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Neutron Diffraction and Scattering Study on M_xWO_3 (M=Rb and K)

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To study the relationship between the lattice instability and the superconductivity of nonstoichiometric hexagonal tungsten bronze, M_xWO_3 , neutron diffraction and scattering studies were made. Two types of the structural phase transitions were observed. One is associated with the distortion of the corner linked WO_6 octahedra. The other is associated with the ordering of the M atoms which partially fill the sites in the WO_3 cage. A long period modulation of the structure appears for some values of x at low temperature. The discussion on the x dependence of the superconducting transition temperature is presented.

§1 Introduction

In the structure of the nonstoichiometric hexagonal tungsten bronzes, M_xWO_3 ($1/6 < x < 1/3$), one dimensional chains of M atoms are embedded in the hexagonal array of the open channels along the c direction which result from the arrangement of the corner linked WO_6 octahedra(1). Metallic conductivity is explained by the presence of the the electrons from M atoms in the WO_3 conduction band(2). Kamitakahara et al.(2) showed that the superconducting transition temperature T_c of $M_{0.33}WO_3$ is quite sensitive to the energy of the nearly dispersionless phonon branch, which can be assigned as the local mode of M atoms in the cage of the corner linked WO_6 octahedra. This mode has been directly observed by neutron inelastic scattering for $K_{0.33}WO_3$ (3), $Tl_{0.33}WO_3$ (2) and $Rb_{0.33}WO_3$ (4). Stanley et al.(5) and Cadwell et al.(6) measured T_c in Rb_xWO_3 and K_xWO_3 as a function of x and found the clear anomaly at $x=0.25$. They also found a resistivity anomaly at a temperature $T_B (>> T_c)$, the x dependence of which is closely related with that of T_c . Sato et al. (7) carried out neutron diffraction and scattering measurements of Rb_xWO_3 . They reported that the M atom in M_xWO_3 undergoes an order-disorder transition at T_S and T_S' , the former agreeing reasonably well with T_B .

This report will present the ordering schemes which contain the long period structure at low temperature. It will also discuss the another structural transition accompanied by phonon softening. This phase transition seems to be mainly associated with the distortion

of the WO_3 cage. The structure proposed by Magneli as the room temperature one for M_xWO_3 is no more correct below the transition temperature T_R ($\approx 420K$ for $x=0.33$). The relationship between T_C and these two types of phase transition will be discussed. The details of the calculation will be published in a future, complete publication.

§2 Expèriment

Single crystals with $x=0.33$ were prepared by the electrolysis as described by Shanks(8). The powder samples were prepared by the solid reactions of the proper amounts of WO_3 , W and M_2WO_4 sealed in a quartz tube. We use here nominal x values determined by the ratio of these elements. The measurements were carried out on triple axis spectrometers at HFBR at Brookhaven National Laboratory and at JRR-2 at JAERI. Phonon measurements have been carried out at various temperatures for the single crystal and the powder sample with $x=0.27$. The powder pattern has been measured at about 10K and at room temperature for all samples. The powder pattern has also been measured at about 490K for the sample with $x=0.27$. Some of the representative superlattice reflections have been measured as a function of temperature.

§3 Structural phase transitions

3.1 Transition associated with the WO_3 cage

Based on X ray diffraction measurement at room temperature, Magneli(1) assigned the space group $P6_3/mcm$ to $Rb_{0.29}WO_3$. This group forbids the

(h0 ℓ) reflections with $\ell=2n+1$. While the neutron powder pattern of $\text{Rb}_{0.27}\text{WO}_3$ at about 490K is fitted well by this space group with position parameters nearly the same as those of Magneli, our room temperature (and lower) scans show a definite peak at (103) Bragg position. This peak does not exist above $T_R=420\text{K}$. In Fig.1, the peak intensity of the (103) reflection is shown as a function of temperature for a single crystal. Other (h0 ℓ) reflections with $\ell=2n+1$ and $h\neq 0$ have also been observed below T_R in this crystal. At this transition, softening of the optical phonon at the Γ point has been observed. An example of the soft phonon profile and the temperature dependence of the soft phonon energy, measured at (103) point, are also shown in Fig.1. These results show that the transition is nearly second order.

