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# Study of Fermi-Surface Topology Changes in Rhenium and Dilute Re Solid Solutions from $T_c$ Measurements at High Pressure

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The superconducting transition temperature has been measured as a function of hydrostatic pressure up to 18 kbar for single-crystal and polycrystal samples of pure rhenium and dilute solid solutions of Mo, W, and Os in rhenium. The pressure dependence for pure Re is anomalous and varies rapidly with solute additions. This anomalous behavior is explained in terms of an abrupt change in Fermi-surface topology under pressure.

## INTRODUCTION

THE superconducting transition temperature $T_c$ for the majority of the known superconducting elements has been studied as a function of pressure.[1] In general, $T_c$ follows a monotonic function with pressure, increasing in a few cases, but usually decreasing. It has recently been demonstrated[2] for lead that, given an adequate knowledge of the pressure dependence of the phonon spectrum, the pressure dependence of $T_c$ calculated from McMillan's[3] expression which includes the effects of strong coupling, is in very good agreement with the experimental value. This agreement will very likely be achieved for all nontransition-metal superconductors, which, with the exception of thallium, exhibit a decrease of $T_c$ with pressure. The situation for the transition-metal superconductors is more complex and a better understanding of the electron-electron interactions is required before such a calculation of the pressure dependence of $T_c$ is possible.

The possibility of a nonmonotonic pressure dependence of $T_c$ arising from pressure-induced abrupt changes in the topology of the Fermi surface has been discussed by Makarov and Bar'yakhtar.[4] It has been suggested that such a transition is responsible for the anomalous pressure dependence of $T_c$ for thallium. The extensive study of the pressure dependence of $T_c$ for Tl and dilute Tl alloys by Lazarev and co-workers[5] provides convincing support for this hypothesis.

The observation of a nonmonotonic pressure dependence of $T_c$ for rhenium has been briefly reported.[6] $T_c$ for both single-crystal and polycrystal rhenium initially decreases with pressure, passes through a minimum at $\sim$7 kbar, and then levels off between 13 and 18 kbar. The addition of Os rapidly displaces the minimum to lower pressures and the anomalous behavior disappeared enitrely in alloys containing more than 0.6-at.% Os, for which $T_c$ decreases almost linearly with pressure. This behavior suggested that an abrupt change in Fermi-surface topology also occurs in pure Re. Further measurements have now been made on dilute solid solutions of W and Mo in Re which support this proposal.

This paper includes full details of the preparation and results that have been obtained for polycrystal and single-crystal samples of pure Re and polycrystal samples of Re-Os, Re-Mo and Re-W solid solutions.

## SAMPLE PREPARATION

Rhenium samples were cut from polycrystalline and single-crystal material obtained from Materials Research Corporation (MRC Grade 1, zone refined, quoted purity: 99.9 wt%). Spectroscopic analysis of a sample of the polycrystal material gave the major impurities in ppm atomic as W 1.4, Mo 12, Ni 9, Fe 4, Ca 2, K 20, and S 12 in reasonable agreement with a "typical" analysis supplied by MRC. Samples cut directly from the "as received" material had superconducting transition widths which extended over more than 1°K. A typical transition curve obtained for a polycrystalline sample (Fig. 1), shows a transition ranging from 3.1 to 1.7°K.

Such broad transitions have been observed in previous investigations and are attributed to the extreme sensitivity of the transition in Re to the amount of

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[1] For a general review see M. Levy and J. L. Olsen, *Physics of High Pressure and the Condensed Phase*, edited by A. Van Itterbeek (North-Holland Publishing Co., Amsterdam, 1965), p. 525.

[2] R. E. Hodder, Phys. Rev. Letters **22**, A8 (1969).

[3] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[4] V. I. Makarov and V. G. Bar'yakhtar, Zh. Eksperim. i Teor. Fiz. **48**, 1717 (1965) [English transl.: Soviet Phys.—JETP **21**, 1151 (1965)].

[5] B. G. Lazarev, L. S. Lazareva, and V. I. Markarov, Zh. Eksperim. i Teor. Fiz. **44**, 481 (1963) [English transl.: Soviet Phys.—JETP **17**, 328 (1963)]; B. G. Lazarev, L. S. Lazareva, V. I. Makarov, and T. A. Ignat'eva, Zh. Eksperim. i Teor. Fiz. **46**, 829 (1964); **48**, 1065 (1965) [English transl.: Soviet Phys.—JETP **19**, 566 (1964); **21**, 711 (1965)]; N. B. Brandt, N. I. Ginzburg, T. A. Ignat'eva, B. G. Lazarev, L. S. Lazareva, and V. I. Makarov, Zh. Eksperim. i Teor. Fiz. **49**, 85 (1965) [English transl.: Soviet Phys.—JETP **21**, 1151 (1965)].

[6] C. W. Chu, T. F. Smith, and W. E. Gardner, Phys. Rev. Letters **20**, 198 (1968).

