SUPERCONDUCTIVITY I N ALKALI TUNGSTEN BRONZES

S. Ruvalds, L. Kahn

SUPERCONDUCTIVITY IN ALKALI TUNGSTEN BRONZES†

J. Ruvalds and L.M. Kahn

Physics Department, University of Virginia, Charlottesville, Virginia 22901, U.S.A.

Résumé.- Le comportement anormal de la température de transition supraconductrice dans quelques bronzes de tungstène alcalin peut être expliqué par le couplage des électrons induit par l'échange de plasmons acoustiques.

Abstract.- The anomalous behavior of the superconducting transition temperature in certain alkali tungsten bronzes is shown to be consistent with electron pairing induced by exchange of acoustic plasmons.

The superconducting properties of certain alkali tungsten bronzes exhibit some highly unusual features which appear to violate the predictions of the BCS theory. These nonstoichiometric compounds are of the form M_xWO_3, where M represents an Alkali atom such as Na, Rb, and hydrogen. As x increases, these compounds become metallic, and the electronic density of states is believed to increase monotonically with the alkali content as indicated by magnetic susceptibility measurements /1/.

On the basis of the BCS theory /2/ the superconducting transition temperature T_c should become higher with increasing electronic density of states at the Fermi energy N(0) according to the relation

$$T_c \simeq 0.7\Theta_D \exp\left[\frac{-1}{g\ N(0)}\right] \qquad (1)$$

Where the Debye temperature is roughly $\Theta_D \simeq 400$ K in these materials and g is a matrix element of the electron-phonon coupling. For a free electron model $N(0) \propto x^{1/3}$, and the predicted T_c increases with x as shown in Figure 1. If the electron density of states increases faster (say $N(0) \propto x$ as in Reference /1/), then the transition temperature of course should rise more sharply as a function of alkali content.

In sharp contrast to these expectations. the experimental data show an enhancement of T_c with decreasing x for Rb_wWO_3 /3,4/ and Na_xWO_3/5/as seen in Figure 1. The low values of the electronic specific heat and magnetic susceptibility in these materials /1/ would seem to rule out spin fluctuation effects, and the extrapolated density of electron states is quite small, resembling the values of Na, Cu, and other non-superconducting metals.

The purpose of the present work is to correlate the anomalous T_c-dependence in these materials with an electron pairing mechanism achieved by virtual exchange of acoustic plasmons.

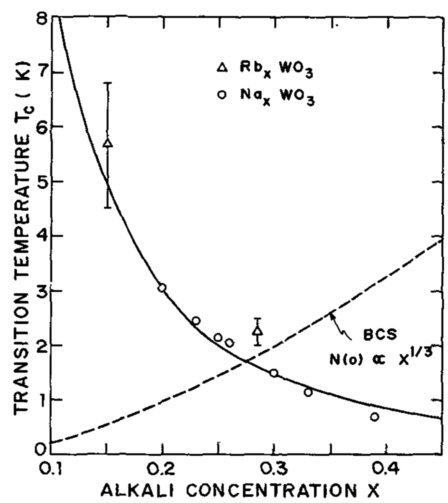

Fig. 1 : Superconducting transition temperature as a function of alkali content for Rb_xWO (References /3,4/) and Na_xWO_3 (Reference /5/). The BCS theory using a free-electron density of states ($N(o) \propto x^{1/3}$) is shown by the dotted line. The solid curve is the result of the present work using the Frohlich expression of Equation (3).

This process was originally suggested by Frohlich /6/ as a possibility in metals with overlapping d and s-electron bands. Acoustic plasmon modes are generated by the screening of the d-plasma

† Supported in part by the National Science Foundation Grant No DMR 77-13167

oscillations by the s-electrons, which yields a linear dispersion for the plasmons of the form

$$\omega_q \simeq cq \qquad (2)$$

where the plasmon "sound" velocity is given by $c=(\omega_d{}^2 m_s/\omega_s{}^2 m_d)^{1/2} v_s$, in terms of the respective (ℓ=d,s) plasma frequencies $\omega_\ell \equiv 4\pi n_\ell{}^2/m_\ell$, the effective masses m_ℓ, and the Fermi velocity v_s of the s-electrons. By treating the acoustic plasmons in direct analogy with ordinary phonons, Frohlich /6/ derived the following expression for the superconducting transition temperature

$$T_c \simeq W e^{-\frac{1}{F}}, \qquad (3)$$

with

$$F \equiv \frac{2\delta^{2/3}}{\pi(3\pi^2)^{1/3}\varepsilon_o (n_d n_s)^{1/6} a^*} \left\{1 - \frac{3 m_s}{\delta^{2/3} m_d} \left(\frac{n_s}{n_d}\right)^{1/3}\right\}, \qquad (4)$$