We also failed to observe the (ho ℓ) reflections with $\ell=2n+1$ in the X-ray powder patterns at room temperature. This implies that the phase transition is mainly associated with the shifts of the oxygen atoms which have a small scattering amplitude for X-rays but a relatively large one for neutrons. Although the lattice parameters suggest the hexagonal or trigonal symmetry, attempts to fit the room temperature ^{neutron} powder pattern of the sample $\text{Rb}_{0.27}\text{WO}_3$ using these symmetries have not been successful. Instead, a reasonable fitting to the orthorhombic space group Cmc2 has been obtained. The structure determined by the fitting can be described by a rotation of the WO_6 octahedra on one of the principal axes in the c plane. In the present paper we use hexagonal indexing, because it does not bring any confusion.

3.2 Transition associated with the ordering of M atoms

Fig.2 shows a part of the powder pattern of $\text{Rb}_{0.27}\text{WO}_3$ measured at 9.5K. Arrow is attached to each superlattice reflection, which does not exist above $T_S \approx 205\text{K}$. T_S agrees reasonably well with T_B , the temperature of the observed resistivity anomaly(5). For this sample all superlattice lines can be indexed by doubling the c axis. We have also studied four additional powder samples of Rb_xWO_3 with $x=0.20, 0.22, 0.24$ and 0.33 . For the sample with $x=0.24$, the transition which involves the doubling of all lattice constants have been observed. For the $x=0.22$ sample, the incommensurate peaks were observed. These transition temperatures are close to T_B . For the $x=0.20$ and 0.33 samples, no clear evidence of a transition has been observed near T_B . Transitions which involve the doubling of an axis in the c plane have been observed at $T_S' \approx 470\text{K}$ and 390K for the samples with $x=0.20$ and 0.22 , respectively.

As stated in ref.7, these transitions are associated with the ordering of the Rb atoms. Rather detailed structure analyses have been carried out to determine the ordering schemes which represent an averaged structure of the nonstoichiometric compounds. We will use the notations of the ordering scheme in the c plane shown in Fig.3a, where only the M atom sites are shown. The open circles are occupied by M atoms and the solid circles are vacant. Two principal ordering schemes (or averaged ordering schemes) are (1×2) and (f) . Three dimensional orderings can be obtained by stacking these plane elements in chosen orders. These are shown in Fig.3b. The first or the second scheme is the one for the sample with $x=0.27$. The

third and ^Vthe fifth schemes correspond to the x values of 1/4 and 1/6, respectively. The averaged structures observed for the x values of 0.24 and 0.20 have these respective schemes. The fourth is the probable intermediate scheme between the third and the fourth. However, the actual result we have obtained for x=0.22 contains the long period modulation along the c axis below T_S . The modulated structure is also seen in the $K_{0.25}WO_3$, whose powder pattern is shown in Fig. 2b. While each superlattice peak of $Rb_{0.27}WO_3$ is at the commensurate position, the corresponding superlattice of $K_{0.25}WO_3$ deviates slightly from the commensurate position indicated by the arrow. This feature can be understood by, for example, inserting one (f) layer at a step of about 100 layer spacing. Bando and Iijima have also observed this long period structure by electron diffraction(9).

In Fig.4, the phase diagram we have determined is shown. Following points may be valuable to be noticed. (a) In the lower vacancy concentration region, the vacancies tend to be confined to one layer or two neighboring layers. (b) The long period structure is stable at low temperature. This situation is opposite that observed for charge density waves. (c) The shifts of the oxygen atoms have also been observed in some cases induced by the coupling between the WO_6 octahedra and the ordering of M atoms.