TABLE I. Summary of metallurgical treatments and atmospheric pressure $T_c$ for a number of Re samples.

| Sample | $T_c$ (°K) | Annealing conditions: Temperature (°C) | Time (h) | Vacuum (mm Hg) | Remarks |
|---|---|---|---|---|---|
| Re (polycrystalline) | | | | | MRC, grade 1, 99.9 wt% purity |
| Re 1*P* | ~3.1 –1.7 | | | | As received |
| Re 2*P* | 1.698–1.694 | | | | Arc melted, He atmosphere |
| Re 3*P* | 1.695–1.692 | 1400 | 1 | $2–3\times10^{-5}$ | |
| Re 4*P* | 1.696–1.694 | | | | Arc melted, Ar atmosphere |
| Re 5*P* | 1.695–1.693 | 1350 | 1 | $\sim7.5\times10^{-5}$ | |
| Re 6*P* | 1.695–1.693 | | | | Arc melted, He atmosphere |
| Re (single crystal) | | | | | MRC, grade 1, 99.9 wt% purity |
| Re 1*S* | ~2.8 –2.0 | | | | As received |
| Re 2*S* | 1.696–1.690 | 1600–1700 | 1 | $3–5\times10^{-5}$ | Spark cut |
| Re 3*S* | 1.696–1.690 | 1500–1680 | 1½ | $\sim10^{-2}$ | Cut on carborundum wheel |
| Re 4*S* | 1.695–1.694 | 1600–1750 | 1 | $2–3\times10^{-5}$ | Cut on carborundum wheel |
| Re 5*S* | 1.695–1.694 | 1500 | 1 | $6.7–7.5\times10^{-5}$ | Cut on carborundum wheel |
| Re 6*S* | 1.695–1.693 | 1500 | 1½ | $4.5–5\times10^{-5}$ | Spark cut |

plastic deformation and internal strain in the material. It was therefore necessary to sharpen the transition before the effect of pressure could be studied and it was found that inductive annealing *in vacuo* or, in the case of the polycrystal samples, arc melting in either a helium or an argon atmosphere produced satisfactory transition curves (Fig. 1). A full symmary of the heat treatments is given in Table I.

Solid solutions of Os, W, and Mo in Re were prepared from MRC polycrystal Re and the appropriate amount of solute by arc melting in an argon atmosphere. In order to promote homogeneity, each sample was turned and remelted at least seven times. The more dilute samples (<0.5-at.% solute) were prepared by the addition of more Re to the alloy of next-highest concentration. As the weight losses which occurred during melting were negligibly small, the quoted compositions are those calculated from the initial relative proportions of the constituents. The transition curves for the arc-melting alloy samples were sharp (between 1.5 and 5 mdeg wide) and this was taken to be indicative of good homogeneity and so no further treatment was given.

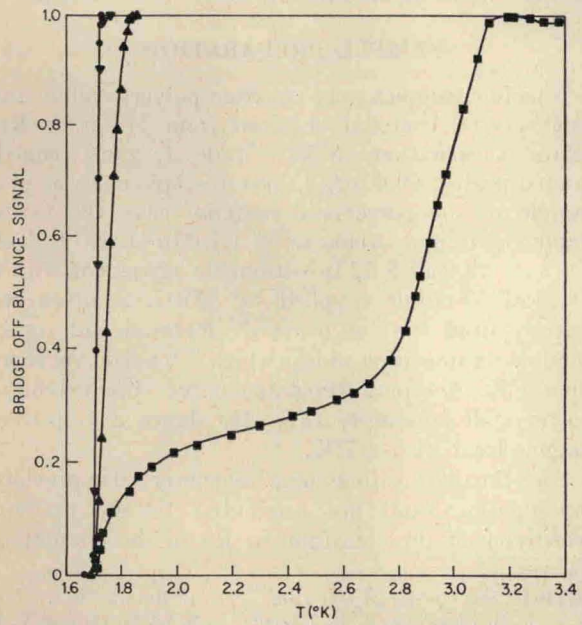


FIG. 1. Effect of strain on the superconducting transition curve for pure polycrystalline Re. ■, as received; ●, after arc melting; ▲, after application of 18.5 kbar (Teflon pressure medium); ▼, after application of 17.3 kbar (fluid pressure medium).