where δ is the degeneracy of the d-band, m_s and m_d denote the number of electrons in the s and d bands respectively, and ε_o is the dielectric constant, and $a^* = \hbar^2/e^2(m_s m_d)^{1/2}$. Similarly, the corresponding plasmon cut-off temperature W can be expressed as

$$W^2 \simeq \frac{\omega d^2}{\varepsilon_o} \left(\frac{m_o}{m_d}\right) \left(1 - 3\frac{n_s D_s}{n_d D_d}\right), \qquad (5)$$

Where D_ℓ is the density of energy levels per electron near the Fermi energy

The acoustic plasmon exchange mechanism favors high temperature superconductivity for two basic physical reasons. First the coupling of electrons to acoustic plasmons is essentially a screened Coulomb interaction which may be expected to be stronger than the usual electron-phonon coupling. Secondly the cut-off frequency W may be of the order of a plasmon frequency (W 10 K) thus overwhelming the phonon contribution which involves a Debye energy cut-off $\Theta_D \sim 400$ K. On the other hand, the formation of acoustic plasmon modes deprives considerable strength from the bulk "optical" plasmons, and therefore decreases the screening of the Coulomb electron-electron repulsion. Finally it should be emphasized that the acoustic plasmons are generated only under restrictive conditions, and their well-defined occurance may be rare.

Applying the Frohlich formulas /3-5/ to the data for the superconducting transition temperature of alkali tungsten bronzes, we obtain the remarkable agreement for the vaiation of T_c with alkali content as shown in Figure 1. The fit to experiment yields values of the coupling F(x=0.1)=0.32 to F(x=0.5)=0.17, and W≃200K. Using realistic ε_F=0.4eV, $m_s = m_o$, $m_d = 3m_o$, $\delta = 5$, and $\varepsilon_o = 10$ yield larger values of F(x=0.1) ≃ 0.8 and W ≃ 10^4 K. Therefore, the competition from the screened Coulomb repulsion cannot be neglected in a quantitative application of the theory. This conclusion is supported by numerical calculations by Pashitskii /7/ and others who obtain $T_c \simeq 100$ K from solutions of the superconducting energy gap equation.

There is some preliminary support for our band model in the optical data /8/ which reveals an absorption edge at Δ∿ 3eV for pure insulating WO_3. As Na_x is added the absorption edge moves higher in energy for x > 0.1, corresponding to a transition from the valence band to the partially filled conduction band. The shift in the absorption edge is roughly 0.3eV which is consistent with our s-band superimposed on a rigid conduction d-band whose bottom is roughly 0.2eV above the s-band minimum.

In summary, the acoustic plasmon mechanism to give a good account of the anomalous concentration dependence of T_c in alkali tungsten bronzes. Further calculations of the reduced Coulomb screening are in progress. Finally it would be interesting to probe the alkali tungsten bronzes by direct electron loss measurements; our calculations yield Landau damping of the acoustic modes, but nevertheless show a significant peak in the structure factor at finite momenta which should be observable by experiment.

It is a pleasure to acknowledge stimulating conversations with B. Deaver, L. De Long, C. Friedberg, I. Lefkowitz, K.L. Ngai, S. Schnatterly and J. Snare.

References

/1/ See for example, Greiner, J.D., Shanks, H.R., and Wallace,D.C., J. Chem. Phys. 36 (1972) 772 and references cited therein.

/2/ Bardeen, J., Cooper, L.N. and Schrieffer, J.R., Phys. Rev. 106 (1957) 162.

/3/ Remeika, J.P., Geballe, T.H., Matthias, B.T., Cooper, A.S., Hull, G.W., and Kelly, E.M., Phys. Lett. 24A (1967) 565.

/4/ Sweedler, A.R. (PhD. Thesis, University of California, La Jolla, California 1969).
For a recent review of T_c enhancement in tungsten bronzes, see I. Lefkowitz, Ferroelectrics 16 (1977) 239.

/5/ Shanks, H.R., Sol. St. Commun 15 (1974) 753.

/6/ Frohlich, H., J. Phys. C.1 (1968) 544.

/7/ Pashitskii, E.A. and Chernousenko, V.M., Soviet Physics JETP 33 (1971) and references cited therein.

/8/ Dickens, P.G., Quillian, R.M.P. and Whittingham, M.S., Mat. Res. Bull. Vol. 3, P. 941, 1968 (Pergamon Press).