Heat capacity of hexagonal tungsten bronzes

A. J. Bevolo, H. R. Shanks, P. H. Sidles, and G. C. Danielson
Ames Laboratory and Department of Physics, Iowa State University, Ames, Iowa 50010
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The heat capacity of four hexagonal tungsten bronzes (K_xWO_3, Rb_xWO_3, Cs_xWO_3, and Tl_xWO_3), WO_3, and cubic Na_xWO_3 have been measured from 1 to 55 K. The excess heat capacity reported by King *et al.* for Rb_xWO_3 and attributed to an Einstein mode is also present in K_xWO_3, Cs_xWO_3, and Tl_xWO_3. The values of x determined from the excess heat capacity agree reasonably well with the nominal composition having $x = 0.33$. The Einstein temperatures Θ_E for the metal ions vibrating in the channels formed by the six-membered rings of WO_6 octahedra were found to be 58 K for Rb, 70 K for Cs, and 38 K for Tl. Two unexplained peaks in the heat capacity of K_xWO_3 near 20 K precluded an accurate determination of Θ_E for this tungsten bronze, but Θ_E is estimated to be between 60 and 90 K. The magnitudes of the Einstein temperatures can be understood in terms of the masses and ionic radii of the metal ions. All four hexagonal tungsten bronzes are superconductors. Measurements of the heat capacity with a magnetic field showed Rb_xWO_3 to be a type-I superconductor, but K_xWO_3 to be a type-II superconductor.

I. INTRODUCTION

Tungsten bronzes are nonstoichiometric compounds with the general formula M_xWO_3, where M is a metal and $0 < x < 1$. The crystal structure has high symmetry for high x values and low symmetry for low x values. In all cases the structure is composed of corner-bonded WO_6 octahedra with the metal ions occupying the interstitial sites. Since WO_3 has a corner-bonded monoclinic structure,[1] the tungsten bronzes may be considered to be high-symmetry forms of WO_3, stabilized by the presence of the metal ions. If M is an alkali metal, Magneli[2] has shown that the hexagonal structure consists of six-member rings forming channels, and the tetragonal-I structure consists of five-member rings forming channels. The cubic structure may be considered as four-member rings.

Superconductivity was first reported by Raub *et al.*[3] in a tetragonal-I sodium bronze with $x \approx 0.3$ and T_c about 0.5 K. The perovskite-related cubic and tetragonal-II structures were not superconducting. Sweedler *et al.*[4] reported that hexagonal K, Rb, and Cs bronzes were superconducting with T_c near 1.5 K. Remieka *et al.*[5] found that acid etching of the alkali-metal hexagonal bronzes increased T_c by a factor of 3, lowered the x value, and produced a contraction of the lattice along the c axis. A magnetic field of 24 kG was required to suppress T_c below 4.2 K with H parallel to the c axis. No corresponding magnetic behavior was reported for the untreated samples. Other hexagonal bronzes (M = Ca, Sr, Ba, In, and Tl) have also been reported[6,7] to be superconducting with T_c from 1 to 3 K. Using a hydrothermal growth process Gier *et al.*[8] have been able to produce hexagonal lithium, sodium, and ammonium bronzes which are superconducting with T_c between 1 and 5.4 K. However, they found that one hexagonal bronze, Sn_xWO_3, was not superconducting above 1 K. Superconductivity has been observed by Hubble *et al.*[9] in the related tungsten fluoroxide bronzes $M_xWO_{3-x}F_x$, where M = K, Rb, and Cs with x values from 0.08 to 0.30. They observed T_c to increase with decreasing x value, similar to the results reported for the acid-etched hexagonal bronzes. Large critical fields, 5 to 10 kG, indicative of type-II behavior were found for the Rb and Cs fluoroxide bronzes.

Low-temperature heat capacity of the tungsten bronzes has been reported by Vest *et al.*,[10] Gerstein *et al.*,[11] Kienzle *et al.*,[12] and King *et al.*[13] Vest *et al.*[10] have reported the specific heat of cubic Na_xWO_3 for several x values from 1 to 4 K and found that $C_p = \gamma T + \beta T^3$ with γ increasing with x and the Debye temperature Θ_D (obtained from β) ranging from 450 to 505 K. The Debye temperatures were obtained from β using $4 + x$ as the number of atoms per formula weight. Gerstein *et al.*[11] measured C_p from 15 to 300 K for cubic $Na_{0.679}WO_3$ and found a minimum in the Debye temperature at about 27 K. Kienzle *et al.*[12] reported on the heat capacity of five different Rb_xWO_3 samples from 1 to 16 K and found T_c to be insensitive to x value within the range $0.27 \leq x \leq 0.32$. A low-temperature anomaly near 2 K prevented the determination of γ and Θ_D. King *et al.*[13] have measured the heat capacity of hexagonal Rb_xWO_3 with $x \sim \frac{1}{3}$ from 1.5 to 16 K and found an excess heat capacity which they could fit to an Einstein contribution with characteristic temperature, Θ_E, of 57 K. Since the hexagonal structure (see Fig. 1) has large channels along the c axis, which contain the Rb^+ ion, it was proposed that the motion of these ions could account for the Einstein excess heat capacity. Although complicated by the presence of this excess

heat capacity and the superconducting jump in C_p near 2 K, they determined that $\Theta_D = 415$ K and $\gamma = 2.2$ mJ/mole K^2.

