The compound has a layer structure consisting of four hexagonal bronze-like layers linked in a fifth layer to the next set of hexagonal ring layers by a trigonal bipyramid of oxygen atoms. The sodium atoms are thought to be in the unaligned hexagonal rings. Recently a lithium analog was prepared in the Ames Laboratory with a lithium concentration of 0.2. In light of the results for the hexagonal tungsten bronzes it appeared of interest to investigate the heat capacity of these compounds at low temperatures.

II. Experimental

Single-crystal samples of the triclinic sodium and lithium tungstates were prepared by electrolysis of fused salts (*4*) of Na_2WO_4–WO_3 and Li_2WO_4–WO_3, respectively. The sodium–tungsten ratio in the $Na_{0.33}WO_3$ sample was determined by neutron activation analysis. The nominal composition $Li_{0.2}WO_3$ for the lithium compound is based on the known composition of the fused salt and the Li_2WO_4–WO_3 phase dia-

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gram. For both compounds, the tungsten–oxygen ratio is written as WO_3 although from structural consideration the correct ratio may be nearer $WO_{3.2}$.

Heat capacity measurements were made from 1 to 60 K by a standard heat-pulse method in a helium cryostat of conventional design. Details of the equipment and the experimental procedures were described previously (*3*, *6*). The single-crystal samples were oriented in the cryostat sample holder with the *c* axis parallel to the copper heat source to maximize thermal conduction through the sample since preliminary thermal conductivity measurements indicate a much higher conductivity in the *a–b* plane than along the *c* axis.

III. Results and Discussion

At low temperatures the heat capacity is given by

$$C_p = \gamma T + \beta T^3, \qquad (1)$$

where γT is the electronic contribution and βT^3 is the Debye lattice contribution. The β term is proportional to θ_D^{-3} and one can obtain values for both θ_D and γ by plotting the heat capacity data as C_p/T vs T^2. The data for the two compounds are illustrated on such a plot in Fig. 1 in the temperature range $1 < T < 6.3$ K. The sodium and lithium tungstates show a linear behavior on this plot below 3.5 and 4.0 K, respectively. From these linear regions one can obtain the values for γ and θ_D listed in Table I. The data for WO_3 reported by Bevolo *et al.* (*3*) and cubic $Na_{0.30}WO_3$ reported by Zumsteg (*7*) are included for comparison. Since these tungstates, like WO_3, are very poor conductors, the electronic contributions to C_p are expected to be small and are indeed comparable with WO_3. The metallic bronzes have γ values between 1 and 3 mJ/mole K (*3*, *7*). The values calculated for θ_D for the two tungstates are not inconsistent with those reported for the other bronzes and WO_3.

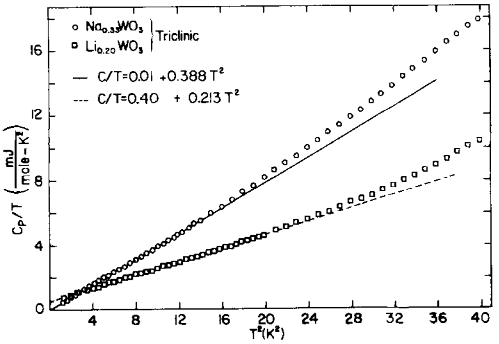

FIG. 1. Heat capacity of the triclinic $Li_{0.2}WO_3$ and $Na_{0.33}WO_3$ crystals in the temperature range $1 < T < 6.3$ K. The dashed and solid lines are the best fits to a normal Debye heat capacity.

Figure 2 shows our results for the two tungstate compounds as well as data from Bevolo *et al.* (*3*) for WO_3 and cubic Na_xWO_3 in the temperature range $1 < T < 20$ K. From this figure it is clear that the tungstates have excess heat capacities with respect to WO_3 or cubic Na_xWO_3 just as Bevolo *et al.* (*3*) reported for hexagonal bronzes. The data in Fig. 3 show that the behavior continues up to 60 K and indeed, the excess term appears to become constant between 40 and 60 K.

