Concentration dependence of superconductivity and order-disorder transition in the hexagonal rubidium tungsten bronze Rb$_2$WO$_3$. Interfacial and bulk properties

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We revisited the problem of the stability of the superconducting state in Rb$_2$WO$_3$ and identified the main causes of the contradictory data previously published. We have shown that the ordering of the Rb vacancies in the non-stoichiometric compounds have a major detrimental effect on the superconducting temperature $T_c$. The order-disorder transition is first order only near $x = 0.25$, where it cannot be quenched effectively and $T_c$ is reduced below 1 K. We found that the high $T_c$'s, which were sometimes deduced from the resistivity measurements and attributed to compounds with $0.25 \leq x \leq 0.30$, are to be ascribed to interfacial superconductivity which generates spectacular non-linear effects. We also clarified the effect of acid etching and set more precisely the low-rubidium-content boundary of the hexagonal phase. This work makes clear that $T_c$ would increase continuously (from $\approx 2$ K up to $\approx 5.5$ K) as we approach this boundary ($x \approx 0.20$), if no ordering would take place—as it is approximately the case in Cs$_x$WO$_3$. This behavior is reminiscent of the tetragonal tungsten bronze Na$_x$WO$_3$ and asks the same question: what mechanism is responsible for this large increase of $T_c$ despite the considerable associated reduction of the electron density of state $D_{FE}$? By reviewing the other available data on these bronzes we conclude that the theoretical models which are able to answer this question are probably those where the instability of the lattice plays a major role and, particularly, the model which call upon local structural excitations (LSE), associated with the missing alkali atoms.

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I. INTRODUCTION

Tungsten bronzes with general formula M$_x$WO$_3$ are the first oxides where superconductivity has been observed in 1964.$^1$ Much attention has been paid to these non-stoichiometric compounds in which it seemed possible to study how the normal and superconducting states react to the filling of the conduction band—as this can be adjusted within rather large ranges by varying the M content (M = alkali). The most extensive investigations have been carried out on Na$_x$WO$_3$—which displays distorted perovskite structures—and particularly on the tetragonal phases, in which a large increase of the superconducting transition temperature $T_c$ has been observed by reducing the Na content ($T_c \approx 0.7$ K for $x = 0.4$ whereas $T_c \approx 3$ K for $x = 0.2$).$^2$ This $T_c(x)$ dependence was rather puzzling because it seemed quite clear that the density of state at the Fermi level $D_{FE}$ was decreasing with $x$. At the same time, an enormous amount of data was accumulated on those properties which are related to the high mobility of the small M atoms, and which could lead to applications in electrophonic devices and solid electrolytes. These highly mobile M atoms—and the associated Einstein-like phonon modes—were also suspected to play a determining role in the electron-phonon coupling; however, no clear correlation has been found between the characteristic energy of these modes and the stability of the superconducting state. Many studies have been also devoted to the hexagonal tungsten bronzes (HTB), where higher $T_c$'s were obtained$^3$ but they yielded many conflicting results, particularly about the $T_c(x)$ dependence, and this apparently discouraged further attempts to get a better knowledge of these systems. Recently, however, this issue came back in the foreground incidentally after superconductivity and even high-temperature (superficial) superconductivity was observed in WO$_3$-$x$$^4$ and Na$_{0.05}$WO$_3$$^5$ respectively. This encouraged us to revisit the HTB, and particularly Rb$_x$WO$_3$ where the highest $T_c$ had been observed.

The structure of these bronzes has been described first by Magnéli.$^6$ It is based on a framework of WO$_6$ (distorted) octahedra which are linked by their corners, as they are in the tetragonal tungsten bronzes (TTB), but forming here hexagonal tunnels in which the alkali atoms are accommodated. This structure is stabilized by these atoms, if they are large enough (K, Rb, Cs) and if they fill more than a half of the tunnel sites ($0.19 \lesssim x \lesssim 0.33$).

The electronic structure of the tungsten bronzes has been calculated only for cubic MWO$_3$ and hexagonal WO$_3$ model systems$^4$ and is in rather good agreement with the results of photoemission measurements carried out on Na$_x$WO$_3$.$^7$ These calculations seem to indicate that the main features of the valence and conduction bands are not very sensitive to the symmetry of the WO$_3$ framework and rather independent of M: the role of the alkali atoms being above all to give their $s$ electrons to the conduction band whose bottom is mainly built of W 5$d$ − t$_{2g}$ orbitals, hybridized with the O 2$p$'s.