We report here a systematic study of the low-temperature heat capacity of four hexagonal tungsten bronzes (M = K, Rb, Cs, and Tl) from 1 to 55 K. Previous heat-capacity measurements on hexagonal tungsten bronzes have been reported only for Rb_xWO_3. Although critical-field measurements on acid-etched and fluorinated hexagonal bronzes suggest type-II superconductivity, no determination of the type of superconductivity has been reported for untreated tungsten bronze samples. Measurements of C_p in a magnetic field provide a clear means of distinguishing between type-I and type-II superconductivity. A magnetic field also allows one to suppress the superconducting jump in C_p so that accurate values of γ and Θ_D can be obtained.

During the course of these investigations it became desirable to know C_p for WO_3 from 1 to 55 K. The only available data[14] below room temperature were from 300 to 63 K, so we have measured C_p for WO_3 from 1 to 55 K. For comparison purposes we have also measured C_p for cubic $Na_{0.8}WO_3$ from 1 to 55 K.

II. EXPERIMENT

Four hexagonal tungsten bronze single crystals were grown electrolytically from a fused salt.[15] Based on previous experience with the growth of these materials, the x values were estimated to be within 10% of 0.33, which is the upper theoretical limit for the hexagonal structure.

Mass spectrographic analyses gave similar results for all four samples. The principal impurities (relative to tungsten having 10^6 parts per million) were alkali metal atoms at a few thousand ppm atomic and Mo and Fe at a few hundred ppm atomic. All other impurities totaled less than 100 ppm atomic. The WO_3, grown by vapor transport, showed 2000-ppm Na and 60-ppm Mo; the sum of all other impurities was less than 20 ppm.

Heat-capacity measurements were made by the heat-pulse method in a He^4 cryostat of conventional design. Samples rested on a copper pan supported by nylon threads. The Ge thermometer was calibrated from 1 to 20 K on a paramagnetic-salt temperature scale,[16] and from 20 to 55 K on the NBS 1955 temperature scale.

A 29-g sample of 99.999% American Smelting and Refining Company (ASARCO) copper was used to determine the overall accuracy of the calorimeter. From the copper reference equation[17] and NBS compilation[18] copper from 25 to 60 K,[18] the measured C_p agreed within 1% of the reference C_p over the whole temperature range. The addenda correction varied from 8 to 32% for the 29-g copper sample. For $T < 25$ K the heat capacity of the 29 g of copper is approximately twice that of a typical bronze sample having a mass of about 8 g. Thus the estimated uncertainty in the C_p of the bronze samples is about 2%. From 25 to 55 K the heat capacity of the bronzes decreases from one-half to one-quarter that of the 29-g copper sample; so the estimated uncertainty above 25 K rises from 2% to 4%.

The magnetic field was supplied by a 12-in. Varian electromagnet. The cryostat tail was designed to fit snugly between the 2-in. gap of this electromagnet. A Hall-probe magnetometer was used to measure the applied field. Considering the homogeneity of the field and the absence of any magnetic materials near the sample, it was estimated that the field at the sample could be measured to within 1 G for fields less than 100 G.

III. RESULTS

A normal metal at low temperatures has

$$C_p = \gamma T + \beta T^3, \tag{1}$$

where γT is the electronic specific heat and βT^3 is the lattice contribution. The lattice coefficient β is related to the Debye temperature Θ_D by[19]

$$\beta = 1944 r \Theta_D^{-3}, \tag{2}$$

where β is in units of J/mole K^4 and r is the number of atoms per formula weight. For the bronzes M_xWO_3, $r = 4 + x$. If the data are plotted as C_p/T vs T^2, Eq. (1) predicts a straight line whose slope is β and whose intercept is γ.

Heat-capacity measurements for the four hexagonal bronzes K_xWO_3, Rb_xWO_3, Cs_xWO_3, and Tl_xWO_3 as well as for the cubic bronze $Na_{0.8}WO_3$ and the WO_3 sample are shown in Figs. 2–5. The magnetic field was less than 1 G. Our data for cubic $Na_{0.8}WO_3$ agree with the measurements of Vest *et al.*[10]

In Fig. 2 the data are plotted as C_p/T vs T^2 for $1 < T < 2.8$ K. Both Cs_xWO_3 and WO_3 have Θ_D equal to 380 ± 15 K, while Na_xWO_3 has a Θ_D of 520 ± 20 K.

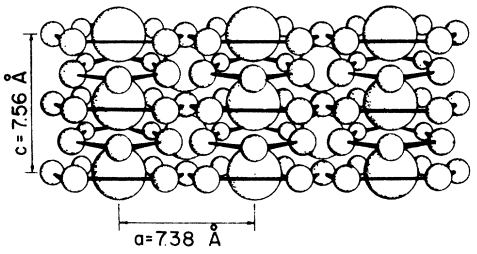

FIG. 1. Perspective view of hexagonal tungsten bronze structure (after Magneli, Ref. 2) showing open channels along the vertical c axis.