Both King *et al.* (*1*) and Bevolo *et al.* (*3*) explained their data with a model in which the lattice heat capacity consists of a Debye term due to the WO_6 octahedra and an Einstein term due to the vibrations of the alkali atoms located in the center of the six-

TABLE I

VALUES OF θ_D AND γ FOR TRICLINIC $Na_{0.33}WO_3$, $Li_{0.2}WO_3$, WO_3, AND CUBIC $Na_{0.30}WO_3$

	θ_D (K)	γ mJ/mole K
$Na_{0.33}WO_3$	280 ± 20	0.01
$Li_{0.2}WO_3$	340 ± 20	0.4
$WO_3^{(3)}$	380 ± 15	0.6
Cubic $Na_{0.30}WO_3^{(7)}$	296	1.16

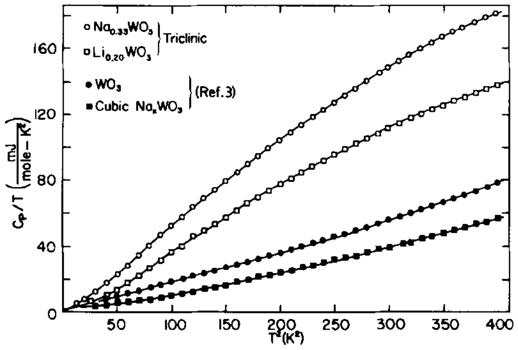

FIG. 2. Heat capacity of the triclinic $Li_{0.2}WO_3$ and $Na_{0.33}WO_3$, crystals from 1 to 20 K. Data for WO_3 and Na_xWO_3 from Bevolo *et al.* (*3*) are included to show the large additional contribution to the heat capacity of the triclinic samples.

sided rings formed by the WO_6 octahedra. King *et al.* (*1*) obtains a value for the Einstein contribution by subtracting $\gamma T + \beta T^3$, with γ and β determined at low temperature, from the total heat capacity. This procedure assumes a constant θ_D over the entire temperature range measured. Because of the variation observed in the value of θ_D as a function of temperature for WO_3 and cubic $Na_{0.8}WO_3$, Bevolo *et al.* (*3*) calculated the magnitude of the Einstein term by subtracting the heat capacity measured for WO_3 from the values obtained for the hexagonal bronzes. This assumes that the temperature dependence of θ_D is the same as that of WO_3.

Because our data extend over a wide temperature range, 1–60 K, we have chosen to use the technique reported by Bevolo *et al.* (*3*). Figure 4 shows the resulting exess heat capacity of the tungstates when the values for WO_3 reported by Bevolo *et al.* are subtracted from our data. The dashed and solid lines in Fig. 4 represent the best fits to the data for a single Einstein mode using the equation

$$C_E = \left(\frac{3R}{4}\right) S \left(\frac{\theta_E}{T}\right)^2 \operatorname{csch}^2\left(\frac{\theta_E}{2T}\right), \quad (2)$$

where R is the universal gas constant, S is the number of atoms contributing to the mode per formula weight, and θ_E is the characteristic Einstein temperature. Details of the technique used to fit the data with the equation are given by Bevolo *et al.* The values of θ_E and S which provide the best fit to the tungstate data are

$\theta_E = 78 \pm 2$ K and

$S = 0.38 \pm 0.03$ for $Na_{0.33}WO_3$

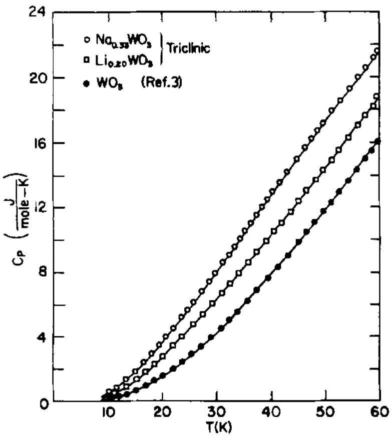

FIG. 3. Heat capacity of the triclinic tungstates and WO_3 from 10 to 60 K showing that the difference in the heat capacity becomes constant at high temperatures.