The hexagonal tunnels running along the $c$ direction
are quite open and this allows the smaller alkali atoms to be very mobile. In the substoichiometric compounds Rb₂WO₃ and K₂WO₃ they tend to order below or near room temperature respectively. According to Sato et al., this ordering could be responsible for the drastic reduction of Tc around x ≈ 0.25 and for the electron-transport anomalies observed by Stanley et al. and Cadwell et al. Similar but much less pronounced behaviors were recognized in Cs₂WO₃ by Skokan et al. as if the larger size of the Cs atoms impeded their ordering. These authors—belonging to what we shall refer as the Florida group—also reported an unexplained anisotropy of the upper critical field and Stanley et al. underlined the poor reproducibility of their data: some Rb₂WO₃ samples displaying large Tc (≈ 7.5 K) whereas no superconductivity was observed in others belonging to the same composition range. Moreover, other investigations detected no anomaly in the transport properties. Another point was left controversial: acid etching was found to increase Tc and it was not clear if it was due to a reduction of the Rb content in the bulk or only at the surface of the samples. These rather confusing results even led Lefkowitz to attribute any higher Tc’s observed in non-stoichiometric samples to sample effects. We have undertaken to resume the experimental investigations on Rb₂WO₃ also encouraged by the acknowledgment that interesting phenomena are often hidden behind poorly reproducible data.

A great part of our work had to deal with physical chemistry issues. It will be described in a forthcoming paper hereafter referred to as II.

II. EXPERIMENTAL

A. Preparation of samples

In the first stage of our investigations, we studied single crystals grown electrolytically from a melt consisting of Rb₂CO₃ and WO₃—according to the method developed by Sienko and Morehouse. Contrary to some authors who claimed to have obtained big single crystals with 0.19 < x < 0.33, we had good results, by this method, only for the stoichiometric (x ≈ 0.33) melt. Moreover, it was very difficult to guarantee that these crystals were completely free from occlusions of the melt. As our aim was, first, to clarify how the superconductor properties depend on x, we needed homogeneous samples and a good knowledge of their composition. Therefore we preferred carrying out this study with powder samples which have been prepared by the usual solid-state reaction: for each nominal x value, the starting material was made up from high-purity Rb₂WO₄, WO₃ and W which were ground together and placed in a quartz tube. Before the tube was sealed, the mixture was pumped to 10⁻⁶ Torr and baked repeatedly at about 150°C until we observed no more outgassing. The tube was then heated at 900°C for 2 days.

As discussed in more details in II, we found no benefit from increasing the temperature above 900°C, as we did not try to obtain single crystals; on the contrary we observed that higher temperatures resulted in attack on the quartz by the rubidium escaping from the Rb-rich samples.

This procedure yields fine crystalline powders with grain sizes ranging between about 10 and 100 µm (bigger crystals being found near the x ≈ 0.33 content). By checking that the X-ray powder diffraction patterns of these samples agree with the HTB symmetry, and display no trace of another phase, we can be quite confident in taking for x its nominal value. This has been confirmed by the micro-probe analysis of some of the samples.

It should be noticed that a solid-state reaction cannot lead to a perfectly homogeneous non-stoichiometric compound: each crystal is poorly connected to its neighbors in a low-pressure vapor and should reach an equilibrium slightly depending on its morphology and neighborhood. From our micro-probe analysis we estimate the dispersion of the Rb content in our batches at 0.005 ≤ δx ≤ 0.01.

B. Characterization of the superconducting transition

We used a mutual-inductance bridge and a standard ⁴He cryostat to systematically characterize the superconducting transition by monitoring the diamagnetic expulsion in a small (〈 2 × 10⁻⁴ T) low frequency (33 Hz) magnetic field. Magnetic susceptibility measurements in static fields have also be done with a SQUID magnetometer. These methods are better suited to the investigations we were concerned with than conductivity measurements. The width of the magnetic transition gives a good picture of the homogeneity of the sample, whereas a zero-resistance state may be due only to minute superconducting sheets or filaments. Moreover, as we shall show later, a crystal which was grown from the vapor and has a suitable size for conductivity measurements may not be representative of the nominal composition of the batch, whereas this can be checked readily on powder samples by taking them from different parts of the powder batch.

We also carried out magnetic susceptibility and conductivity measurements on various single crystals but these experiments—which will be discussed in due course—will not be included in our determination of the Tc vs x dependence.

The amplitude of the magnetic transition of the powder samples could vary on a rather large range (±20%), but we determined that this was only related to the size and morphology of the grains as well as to the compactness of the samples.
III. RESULTS

We tried to find out the cause(s) of the non-reproducibility of the superconducting transition temperature \( T_c \) by first looking for a phase transition between room temperature and 900°C. We used differential thermal analysis (DTA), differential scanning calorimetry (DSC) and tried to anneal and quench the samples from various temperatures but we found no sign of a phase transition. However, these heat treatments have brought to light some aspects of the physical chemistry of these compounds which could explain a part of the discrepancies previously noticed. We shall deal with this in II and here describe what appeared to be the major cause of these discrepancies: the \( T_c \) of the non-stoichiometric compounds is sensible to the cooling rate below room temperature. This was the expected consequence of an ordering of the Rb vacancies like the one described by Sato et al.\textsuperscript{11} but we first missed this cooling-rate effect because we tried to detect it in the region of the composition range where the previously observed dispersion of \( T_c(x) \) was the highest, i.e. near \( x \approx 0.25 \). In this range, we never observed superconductivity above 1 K, contrary to what claimed Stanley et al.\textsuperscript{23}