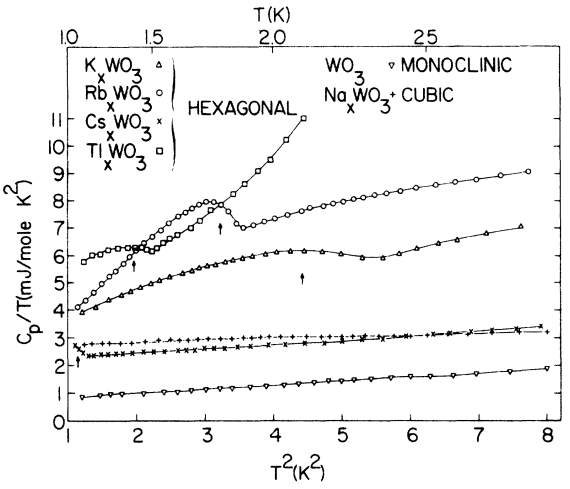

FIG. 2. Heat capacity of WO_3, cubic Na_xWO_3, and four hexagonal bronzes for $1 < T < 2.8$ K. The superconducting transitions for the four hexagonal bronzes are shown by arrows. The plot of C_p/T vs T^2 is linear for WO_3, Na_xWO_3, and Cs_xWO_3 in this temperature range.

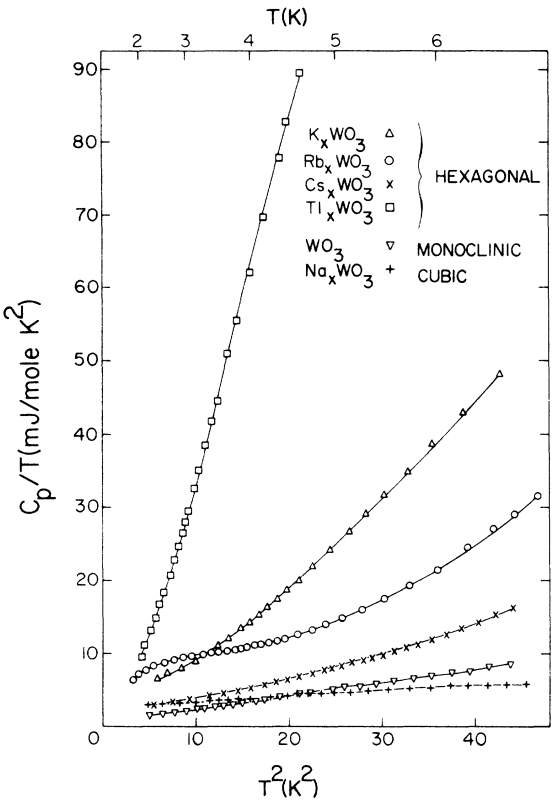

FIG. 3. Heat capacity of WO_3, cubic Na_xWO_3, and four hexagonal bronzes for $2 < T < 6.5$ K. All four hexagonal bronzes show an excess heat capacity with respect to WO_3 and Na_xWO_3, which retain their linear behavior. The excess heat capacity of Tl_xWO_3 is enormous. The Rb_xWO_3 curve exhibits an added shoulder.

The γ values, in units of mJ/mole K^2, are 0.6, 2.15, and 2.70 for WO_3, Cs_xWO_3, and Na_xWO_3, respectively. Since WO_3 is an insulator, γ should be zero. The origin of this linear term in the heat capacity of WO_3 is unknown. Additional contributions to the heat capacity for K_xWO_3, Rb_xWO_3, and Tl_xWO_3 preclude the determination of γ and Θ_D for these tungsten bronzes. In Fig. 2 the superconducting transitions for the four hexagonal bronze samples are indicated by vertical arrows.

In Fig. 3 the C_p of the same six samples are shown again in a C_p/T-vs-T^2 plot, but now for the temperature range $2 < T < 6.5$ K. Only Na_xWO_3 and WO_3 retain their linear form. The four hexagonal bronzes show widely varying amounts of excess heat capacity with respect to the heat capacity of Na_xWO_3 or WO_3. The excess heat capacity for Rb_xWO_3 is qualitatively different from the excess heat capacity of the other three hexagonal bronzes below 5 K. Rb_xWO_3 exhibits an added shoulderlike behavior. A magnetic field of 16 kG produced no significant change in this feature. This effect was not reported by King *et al.*,[13] and may be caused by impurities in our samples. Unfortunately this shoulder prevents the determination of γ and Θ_D for Rb_xWO_3. The large excess C_p for Tl_xWO_3 and K_xWO_3 also precluded the determination of γ and Θ_D for these tungsten bronzes.