54 Relationship between the structural phase transitions and the superconductivity

Three types of the lattice excitations in M_xWO_3 may be relevant to the superconductivity. These are phonons of the WO_3 cage, local modes

of M atoms and local structural excitations(LSE). Importance of LSE is emphasized by Vujicic et al.(10). The new periodicity of the lattice due to the order-disorder transition may produce a gap at a part of the Fermi surface, which is probably largest at $x=0.25$ as suggested by the resistivity data(5,6). This may be the reason of the anomalous x dependence of T_c found for Rb_xWO_3 (5) and K_xWO_3 (6). However, the effects of the transition on the lattice excitations mentioned above may be also important for T_c . Kamitakahara et al.(2) mentioned that the contribution of the phonon of the WO_3 cage is not negligible and that it makes T_c very sensitive to the local mode energy of M atoms. This fact seems to have close connection with the existence of the transition associated with the distortion of the WO_3 cage. In M_xWO_3 , the local redistribution of the vacancies which often couples, as we have observed, with the distortion of the WO_3 cage may have a role of LSE. Then, the ordering of M atom suppresses the contribution of the LSE to the superconductivity(10) and we can expect the x dependence of T_c consistent with the observed one. Although any correlation of the local mode energy of M atoms with the x dependence of T_c has not been observed at room temperature(7), the low temperature data is necessary to exclude the possibility that the change of the local mode energy due to the transitions has an important role for the value of T_c .

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References

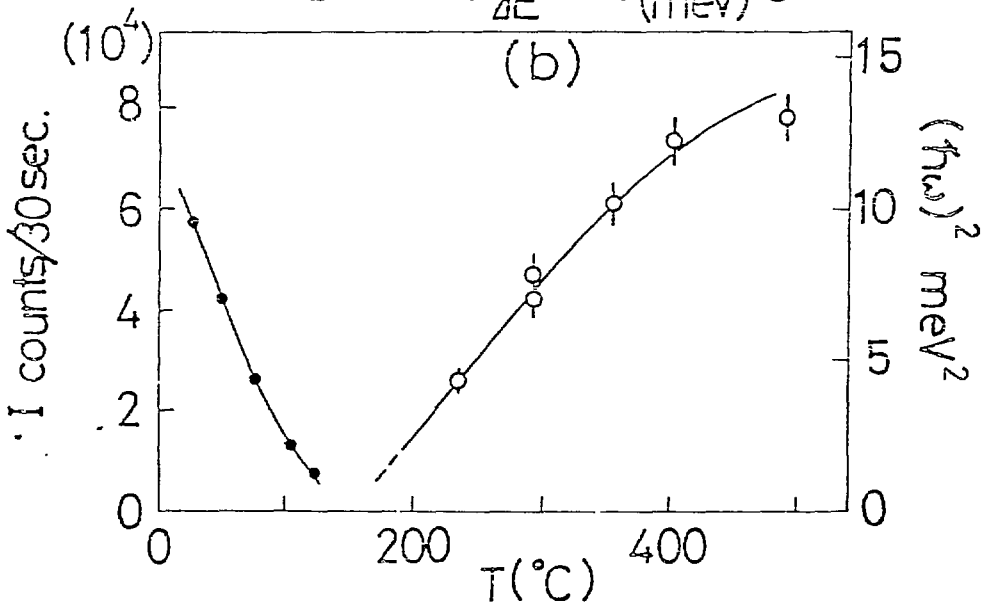
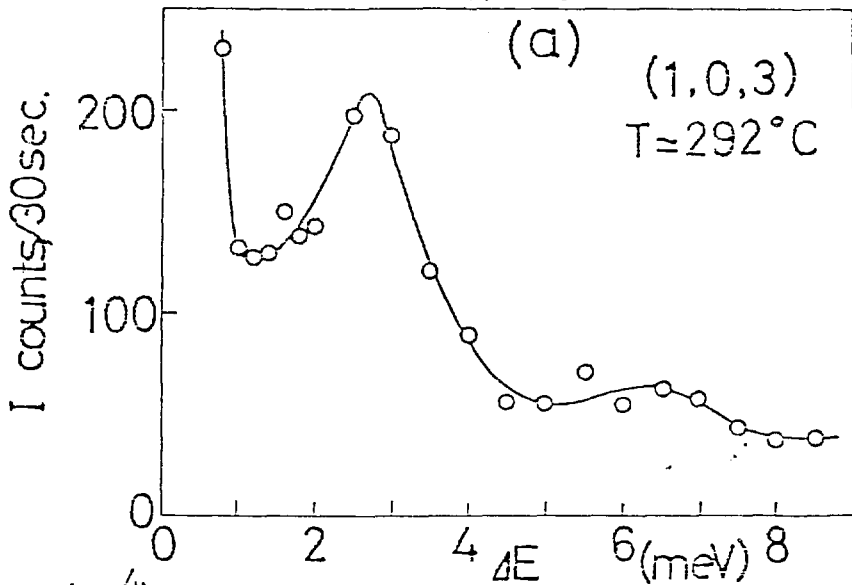
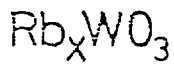
1. A. Magneli Acta Chem. Scand. 7 315 (1953)
2. W.A. Kamitakahara, K. Shanberg and H.R. Shanks Phys. Rev. Lett. 43 1607 (1979)
3. N.J. Chesser, J.G. Traylor, H.R. Shanks and S.K. Sinha Ferroelectrics 16 115 (1977)
4. M. Sato J. Phys. C13 L481 (1980)
5. R.K. Stanley, R.C. Morris and W.G. Moulton Phys. Rev. B20 1903 (1979)
6. L.H. Cadwell, R.C. Morris and W.G. Moulton Phys. Rev. B23 2219 (1981)
7. M. Sato, B.H. Grier, G. Shirane and H. Fujishita Phys. Rev. B25 501 (1982)
8. H.R. Shanks J. Cryst. Growth 13/14 433 (1972)
9. Y. Bando and S. Iijima Twelfth Int. Cong. Cryst. ed. M. Przybylska, Ottawa (1981)
10. G.M. Vujičić, V.L. Aksenov, N.M. Plakida and S. Stamenković J. Phys. C14 2377 (1981)