A. The cooling rate effect

We have observed this effect for \( 0.29 \lesssim x \lesssim 0.31 \) and for \( 0.19 \lesssim x \lesssim 0.23 \), and it is exemplified in Fig. 1: the “slowly-cooled” sample has been cooled down to 90 K within a few hours before we transferred liquid helium; the “quenched” same sample reached 4.2 K within a couple of minutes after it has been introduced directly in the cryostat filled with liquid helium. As shown in Fig. 1, it is the “slowly-cooled” samples which have a lower \( T_c \), contrary to what is expected—and most usually observed—for a better ordered state. We also experimented with a faster cooling down to 90 K by dropping and stirring the sample in liquid nitrogen but we observed no further increase of \( T_c \). We also observed that the quenched state can be annealed at temperatures above \( T_m \approx 110 \pm 10 \) K and, in this respect, we saw no difference between the three samples studied with \( x = 0.19 \), \( x = 0.22 \) or \( x = 0.29 \).

The cooling rate effect clearly confirms the ordering of the Rb atoms in the non-stoichiometric HTB and their extreme mobility. We shall present now the other information we got on the order-disorder transformation.

B. Calorimetric study of the order-disorder transformation

After several unsuccessful attempts, we finally observed the enthalpy anomaly accompanying this transformation, but only in the samples with \( x \approx 0.25 \). The apparatus we used was a Perkin-Elmer DSC-7 differential scanning calorimeter and our measurements extended down to \( \sim 100 \) K. As the anomaly is quite weak, we had to use rather sizeable powder samples and high heating or cooling rates. This could partly explain the large temperature range of the anomaly and the thermal hysteresis which are exemplified in Fig. 2. However, by comparing the behaviors of different samples, it appears that the width of the anomaly is mainly related to its strong \( x \) dependence and to the imperfect homogeneity of the samples: the data presented in Fig. 2 indicate that a composition difference \( \delta x \approx 0.01 \) in the neighborhood of \( x = 0.25 \) leads to a shift of the anomaly by about 20 K—the largest extrapolated peak onset temperature we observed being about 240 K.

Our results are in rather good agreement with those of Sato et al.\textsuperscript{23} however, we observed no anomaly for \( 0.16 \lesssim x \lesssim 0.23 \) and \( 0.27 \lesssim x \lesssim 0.33 \) which shows that the transition is first-order only for \( x \) in a narrow range around \( x = 0.25 \). Outside this range, the transition should become continuous and, actually, it is what is observed in the powder-diffraction pattern of Rb\(_{0.27}\)WO\(_3\).

In our \( x \approx 0.25 \) samples, we estimate the maximum

\( \Delta M(mH) \)

\( \Delta \)

\( 0 \)

\( 0.02 \)

\( 0.04 \)

\( 0.06 \)

\( 0.08 \)

\( 0.12 \)

\( T(K) \)

\( T(K) \)

FIG. 1: Superconducting transitions (mutual inductance variations) of a powder sample of Rb\(_0.22\)WO\(_3\) after different coolings.

FIG. 2: DSC thermograms observed on a powder sample of Rb\(_{0.25}\)WO\(_3\) (\( \approx 50 \) mg) on heating and on cooling at \( \pm 10 \) K/min.
heat absorption $\Delta H$ which accompany the order-disorder transition to be $80 \pm 10$ J/mol K, and the maximum entropy increase $\Delta S$ to be $0.35 \pm 0.05$ J/mol K. This value indicates that the degree of order in $\text{Rb}_{0.25}\text{WO}_3$ is quite low just before it transforms into the high-temperature disordered state. Actually, the molar configurational entropy of the disordered state is then associated with the temperature $T$.

$$w = \frac{N!}{(\frac{N}{3})! (\frac{N}{3})!}, \quad N = N_0/3,$$

as $x = 0.25$ corresponds to $1/4$ of the Rb atoms missing on the $N_0/3$ sites per mole available in the HTB structure. It gives $S_{\text{dis}} = 1.56$ J/mol K. If we eliminate all the arrangements where two vacancies or more are first neighbors we find that $w$ should be:

$$w = \frac{3N!}{(\frac{N}{3})! (\frac{N}{3})!}, \quad \text{which gives } S_{\text{dis}} = 1.32 \text{ J/mol K.}$$

Accordingly, the increase of entropy $\Delta S$ we observed at the first-order transition amounts to about 22–26% of $S_{\text{dis}}$. This is in rather good agreement with the simple Bragg-Williams approximation applied to AB$_3$ alloys, which gives $\Delta S/S_{\text{dis}} = 17.5\%$.