Figure 4 shows the data, still plotted as C_p/T vs T^2, for temperatures up to 18 K. It is clear from these data that the C_p of the hexagonal tungsten bronzes are qualitatively different in magnitude from either Na_xWO_3 or WO_3. The heat capacity of

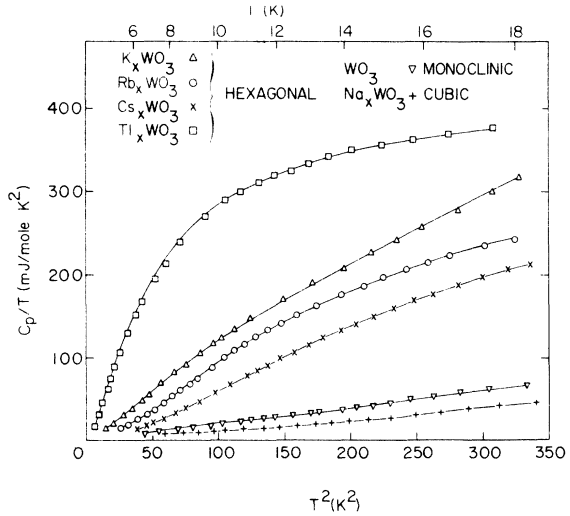

FIG. 4. Heat capacity of WO_3, cubic Na_xWO_3, and four hexagonal bronzes for $T < 18$ K. The excess heat capacity is conspicuous for all four of the hexagonal bronzes.

Tl_xWO_3 is enormous compared to that of most materials.

Figure 5 shows C_p vs T up to our highest temperature, 55 K. Several new features are shown in Fig. 5. Above 40 K the difference between the heat capacity of a hexagonal bronze and the heat capacity of WO_3 is nearly independent of temperature. Such is not the case for the heat capacity of Na_xWO_3 which, above 40 K, appears to be converging to the heat capacity of the hexagonal bronzes. Near 20 K, K_xWO_3 exhibits two closely spaced peaks in the heat capacity. These peaks occur only for this material. Measurement on three samples from the same crystal showed that neither annealing at 600 °C nor cold working nor a magnetic field of 1000 G had any influence on these peaks. A sample grown from a different fused salt exhibited a single broad peak centered at the midpoint between the two peaks shown in Fig. 5.

Figure 6 shows the heat capacity of Rb_xWO_3 near the superconducting transition with the applied magnetic field perpendicular to the c axis. A prominent feature of the data in Fig. 6 is the existence of excess heat capacity near T_c in the presence of a nonzero magnetic field. These data were taken by cooling the sample to 1 K in zero magnetic field, after which the desired magnetic field was applied. At this constant magnetic field, heat capacity data were measured from 1 K to temperatures somewhat higher than T_c. Before beginning the next set of data at a different magnetic field, the field was reduced to zero and the sample warmed to at least 4.2 K. The sample was then cooled to 1 K again in zero magnetic field, and the new field applied. This procedure was designed to eliminate any trapped flux in the sample. Data taken when the sample was cooled in a magnetic field gave evidence of trapped flux in the form of reduced excess heat capacity near T_c. The width of the transition shows a noticeable sharpening when the magnetic field is increased from zero to 7.5 G. As the field is further increased, the transition becomes broadened until at fields near 40 G the width is comparable to that observed at zero field.

The jump in heat capacity ΔC, the transition temperature T_c, and the width of the transition ΔT_c were obtained for each value of the magnetic field by the method shown in Fig. 7. The value of ΔC in zero field is found to be 4.2 ± 0.9 mJ/mole K. The large uncertainty in ΔC is caused by the broadening of the transition in zero field and by the nonlinear behavior of the heat capacity in the normal state.

The critical-field curve, H_c vs T^2, for Rb_xWO_3 is shown in Fig. 8. The data for zero field and for fields above 40 G are less reliable, owing to the considerable broadening of the transitions. The straight line drawn through the more reliable points (7.5 to 40 G) in Fig. 8 gives $T_c(0) = 1.82 \pm 0.05$ K and $H_c(0) = 94 \pm 5$ G. The error bars for the points in Fig. 9 represent the full width of the transition ΔT_c obtained by the method shown in Fig. 7.

An unetched Rb_xWO_3 sample was found to have a T_c of 2.1 K as determined by ac mutual inductance