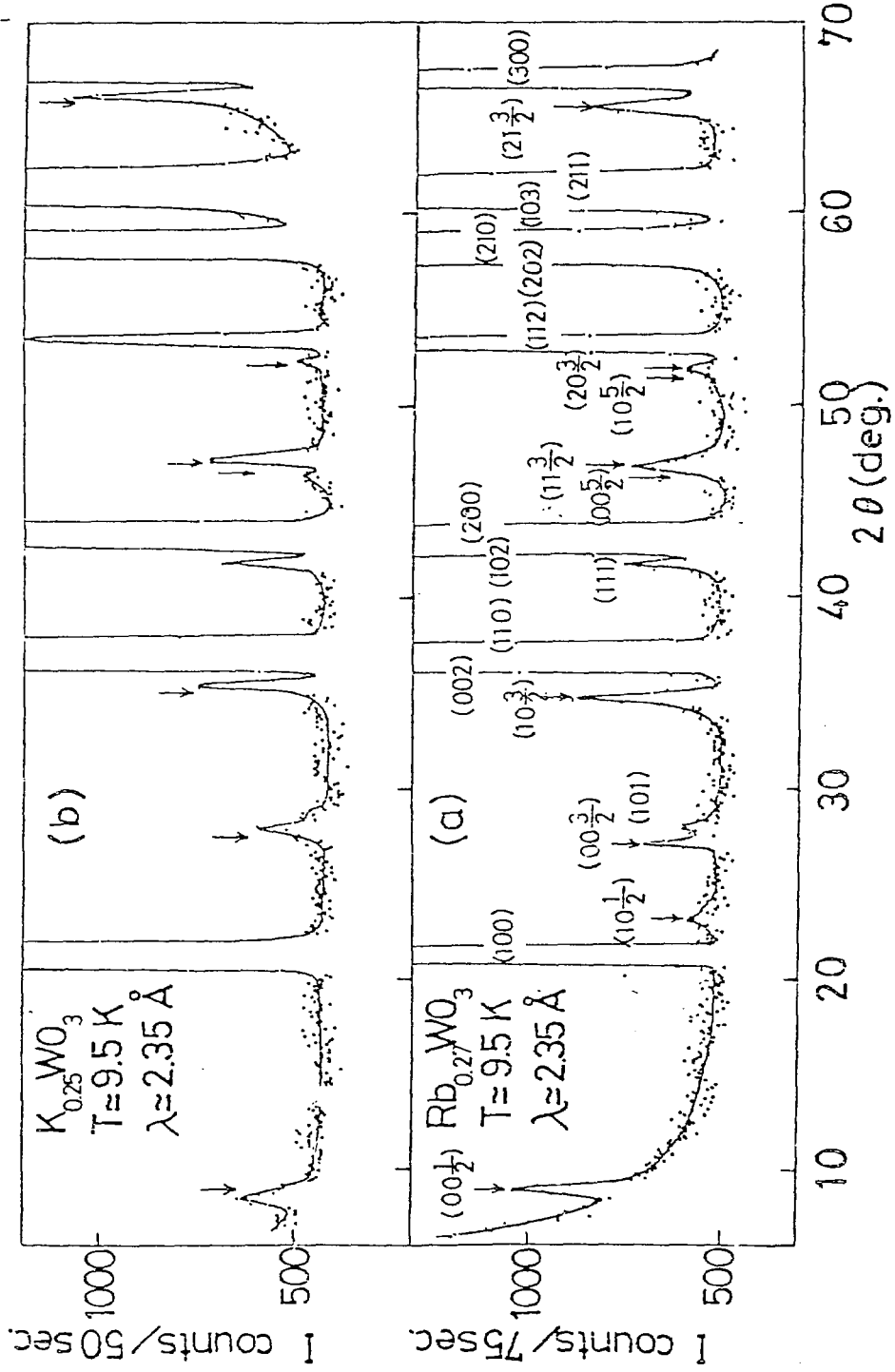
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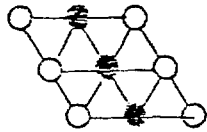
Figure captions