C. The resistivity anomaly

As mentioned earlier, Sato et al. had noticed that the order-disorder transition temperature $T_\text{tr}$ they determined from their neutron diffraction data seemed to correspond to the temperature $T_\text{B}$ of the resistivity anomaly observed by Stanley et al. It was therefore very tempting to attribute this anomaly to the ordering of the Rb atoms. Since our results clearly confirmed this ordering and showed its strong effect on the stability of the superconducting state, it was still more difficult to understand why this resistivity anomaly had not been observed by other authors. This led us to undertake new resistivity measurements on single crystals obtained by following the same procedure as Stanley et al., i.e., a solid state-reaction at $950^\circ$C for 5 days. We prepared in this way about 5 g of $\text{Rb}_{0.26}\text{WO}_3$ and obtained the usual poorly crystallized, partly sintered powder, plus a few mg of needle-like crystals. These often radiate in bundles from tiny crystals attached to the quartz surface; this shows that they grew from the vapor. Most of these needles were dark blue and displayed the hexagonal symmetry of the HTB, but we also observed light-blue whiskers and even transparent ones, some of which were curved and even spiraled. We selected some of the dark blue needles, which were about 5 mm long in the c axis direction and rather ribbon-shaped, therefore well suited to resistivity measurements (about 20–50 $\mu$m in width and 2–5 $\mu$m in thickness).

Silver or gold paints, which are usually used to attach current and potential leads to small samples, do not give satisfactory electrical contacts on $\text{Rb}_3\text{WO}_3$, even by using freshly prepared crystals. While evaporated coatings are not very effective, we obtained very good results by first sputtering gold on the contact areas. This nonconducting behavior of the sample surface will be considered in II. The device we used produces contact areas partly enveloping the samples, specially at their ends, which should allow fairly uniform current lines.

We measured the temperature dependence of the resistivity of seven of these samples between 300 K and 1.2 K, by using always slow cooling or heating rates (about 2 K/min) and we observed:

- in two samples (A), an anomalous hump in the resistivity ($\rho$) as a function of temperature (Fig. 4) —similar to the one observed by Stanley et al.,

- in the other samples (B), a low-temperature upturn of $\rho$ (Fig.),

- in all samples, a vanishing of $\rho$ occurring between $\approx 8$ K and $\approx 2$ K. (Fig. whereas, as usual, no sign...
of superconductivity was detected in the magnetic susceptibility of the powder samples of the batch, and large non-linear effects, in the same temperature range (see Sec. III D).

These conflicting observations prompted us to question the identity of these fibers and to carry out their examination with a JEOL 840-A scanning electron microscope (SEM) fitted with an energy dispersive spectrometer (EDS). This revealed that none of these vapor-transported crystals are really representative of $\text{Rb}_2\text{WO}_3$: their rubidium content are much higher than the nominal content of the batch, samples B being structurally and chemically more homogeneous. We suspect that the special transport properties of these fibers are consequences of their structural non-homogeneity which could affect microscopic as well as mesoscopic scales. We suggest that crystallization from the vapor might lead to the growth of rather decoupled layers of HTB with sometimes, possibly, really different Rb contents. Besides, each layer or strip might be often perturbed by extended defects. We shall discuss the possible nature of these interlayer and interlayer defects in II.

Within this framework we propose the following description of the features listed above:

- The main decrease of the resistance—occurring at about 2.5 K in samples A—is probably associated with the superconducting transition of nearly stoichiometric $\text{Rb}_{0.33}\text{WO}_3$ strips. But in some samples, and particularly in samples B, the resistance begins to decrease at about 8 K, which is much higher than the highest $T_c$’s ever observed in HTB via magnetic measurements (cf. Sec. III E). We think we are not dealing here with intrinsic superconductivity but rather with superficial or filamentary effects similar to those observed in NbSe$_3$ for instance.

- The low temperature non-linear conductivity is a symptom which is related to the defects mentioned above.

D. The non-linear resistivity behavior of the vapor-grown fibers

At temperatures below about 2 K, the differential resistance $dV/di$ steeply rises when the bias current exceeds a critical value $I_c$ and then decreases toward the value of the normal state resistance (Figs. 7 and 8). Sweeping the bias current up or down at different rates does not modify significantly the current dependence of $dV/di$ which is not very sensitive either to thermal cycling. Well below and also beyond $I_c$ the differential resistance displays rather erratic features which seem to be related to noise generating instabilities.

Assuming a uniform current distribution, the $I_c$ values at $\approx 1.2$ K would correspond to current densities $j_c$ ranging between about 0.05 A/mm$^2$ and 20 A/mm$^2$, depend-
tion is certainly not merely a matter of chance. At the same temperature range as the order-disorder transition being discussed, the homogeneity of the samples. However, its occurrence in the resistivity anomaly is extrinsic and related to the inhomogeneity of the samples. On the other hand, in the vapor-grown samples, the loss of conductivity associated with the structural defects—including those revealed by the non-linear effects described above—could be enhanced by the reduction of $D_F$ and lead to the hump observed.