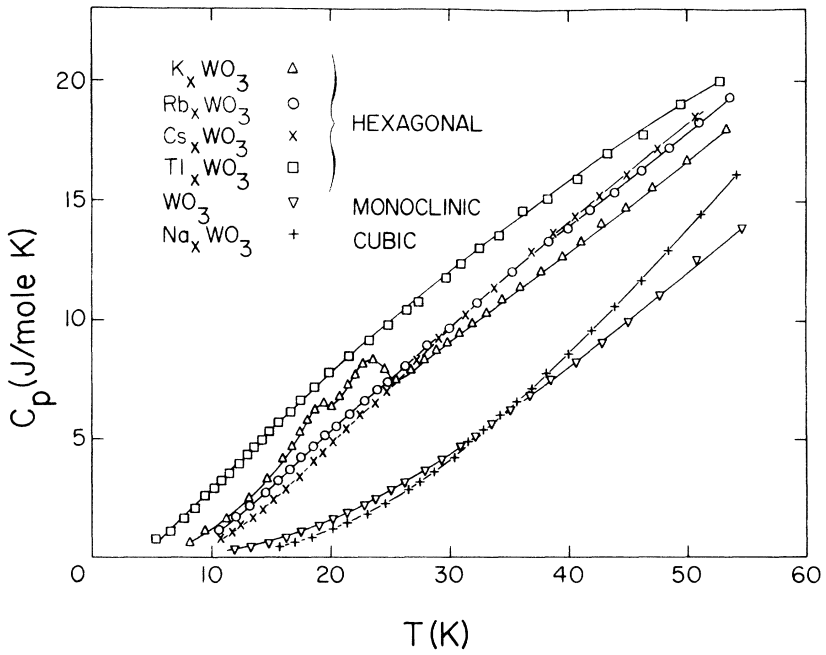

FIG. 5. Heat capacity of WO_3, cubic Na_xWO_3, and four hexagonal bronzes for $T < 55$ K. Above 40 K the difference between the heat capacity of a hexagonal bronze and the heat capacity of WO_3 is nearly independent of temperature as one would expect if this difference is due to an Einstein contribution. Near 20 K the curve for K_xWO_3 exhibits two closely spaced peaks, which are unexplained.

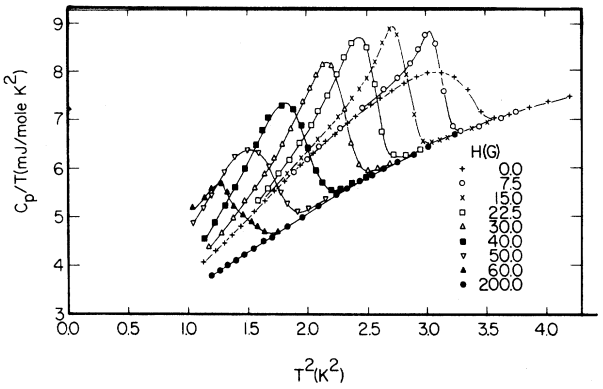

FIG. 6. Heat capacity of hexagonal Rb_xWO_3 in the presence of a magnetic field. The extra heat capacity (latent heat) near T_c associated with the application of a magnetic field is characteristic of a type-I superconductor.

and by heat-capacity measurements. After treatment at 150 °C for several hours with H_2SO_4 in a pressure vessel, the mutual-inductance measurements revealed a broad superconducting transition from 3 to 5 K, while the heat capacity showed a single peak at 2.1 K. For this particular acid treatment on an Rb_xWO_3 single crystal, the increase in T_c was evidently a surface effect.

IV. DISCUSSION

According to the model suggested by King *et al.*[13] the lattice heat capacity of the hexagonal bronzes consists of two parts; a lattice term due to the WO_6 octahedra and an Einstein contribution due to the motion of the metal ions in the channel site. The measurement gives only the sum of these two heat-capacity contributions. In order to find the Einstein contribution, we need to obtain the WO_6 lattice term by itself. An ideal solution would be to measure the heat capacity of a hexagonal-phase WO_3 sample and subtract it from that of the hexagonal bronzes. The low-temperature (1–55 K) phase of WO_3 is not known, but it is probably not hexagonal. However, WO_3 in all its low-temperature phases has the same basic structural unit as the bronzes, namely corner-bonded WO_6 octahedra.[20] In addition, our results for $T < 3$ K give very similar Debye temperatures for WO_3 and for the hexagonal bronze Cs_xWO_3 (380 K for WO_3 and 380 K for Cs_xWO_3). Also these values of Θ_D are very near the value of Θ_D for Rb_xWO_3 (415 K) found by King *et al.*[13] These results suggest that, despite the difference in crystal symmetry, the low-frequency WO_6 lattice modes for WO_3 and the hexagonal bronzes are very similar.

On the other hand, the low-frequency modes for cubic Na_xWO_3 are not the same as for the hexagonal bronzes, and it is not appropriate to subtract the heat capacity of cubic Na_xWO_3 from the heat capacity of the hexagonal bronzes to obtain the excess heat capacity. Although the fourfold WO_6 bonding is nearly the same for cubic Na_xWO_3 and for WO_3, the larger Debye temperature for the cubic bronze (near 500 K) suggests that the sodium ions are strongly coupled to the WO_6 octahedra in Na_xWO_3. This strong coupling is not unexpected when it is noted that the metal-oxygen interatomic distance in the cubic sodium bronze (1.95 Å) is considerably smaller than that found in the hexagonal bronzes (3.29 Å).