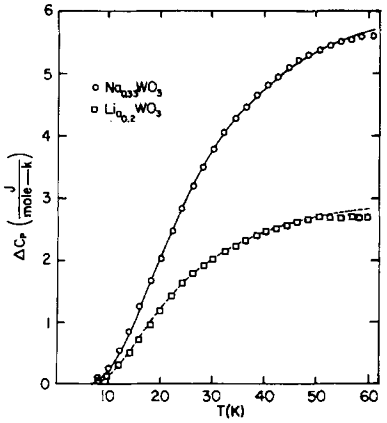

FIG. 4. The excess heat capacity of the triclinic $Na_{0.33}WO_3$ and $Li_{0.2}WO_3$ samples vs temperature. The dashed and solid lines represent the best fits to single Einstein modes.

TABLE II

EINSTEIN TEMPERATURE, NUMBER OF OSCILLATORS, AND RELATED CONSTANTS FOR THE TUNGSTATES AND TWO TUNGSTEN BRONZES

	$Li_{0.2}WO_3$ (triclinic)	$Na_{0.33}WO_3$ (triclinic)	Rb_xWO_3[a] (hexagonal)	Cs_xWO_3[a] (hexagonal)
θ_E (K)	71 ± 2	78 ± 2	58 ± 2	70 ± 2
S	0.17 ± 0.03	0.38 ± 0.03	0.29 ± 0.02	0.32 ± 0.02
M (amu)	7	23	86	133
k (N/m)	1	4	8	19

[a] Reference (3).

and

$$\theta_E = 71 \pm 2 \text{ K and}$$

$$S = 0.17 \pm 0.03 \text{ for } Li_{0.2}WO_3.$$

The values obtained for S are in agreement with the number of alkali ions present within the combined errors of the compositional analysis and the calculation of the excess heat capacities. In the temperature range $15 < T < 40$ K the excess heat capacities of each tungstate can be fit to a single Einstein mode within 2%, suggesting that the Li and Na ions oscillate isotropically within the six-sided channels. However, it should be noted that the excess heat capacity data were obtained with the assumption that the Debye term remains the same as that of WO_3 and that the heat capacity data are likely to be rather insensitive to small anisotropies in the oscillation of the alkali ions.

In the temperature range investigated here, the alkali ions can therefore be approximated as independent particles executing simple harmonic motion in three dimensions with a frequency

$$\nu_E = k_B\theta_E/h, \tag{3}$$

where k_B is the Boltzmann constant and h is Planck's constant. For simple harmonic motion,

$$\nu_E = \left(\frac{\pi}{2}\right)\left(\frac{k}{m}\right)^{1/2}, \tag{4}$$

where k is the force constant associated with the restoring force acting on the alkali ions and m is the mass of the alkali ions. By combining Eqs. (3) and (4) one obtains an expression for θ_E as a function of the mass of the ion and the restoring force constant:

$$\theta_E = \left(\frac{\hbar}{k_B}\right)\left(\frac{k}{m}\right)^{1/2} \tag{5}$$

The overlap of the alkali ion orbitals with the orbitals of the surrounding oxygen atoms presumably produces the restoring force. Since the rings formed by the WO_6 octahedra remain nearly constant in size for all the compounds discussed here, the radius of the alkali ion should be the major determining factor in the value of the force constants.

Table II lists the various parameters associated with the fit to a single Einstein mode for each of the tungstates and two hexagonal tungsten bronzes. It can be seen from Table II that the force constant increases with increasing ion radius as one would expect; the Na^+ ion with a radius of about 0.95 Å has a larger force constant than the Li^+ ion with a radius of about 0.68 Å because of the increased overlap of the orbitals with nearest-neighbor oxygen orbitals.

IV. Summary

The low-temperature heat capacity data obtained for the two triclinic tungstates, $Li_{0.02}WO_3$ and $Na_{0.33}WO_3$, shows a contribution in addition to the Debye term which can be fit to a single Einstein mode associated with oscillations of the alkali ion in the six-sided channel formed by the WO_6 octahedra. The Einstein characteristic temperatures obtained are 71 ± 2 K for $Li_{0.2}WO_3$ and 78 ± 2 K for $Na_{0.33}WO_3$. These results are similar to and consistent with the results obtained earlier for the hexagonal bronzes.

Acknowledgments

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