We shall now sum up the information we have on the anomalous hump in resistivity which motivated this study: we only observed this hump in two of seven vapor-grown samples and never observed it—whatever the Rb content—in the more massive crystals prepared by fused-salt electrolysis. In these the resistivity decreases quite linearly with temperature down to about 100 K, before it progressively saturates (Fig. 6). This is the behavior also observed by Aristimuno et al. in crystals which were carefully selected to be electrically homogeneous. On the contrary, we showed that the vapor-grown crystals are not homogeneous and display a transition towards a zero-resistance state which begins at about 8 K. This resistance anomaly is not observed magnetically in any bulk HTB. The foregoing remarks lead us to suspect that the resistivity anomaly is extrinsic and related to the inhomogeneity of the samples. However, its occurrence in the same temperature range as the order-disorder transition is certainly not merely a matter of chance. Actually the same Florida State University group observed the same anomalies in $K_xWO_3$ but at higher temperatures, and no anomaly in $Cs_xWO_3$—which is consistent with the greater tendency for the smaller ions to order. As described below, this also agrees with the quite different $T_c(x)$ dependences observed in the three bronzes.

The only explanation we can offer to rationalize these behaviors is the following: the ordering of the Rb atoms leads to a reduction of the density of states at the Fermi level $D_F$ which destabilizes the superconducting state but has only a minute effect on the resistivity of the normal state in the massive samples. On the other hand, in the vapor-grown samples, the loss of conductivity associated with the structural defects—those revealed by the non-linear effects described above—could be enhanced by the reduction of $D_F$ and lead to the hump observed.

E. The $T_c(x)$ phase diagram

The information collected above confirms that we should not rely on the composition of the vapor-grown samples to establish the tungsten bronzes $T_c(x)$ phase diagram. It also allows us to dismiss the high values of $T_c$ observed by Stanley et al. near $x = 0.25$. As we just saw, they are probably to be ascribed to a kind of filamentary superconductivity, whereas the $T_c$’s of the corresponding bulk material deeply decrease—as a result of the ordering of the Rb vacancies. The dependence of $T_c$ therefore displays a pronounced dip near this Rb content which allows the greatest degree of order and leads to the highest transformation temperature $T_{ord}$ (Fig. 7). This dip is less pronounced when the samples are quenched from room temperature but ordinary quenching rates are not sufficient to prevent a significant ordering when $0.23 \lesssim x \lesssim 0.28$, and superconductivity cannot develops above $\approx 1$ K within this composition range.
range. Beyond this range, $T_c$ steeply increases with $x$, up to $T_c \approx 3$ K for $x \approx 0.30$, and then slowly decrease down to $T_c \approx 2$ K, when the Rb content approaches the stoichiometric value. On the other side of the dip, $T_c$ increases still more abruptly with the decrease of the Rb content and seems to level off at $T_c \approx 5$ K for $x \lesssim 0.21$. However, this asymptotic behavior seems to conflict with the higher $T_c$'s ($\approx 5.5$ K) we can obtain in samples in which the Rb content has been reduced by acid etching or by a slight oxidation.

This inconsistency prompted us to question the stability of the HTB phase for $x \lesssim 0.22$. By examining more systematically the X-ray powder patterns, we found that the $x$ dependence of the lattice parameters shows a discontinuity near $x \approx 0.215 \pm 0.005$ in samples prepared by the usual solid-state reaction method (Fig. 10). This clearly indicates that another phase coexists with the HTB's when the rubidium content falls below this value. In the slowly cooled samples, the corresponding diffraction peaks begin to appear unambiguously only when $x \lesssim 0.19$, a value which was therefore associated, up to now, with the boundary of the HTB-phase region. In these samples, we found it is WO$_3$ which coexists with the HTB phase and gives hardly perceptible diffraction peaks—which agree with the fact that Rb$_{0.21}$WO$_3$ should be in equilibrium with only about 10% of WO$_3$ when the nominal Rb/W ratio is 0.19. In samples which were quenched at the end of their otherwise similar preparative treatment, the larger additional peaks can be attributed to the ITB phases and seem compatible with a content amounting to 20%. These observations are consistent with an ITB-WO$_3$ boundary situated near 700°C–800°C, as proposed by A. Hussain.

On the other hand, the acid-etched or slightly oxidized samples in which we observed the highest $T_c$'s, display also the lowest $c$-parameter values. Moreover, these values correspond to what is expected for an HTB phase with $0.19 \lesssim x \lesssim 0.20$—extending the linear decrease of $c$ with $x$ observed at higher Rb contents (see Fig. 10). Correspondingly, we think that the superconducting transitions which begin above 5 K in the latter samples are to be attributed to this structure and rubidium content.

This led us to complete the low-$x$ region of $T_c(x)$ diagram as displayed in Fig. 11. The transition temperature $T_c$ has been defined here at the onset of the diamagnetic expulsion, as the width of the transition considerably depends on the samples: it can be only about 0.2 K in nearly stoichiometric samples ($x \lesssim 0.30$) which are less sensitive to the ordering transformation, but it can be more than 1 K when the Rb content of the samples leads to the stronger cooling-rate effect. We also observed that powder samples with $x \lesssim 0.23$, which were annealed at 950°C and partly sintered, displayed much steeper transitions, but they recover their pristine behavior when they are powdered again. This probably indicates that the penetration depth $\lambda$ in these samples is close to the size of a notable proportion of the grains, i.e. of the order of 1 µm at least.