This method of obtaining the excess heat capacity, by subtraction of C_p of WO_3 from that of the hexagonal bronzes, differs from the method used by King *et al.*[13] in their analysis of Rb_xWO_3. They subtracted $C_p = \gamma T + \beta T^3$ from the total heat capacity, with β a constant determined by measurements near 3 K. The Debye temperature, and hence β,

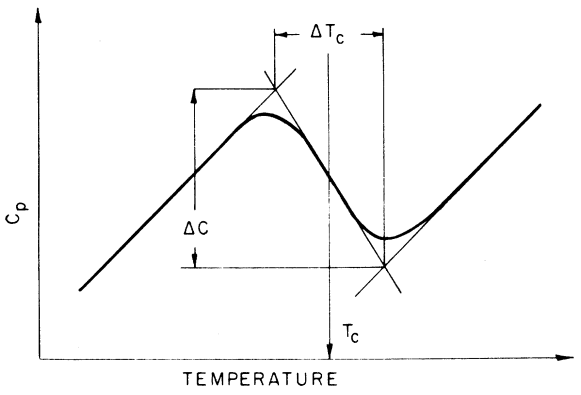

FIG. 7. Method of construction to obtain the jump in heat capacity ΔC, the superconducting transition temperature T_c, and the width of the transition ΔT_c.

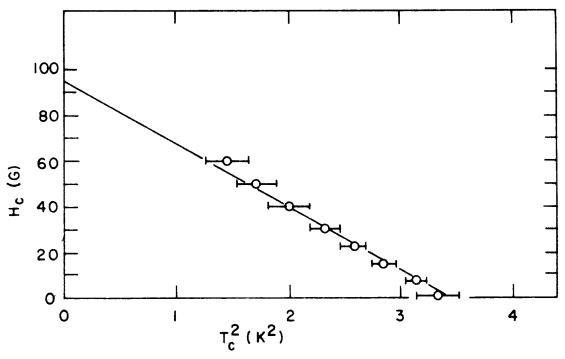

FIG. 8. Critical field curve for hexagonal Rb_xWO_3. Error bars represent the full width of the transition ΔT_c. The straight line determines $T_c(0) = 1.82 \pm 0.05$ K and $H_c(0) = 94 \pm 5$ G.

is probably not a constant for the tungsten bronzes. For WO_3, Θ_D at 17 K is 15% smaller than Θ_D at 3 K (or at 0 K). The assumption that Θ_D is a constant overestimates the excess heat capacity. If Θ_D decreases by 15%, then β will increase by 50%, so that the C_p subtracted may be 50% too small at the minimum in the Debye temperature.

Our method of subtracting the heat capacity of WO_3 from the hexagonal bronzes will tend to compensate for the variation of Θ_D with T and lead to a more accurate estimate of the excess heat capacity at higher temperatures.

After subtracting the heat capacity of WO_3 from that of the hexagonal bronzes, we obtained the excess heat capacity shown in Fig. 9 for Tl_xWO_3, Rb_xWO_3, and Cs_xWO_3. Although K_xWO_3 has the same type of excess heat capacity (see Fig. 5), the presence of the two peaks near 20 K makes a quantitative analysis difficult. The fit of the excess-heat-capacity curves in Fig. 9 to a single Einstein heat-capacity function was tested as follows. The Einstein heat capacity can be written as

$$C_E = \tfrac{1}{4} C_M \alpha^2 \csc^2(\alpha/2), \tag{3}$$

where

$$C_M = 3Rs, \tag{4}$$

R is the universal gas constant, s is the number of atoms per formula weight contributing to the Einstein heat capacity,

$$\alpha = \Theta_E/T, \tag{5}$$

and Θ_E is the Einstein temperature.

Equation (3) has two unknowns, s and Θ_E. Taking the values of excess heat capacity from the curves in Fig. 9 at 10 and 30 K, two transcendental equations involving s and Θ_E were obtained. A hyperbolic function identity allowed these two equations to be reduced to a single easily solved transcendental equation. From Θ_E and s obtained in this manner, values of C_E at other temperatures were calculated and compared to the observed excess heat capacity. In all three cases the observed excess heat capacity could be fitted within experimental error by the values of Θ_E and s shown in Table I.

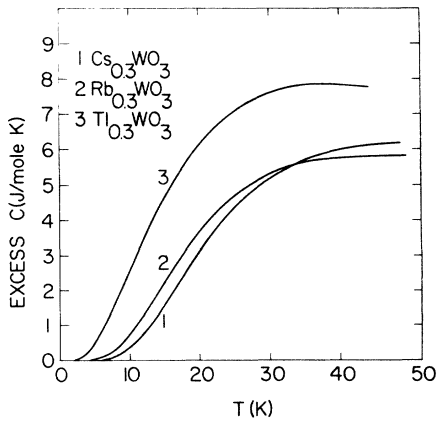

FIG. 9. Excess heat capacity of Cs_xWO_3, Rb_xWO_3, and Tl_xWO_3 obtained by subtraction of the heat capacity of WO_3 from the total heat capacity. In each case, the excess heat capacity can be fitted to a single Einstein heat-capacity function.

The excess heat capacity in Fig. 9 is given to temperatures only up to 45 K, because the excess heat capacity becomes a smaller part of the total heat capacity with increasing temperature. In addition, the germanium thermometer has less sensitivity at the higher temperatures. These two effects combine to increase the error in the excess heat capacity from 4% at the lower temperatures to 8% at 45 K.

The agreement between the x values of these three samples and the s values obtained from the excess heat capacity confirms the hypothesis that this excess heat capacity is due to the metal ions.