- Fig.1 (a) An example of the soft phonon profile of Rb_xWO_3
(b) Square of the soft phonon energy (open circles) and peak intensity of the (103) reflection (solid circles) are shown as a function of T.
- Fig.2 (a) Neutron powder pattern of $\text{Rb}_{0.27}\text{WO}_3$. Peaks with arrows are the superlattice reflections.
(b) Neutron powder pattern of $\text{K}_{0.25}\text{WO}_3$
While for $\text{Rb}_{0.27}\text{WO}_3$ each superlattice peak falls at the commensurate position with a half integral l , the superlattice line of $\text{K}_{0.25}\text{WO}_3$ has a slight deviation from the corresponding commensurate position indicated by the arrow.
- Fig.3 The ordering schemes of Rb atoms. Solid and open circles indicate the vacant and the occupied sites, respectively.
(a) Definition of the ordering schemes within the c plane
(b) Principal schemes of stacking of the layers in the commensurate phases are shown in order of increasing vacancy concentration. The first and the second schemes do not have a long range order of the vacancies within a plane.
- Fig.4 Phase diagram of Rb_xWO_3 . T_R at $x=0.33$ is determined for the single crystal. The others are for powder samples. T_B shown by the broken line is determined by Stanley et al.(8). The shaded region with no clear boundary indicates the presence of the long period structure.

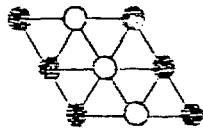




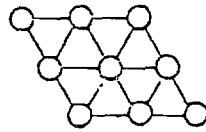
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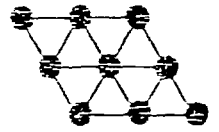
(1x2)



(1x2)'



(f)



(f)'

(b)