Although at first sight it looks quite different, this $T_c(x)$ diagram cannot but recall the corresponding Cs$_2$WO$_3$ diagram which displays a monotonic increase of $T_c$ with decreasing $x$. Actually, the strong reduction of $T_c$ near $x \approx 0.25$ in Rb$_x$WO$_3$ is the signature of the rubidium vacancies ordering. This effect is still more pronounced in K$_x$WO$_3$—where the ordering is very easy—whereas it is absent in the cesium tungsten bronze, where no noticeable ordering seems to occur. In other words, the $T_c(x)$ diagrams of the potassium and rubidium hexagonal tungsten bronzes would be quite similar to the diagram of Cs$_2$WO$_3$, if we could prevent the smaller alkali ions from ordering. Finally, we shall notice that the $x$ dependences we obtained for the lattice parameters in Rb$_x$WO$_3$—as displayed in Fig. 10—are now quite similar to the corresponding ones in Cs$_2$WO$_3$: the decrease of the alkali-metal content leads to a decrease of the $c/a$ ratio; the larger alkali metals giving the larger effect and, probably, playing a more effective role in the stabilization of the HTB phase, as indicated by the fact that they lead to a farther extended homogeneity range, on its low-$x$ side.

![Fig. 10](image-url)
IV. DISCUSSION

A. The $T_c(x)$ issue

We shall first remark that this increase of $T_c$ with decreasing $x$ was also observed in the tetragonal tungsten bronzes (TTB) $\text{Na}_x\text{WO}_3$ and $\text{K}_x\text{WO}_3$. Well before the discovery of the high $T_c$ cuprates, this behavior aroused a great interest. The point is that it seems to conflict with the simple BCS model because a decrease of the alkali content should correspond to a decrease of the density of state at the Fermi level $D_{FE}$ for $x$ in these compounds is therefore probably due to an enhancement of the electron-electron interaction in the low-$x$ range. Although we have less clues to support this diagnosis as far as $\text{Rb}_x\text{WO}_3$ is concerned, we think it remains the most likely in view of the many analogies between the two systems.

Salchow et al. attributed the increase of $T_c$ with increasing $x$ to a better screening of the electron-phonon interaction. We think that this mechanism is probably not very effective in the HTB, because it would imply that the ordering of the alkali vacancies—which certainly reduces $D_{FE}$—would increase $T_c$, whereas it is drastically reduced. Another mediation of the electron-electron interaction has been proposed by Kahn and Ruvalds. They invoked acoustic phonons but, at the moment, we consider that the reliable experimental data on these bronzes are in favour of those models which rely on the lattice instability.

Actually the crystal structure of these bronzes is not very stable: according to Sato et al. a distortion of the $\text{WO}_3$ cage takes place in $\text{Rb}_x\text{WO}_3$ below about 420 K. Above this transition the space group is $P6_3/mcm$, but below this temperature the exact structure remained unsolved at that time. A similar poor agreement with any structural model is observed in $\text{K}_x\text{WO}_3$. Most of these studies indicate that the topology of the oxygen octahedra is disturbed around an alkali vacancy. Moreover, the great versatility of these octahedra is well known: they are able to join along different directions by sharing their corners, or even their edges, and to yield to various deformations—which makes the structures they form able to sustain large deviations from stoichiometry. This leads to the spectacular “crystallographic shear” (CS) planes in $\text{WO}_3$—to the lamellar intergrowth of HTB and $\text{WO}_3$ in low-alkali-content “intergrowth tungsten bronzes” (ITB) and to many $\text{WO}_6$-based metastable structures formed at rather low temperatures, via the methods of soft chemistry.

On the other hand, we have many evidences of the great mobility of the small alkali atoms in the tungsten bronzes. In the HTB, particularly, low-frequency Einstein-like phonon modes are associated to the vibrations of these atoms within the large channels running along the $c$-direction. These modes were made responsible for the “excess” heat capacity observed above about 10 K, and which can be fitted—in $\text{Rb}_x\text{WO}_3$—by an Einstein contribution with $\Theta_E \approx 60 \text{ K}$. However, as their characteristic energy seems to hardly depend on $x$, they probably are not the main cause for the anomalous $T_c(x)$ dependence.

Other special phonons have been invoked, originally by Shanks and have given rise to the LSE model proposed by Ngai et al. then treated by Vujčič et al. They attribute the enhancement of the electron-electron attractive interaction, in the tungsten bronzes, to local structural instabilities: their model is based on the idea that a local ground-state configuration could be separated from one or more other configurations by a small amount of energy and by a potential barrier. According to these authors, the excitations between these local states—they called “local structural excitations” (LSEs)—could not only enhance the phonon pairing of electrons but also mediate a supplementary effective electron-electron interaction through a specific electron-LSE interaction.