For these temperatures ($T < 55$ K) the metal ions can be thought of as a collection of nearly independent particles executing three-dimensional simple harmonic motion with frequency

$$\nu_E = k_B \Theta_E/h, \tag{6}$$

where k_B is the Boltzmann constant and h is Planck's constant. The frequency of vibration is

$$\nu_E = (\tfrac{1}{2}\pi)(k/m)^{1/2}, \tag{7}$$

where k is the force constant associated with the restoring forces acting on the M^+ ions and m is the mass of the M^+ ions. Solving Eqs. (6) and (7) for Θ_E, we obtain

$$\Theta_E = (\hbar/k_B)(k/m)^{1/2}. \tag{8}$$

The masses of the metal ions are well known and are given in Table I in amu. The force constants calculated from these masses and the measured values of Θ_E are shown in Table I.

The volume of a channel site containing the metal ion does not change appreciably from one hexagonal bronze to another, since the unit-cell dimensions (see Table I) do not change. Thus the overlap of the M^+ ion orbitals with the nearest-neighbor-oxygen orbitals, which presumably produces the restoring force, will depend primarily on the ionic radius of the M^+ ion. The larger the M^+ ion, the greater the overlap and the greater the force constant k. This conclusion, that k depends largely on the ionic radius, helps to account for some of the numbers in Table I. Both the Tl^+ and Rb^+ ions have the same ionic radius, and they do indeed have the same force constant. Also consider Θ_E of Rb_xWO_3 and Cs_xWO_3. The heavier Cs^+ ion

should, by Eq. (8), produce a smaller Θ_E for the same k. The fact that Θ_E for Cs_xWO_3 is larger than Θ_E for Rb_xWO_3 can be explained by its larger ionic radius, which produces a larger force constant. These simple assumptions give a qualitative understanding of Θ_E for the hexagonal tungsten bronzes.

It is difficult to determine Θ_E for K_xWO_3 in the presence of the large peaks near 20 K. However, we can make a fair estimate of Θ_E for K_xWO_3. The ionic radius of K^+ is 1.33 Å, which is smaller than Rb^+, so we expect a smaller force constant for K_xWO_3. A maximum value of 90 K for Θ_E of K_xWO_3 is obtained from Eq. (8) with $m = 39.1$ amu and k equal to the value for Rb_xWO_3. To obtain a minimum value of Θ_E for K_xWO_3, we observe from Fig. 6 that for $T > 30$ K the heat capacity of K_xWO_3 is less than the heat capacity of Rb_xWO_3. This lower value for K_xWO_3 is probably caused primarily by a high Θ_E rather than by a low x value, since the nominal x value for K_xWO_3 is 0.33, which is higher than the x value for Rb_xWO_3. Thus Θ_E for K_xWO_3 is larger than Θ_E for Rb_xWO_3 (57 K). The Einstein temperature for hexagonal potassium tungsten bronze very likely lies between 60 and 90 K.

The anomalous peaks in the heat capacity of K_xWO_3 are not understood. They may be due to impurities, although their existence in four samples (two different melts) makes this explanation doubtful. The peaks might be caused by latent heat from a low-temperature change in crystal structure. X-ray diffraction near 20 K would be desirable to investigate this possibility.

Considering the structure of the channel site which contains the M^+ ion, one would expect an anisotropy in the force constants which would lead to two Einstein temperatures. McColm *et al.*[21] have obtained the Mössbauer spectra at low temperature ($T \sim 4.2$ K) for hexagonal Sn_xWO_3. These spectra show anisotropy which the authors attribute to anisotropy of the metal-ion motion in the channel sites. Within the errors in Θ_E shown in Table I we find no such anisotropy in the K, Rb, Cs, and Tl hexagonal bronzes.

TABLE I. Einstein temperatures Θ_E and related data for three hexagonal bronzes. Θ_E and s, the number of atoms per formula weight contributing to the excess heat capacity, are obtained from curves shown in Fig. 9. The mass and ionic radius of the metal ions are given by m and R, respectively. The force constants k are obtained from m and Θ_E using Eq. (8). The dimensions of the unit cell are c and a.

	Rb_xWO_3	Cs_xWO_3	Tl_xWO_3
Θ_E (K)	58 ± 2	70 ± 3	38 ± 3
s	0.29 ± 0.02	0.32 ± 0.02	0.33 ± 0.02
m (amu)	86	133	204
k (N/m)	8	19	8
c (Å)	7.56	7.60	7.52
a (Å)	7.38	7.41	7.38
R (Å)	1.49	1.65	1.49

Our value for the Debye temperature of hexagonal Cs_xWO_3 (380 K) is about the same value (415 K) King *et al.*[13] obtained for hexagonal Rb_xWO_3. In contrast the value of Θ_D for cubic Na_xWO_3 is about 500 K. This lower value of Θ_D for the hexagonal structure is expected, owing to the reduced coupling of the metal ions to the WO_6 octahedra in the hexagonal structure.