One of the strong points of this model lies in the fact that the local structural instabilities are associated with the alkali vacancies and it is conceivable that increasing their content should increase the instability of the lattice and the part of the LSE in its dynamics, whereas the ordering of these vacancies should have the opposite effect. Following the approach of Ngai et al. we may imagine, in the case of $\text{Rb}_x\text{WO}_3$, that there are microscopic regions where the local density $x_f$ is smaller than the average value $x$ and thus where there is a tendency, for the $\text{WO}_6$ octahedra, to collapse into a $\text{WO}_3$ structure—which reminds us of the intergrowth mechanism leading to the ITB phases when $x \leq 0.2$. Where a local transformation has occurred, a kind of $\text{WO}_3$ defect has been formed. On the other hand, if the local transformation has not condensed, the local structural instability is preserved, and the elemental $\text{WO}_3$ defect can be viewed as an excited state of the local group of atoms and bonds. Finally, it is also tempting to speculate that the large amplitude vibrations of the alkali atoms could facilitate the tunneling between the free-energy minima of two structural configurations or, more generally, that combinations of these local instabilities with the alkali-atom vibrations could lead to a specially effective coupling with the conduction electrons.

The LSE model has been adopted by Sato et al. and applied to $\text{Rb}_x\text{WO}_3$ by using the McMillan’s equation where they introduced an electron-phonon coupling parameter $\lambda_{\text{LSE}}$ proportional to $\nu_{\text{LSE}}$—the number of LSE—and to $D_{FE}$. This simple approach is able to describe the $x$ dependence of $T_c$ as it provides the necessary increase of $\lambda$ with the decrease of $x$. However the inelastic neutron scattering experiments undertaken by these authors on powder samples have not allowed to observe any significant $x$ dependence. As proposed by these authors, a tentative explanation of this failure could lie in the broadness of the LSE spectrum; however that may be, this issue should deserve to be experimentally settled.
B. Interfacial superconductivity

Besides this problematic $T_c(x)$ dependence, superconductivity in $\text{Rb}_x\text{WO}_3$ displays another unusual feature which has been revealed by our resistivity measurements on the vapor-transferred samples, namely its stabilization—at temperatures above the highest $T_c$’s of the bulk material—in probably interfacial regions. Such a phenomenon has been observed in $\text{WO}_{3-x}$ and attributed to twin walls. Sheet superconductivity also develops on the surface of $\text{WO}_3$ crystals which have been subjected to a slight superficial enrichment of sodium. The very high $T_c$’s observed in the later case (up to 91 K) is evidently far from being explained but indicates how much the interfacial properties of these materials could be promising. The great versatility of the $\text{WO}_6$ octahedra we discussed above, certainly plays a part in these superficial or interfacial properties.

An explanation of such enhancements of $T_c$ was proposed, twenty five years ago, by Lefkowitz who thought that the anomalous $T_c(x)$ dependence in the tungsten bronzes was a surface effect: he stressed that a ferroelectric instability can condense at low temperatures in $\text{WO}_3$ and hypothesized that this could lead to high electric fields at the boundary between the insulating material and the doped regions—this inducing a new electron density of states at the Fermi level. Although we are now quite sure that the increase of $T_c$ with the reduction of the alkali content, in these bronzes, is really a bulk property, the Lefkowitz’s proposition seems fairly seductive when considering the phenomenon we observed in the vapor-transferred samples.

C. The order-disorder transformation

Finally we shall add a few comments about the order-disorder transition of the rubidium vacancies in $\text{Rb}_x\text{WO}_3$. It was observed first by neutron diffraction measurements and then by electron diffraction measurements. Our calorimetric measurements have shown that this transformation was first-order only for $x \approx 0.25$, which corresponds to one forth of the Rb atoms missing, to the most stable ordering and to a doubling of the lattice constants. It appears that the positions of the O atoms are modulated to some extent by the alkali vacancies, therefore a gap at the Fermi surface is certainly induced by this new periodicity. Subsequently, the K ordering in $\text{K}_x\text{WO}_3$ was also studied and different ordering schemes have been proposed. A quite complex picture emerge from these studies, which indicates, one more time, that we are dealing with an “infinitely adaptive structure.”

When we move away from $x \approx 0.25$, the transition temperature $T_{\text{ord}}$ rapidly decreases: it is only about 200 K in $\text{Rb}_{0.22}\text{WO}_3$ and about 123 K in $\text{Rb}_{0.20}\text{WO}_3$, i.e., very near from our estimate of the rubidium mobility threshold $T_{\text{mob}}$, and this agrees with our observation that the disordered state, then, can be quenched more effectively. Conversely, the low-temperature state will be usually less ordered. Moreover, the complex ordering taking place when $x \leq 0.25$ has probably a weaker effect on the Fermi surface. Therefore, both mechanisms contribute to reduce the cooling-rate effect when $x$ approaches its minimum value.