Comparison of the heat capacity of Rb_xWO_3 in a magnetic field near T_c (see Fig. 6) with the classical calculations of Peierls[22] clearly reveals the latent heat associated with type-I superconductivity. We conclude that Rb_xWO_3 is a type-I superconductor. Although γ could not be determined directly for Rb_xWO_3, owing to the anomalous hump in the heat capacity, a not-unrealistic γ of 1.9 mJ/mole K^2 gives a jump in heat capacity $\Delta C = 1.43\gamma T_c$ in accord with BCS[23] theory at $H = 0$. From the critical-field curve of Rb_xWO_3, we obtain $(dH_c/dT)_{T=T_c} = 94 \pm 5$ G/K, and $T_c = 1.82$ K at $H = 0$. The molar volume V of Rb_xWO_3 is 26 (cm)^3/mole. From Rutgers's formula[24]

$$\Delta C = \left(\frac{VT_c}{4\pi}\right)\left(\frac{dH}{dT}\right)^2_{T=T_c}, \tag{9}$$

we calculate a jump in specific heat of 4.6 mJ/mole K in agreement with the experimental value 4.2 ± 0.9 mJ/mole K.

Data (not shown) for C_p of K_xWO_3 in a magnetic field are marred by large irreversible heating effects. However, no latent heat was found at $T = T_c$, which implies type-II superconductivity. While a field of approximately 300 G was required to suppress T_c below 1 K for K_xWO_3, a field of only 100 G was required for Rb_xWO_3. Because of the possible effects of impurities it is not known whether pure K_xWO_3 is an intrinsic type-I or type-II superconductor.

At low temperatures ($T \sim \Theta_E$) the Einstein modes dominate the phonon spectra of the hexagonal tungsten bronzes. Properties such as superconductivity, thermal conductivity, Debye-Waller factor,[25] and inelastic neutron scattering may be strongly affected by these Einstein modes. A crude estimate may be made of the relative numbers of Einstein modes of the metal ions to the Debye modes of the WO_6 octahedra excited at the Einstein temperature. The number of Einstein modes $N_E = 3N_0 x$, where N_0 is Avogadro's number. The number of Debye modes, if we assume the density of states $g(\nu) = 9N_0\nu^2/\nu_D^3$, is

$$N_D = \int_0^{\nu_E} g(\nu)\, d\nu = 3N_0(\Theta_E/\Theta_d)^3 . \tag{10}$$

The ratio $N_E/N_D = x(\Theta_E/\Theta_D)^3$. For $x = 0.3$ and $\Theta_D = 400$ K, N_E/N_D is 100 for Rb_xWO_3, 60 for Cs_xWO_3, and 400 for Tl_xWO_3. The Einstein modes are much more numerous than the Debye modes near the Einstein temperature.

It is tempting to suggest that the large number of Einstein phonon modes generated by the M^+ ions in the hexagonal bronzes may be responsible for their superconductivity through an enhanced electron-phonon interaction. The tetragonal-I bronzes, with T_c near 0.5 K, have five-, four-, and three-member channel sites in their structure. One would expect that the smaller five-member rings, when occupied by the M^+ ions, would produce larger force constants than those associated with the six-member sites of the hexagonal structure. These larger force constants would lead to higher Θ_E, which would reduce the number of phonon modes at low temperatures and thereby lower T_c, as observed. The perovskite structure, characteristic of the cubic bronzes which are not superconducting, has still smaller four-member channel sites. Indeed the metal ions become strongly coupled to the WO_6 octahedra. The higher force constants would lead to an even higher Θ_E. Therefore, we would expect a T_c lower than the T_c associated with the tetragonal-I structure. Thus a mechanism based on an enhanced electron-phonon interaction arising from the vibration of the M^+ ions in the various-size channel sites seems to account for the structure dependence of the superconductivity of the tungsten bronzes.

However, closer inspection of this model leads to difficulties. A clear prediction of this mechanism is that T_c ought to scale inversely with Θ_E. In fact, Tl_xWO_3 has T_c lower than T_c for K_xWO_3 or Rb_xWO_3, and its Θ_E is also lower. The increase in T_c with decreasing x value observed for acid-etched samples is also exactly opposite to what should occur. The fewer the M^+ ions the fewer the phonon modes and T_c should decrease. On the whole the Einstein phonon modes associated with the M^+ ions can be considered, at best, as only partly effective in accounting for the superconducting properties of the tungsten bronzes.

V. CONCLUSIONS

An excess heat capacity has been observed in four hexagonal tungsten bronzes. Choosing WO_3 as a reference, quantitative analysis of this excess heat capacity for three samples (Rb_xWO_3, Cs_xWO_3, and Tl_xWO_3) in the temperature range 1 to 45 K gave an Einstein contribution characterized by a single Einstein temperature. This excess heat capacity has been shown to result from the vibration of the M^+ ions in the hexagonal channel sites. A semiquantitative understanding of the size of the Einstein temperatures has been obtained from an analysis involving the mass and ionic radius of the M^+ ion. The phonon spectra of the hexagonal bronzes at low temperatures are dominated by these local Einstein phonon modes and should have dramatic effects on some of the other low-temperature properties of these materials.

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