Let us finally notice that similar issues, concerning order-disorder phenomena and their influence on superconductivity, have been raised in the high-$T_c$ cuprates. A thermodynamical model for the ordering schemes of the oxygen vacancies has been proposed which leads to a concentration dependence of the ordering temperature quite reminiscent of the $T_{\text{ord}}(x)$ behavior observed in $\text{Rb}_x\text{WO}_3$: in particular, a first-order transition is predicted only in a part of the concentration range. However, ordering increases $T_c$ in these cuprates as well as in the low-$T_c$ organic superconductors, whereas it is just the opposite in the HTB.

V. CONCLUSION

We have identified the main reasons why the available results on the physical properties of the HTB $\text{M}_x\text{WO}_3$ were so contradictory. We have described here the effect of the order-disorder transition and interface-related artifacts; other causes of discrepancies result from the physical chemistry of these compounds and will be described in the forthcoming paper II. We have now a much clearer vision of the HTB, which brings to the fore a common unusual feature of the superconducting state whose critical temperature $T_c$ increases when the M content $x$ and $D_{\text{PE}}$ decrease. This behavior is also shared by the tetragonal tungsten bronze $\text{Na}_x\text{WO}_3$. After reviewing the reliable available information on these systems we concluded that a strong-coupling mechanism was probably responsible for this feature. At this respect, the model appealing to local structural excitations (LSE) seems the most attractive, and it is backed up by our observations that the superconducting state is destabilized by the ordering of the M vacancies, whereas $T_c$ increases with their number. Actually, it is the only model, up to now, able to conciliate these two features. However, we established that superconductivity is nearly completely suppressed in the HTB when 1/4 of the M atoms are missing and ordered, and this cannot be due only to the LSE mechanism as superconductivity exists up to 2 K in the stoichiometric HTB. Thus, the M-atoms ordering also has a deep effect on the Fermi surface—in contradiction with the previous rigid-band descriptions. Conversely, this indicates that the strong-coupling LSE mechanism—if present—must be the most effective when $T_c$ is the highest and $D_{\text{PE}}$ is simultaneously reduced by the highest vacancy content and by their ordering, i.e. for $x = 0.19$. It is therefore near this concentration that more extensive lattice-dynamic studies should be carried out. More generally, from a fundamental point of view and irrespective of the quest...
for room-temperature superconductivity, we think that the possible building up of an attractive electron-electron coupling via localized interactions should be investigated most seriously and that Rb$_3$WO$_3$ is now a system where this task may be tackled profitably.

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22 We have prepared some non-stoichiometric crystals by annealing stoichiometric electrocrystallized crystals within a large sample of compacted non-stoichiometric powder, or by acid etching (see II).
23 Resistivity measurements are not always able to detect rather large changes in $\Delta_{FE}$, as for instance in (TMTSF)$_2$ClO$_4$ (D.U. Gubser, W.W. Fuller, T.O. Poehler, J. Stokes, D.O. Cowan, M. Lee, A.N. Block, Mol. Cryst. Liq. Cryst. 79, 225 (1982)); and Tl$_2$Mo$_6$S$_8$ (R. Brusetti, A. Briggs, L. Laborde, M. Patel, P. Gougeon, Phys. Rev. B 49, 8931 (1994)).
24 It was known for a long time that acid etching could remove the Rb ions from the HTB and considerably enhance $T_c$. We have investigated this effect and we propose a description of the chemical process involved in II. There we also describe how a moderate oxidation, at about 450°C, can have a similar effect on the sample core, by driving the Rb ions towards the supercritical tungstate layer.
25 The corresponding increase of the a parameter is more difficult to bring to the fore because about four times smaller. Moreover, in the oxidized samples it is somewhat obscured by the presence of tungstate diffraction peaks.
26 The decrease of the c-axis lattice constant with decreasing rubidium concentration and the corresponding slight increase of a-dimension was already observed by Hussain and by Wanlass and Sienko. Our results are in better quantitative agreement with the latter ones. Shanks and Danielson referred to an opposite dependence of the c-dimension, from which they extrapolate the $x$-values in their samples prepared by the electrolytic method (H.R. Shanks, G.C. Danielson, in Proceeding of the Twelfth International Conference on Low Temperature Physics, Kyoto, Japan, edited by E. Kanda (Academic Press, New York, 1970), p. 359).
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28 Experimental evidences (specific heat and photoemission spectroscopy) and band structure calculations are discussed in Ref. 38 for instance.
29 In the case of Rb$_3$WO$_3$, we have only rough estimates of $\Delta_{FE}$: one can be derived from the Paris-Peierls-type contribution to the magnetic susceptibility i.e., $\Delta_{FE} \approx$
0.3 state/eV.mol—with no sensible variation with \( x \)—and another is provided by the thermodynamical properties of the superconducting state, i.e., \( \Delta_{FE} \approx 0.7 \) state/eV.mol in Rb\(_{0.33}\)WO\(_3\). These estimates are quite similar to the values obtained in Na\(_x\)WO\(_3\) and, in both cases, are compatible with what can be expected from a nearly-free-electron band, accommodating the electrons donated by the alkali atoms.

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