## EXPERIMENTAL DETAILS

The sensitivity of the superconducting transition of Re to inhomogeneous strain[7] placed stringent requirements on the achievement of hydrostatic pressures. A pressure transmission medium of micron-size Teflon particles, which has been used successfully in a number of previous investigations of the pressure dependence of $T_c$, was found to be unsuitable for the present measurements since it was observed that after the application of pressure there was a large irreversible shift in the zero-pressure value of $T_c$. This is illustrated in Fig. 1 which shows the effect on the transition curve of applying a pressure of 18.5 kbar with this medium. This led us to try a fluid medium of a 1:1 mixture of *n*-pentane and isoamyl alcohol contained in a self-sealing Teflon cell similar to that described by Jayaraman *et al.*[8] The cell was pressurized at room temperature between two high-density alumina pistons in a ¼-in. id hardened Cu-Be cylinder. The pressure was retained by a clamp arrangement for cooling to liquid-helium temperature. Cooling produced a pressure loss of 3–4 kbar. Pressures, as measured by a superconducting tin manometer,[9] were achieved up to 19 kbar. Following the application of the maximum pressure with this arrangement the zero-pressure transition curve was found to be reproducible to within a millidegree. Some initial measurements were made using a hydraulic oil

[7] J. J. Hauser and E. Buehler, Phys. Rev. **125**, 142 (1962); N. E. Alekseyevsky, M. N. Mikheyeva, and N. A. Tulina, Zh. Eksperim. i Teor. Fiz. **52**, 875 (1967) [English transl.: Soviet Phys.—JETP **25**, 575 (1967)].

[8] A. Jayaraman, A. R. Huston, J. H. McFee, A. S. Coriel, and R. G. Maines, Rev. Sci. Instr. **38**, 44 (1967).

[9] T. F. Smith, C. W. Chu, and M. B. Maple, Cryogenics **9**, 53 (1969).

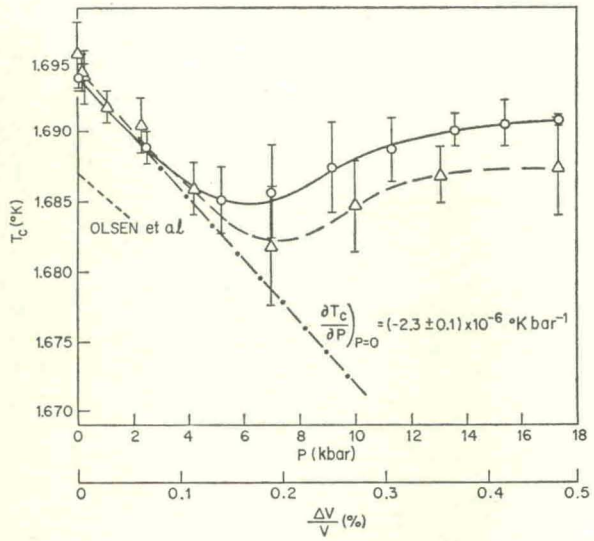


FIG. 2. Pressure dependence of $T_c$ for polycrystalline Re. △ is Re2$P$; ○ is Re5$P$.

which froze ($\gtrsim$7 kbar) at room temperature during the pressure application. This produced broadened transition curves and clearly illustrated the sensitivity of the rhenium transition to nonhydrostatic conditions.

The transition to the superconducting state was detected by an ac bridge technique with a single frequency of 150 cps. After suitable amplification and rectification the bridge output was displayed on the $Y$ axis of a $X$-$Y$ recorder. The $X$ axis was driven from the voltage drop across a germanium resistance thermometer which was calibrated against the 1958 He$^4$ vapor-pressure scale of temperature on each run. The uncertainty associated with the temperature was better than 0.5 mdeg. The pressure could be determined to about ±2%.

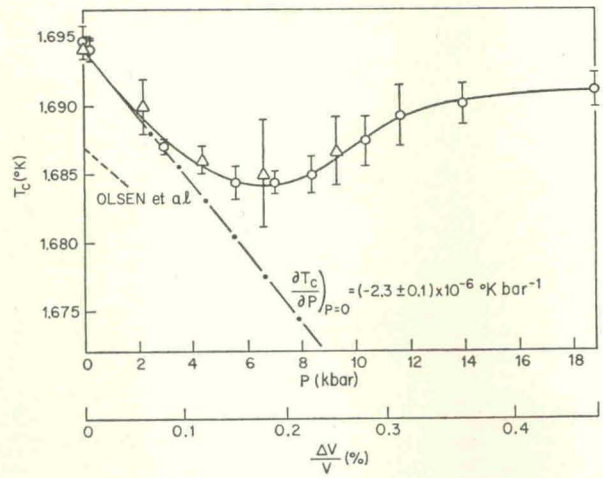


FIG. 3. Pressure dependence of $T_c$ for single-crystal Re. △ is Re5$S$; ○ is Re4$S$.

## EXPERIMENTAL RESULTS

### Rhenium

Zero-pressure transition temperatures for five single-crystal and five polycrystal samples are listed in Table I. From these determinations the mean value of $T_c$, as represented by the midpoint of the transition, is (1.695 ±0.001)°K, in very good agreement with the values reported by Hulm and Goodman[10] and Blanpain[11] but slightly lower than the recent value of Maxwell, Strongin and Reed.[12]

Detailed plots of $T_c$ as a function of pressure for two polycrystalline and two single-crystal samples are shown in Figs. 2 and 3. It can be seen that $T_c$ decreases initially, passes through a minimum, and then levels off at about 17 kbar. The results for Re 5$P$, Re 4$S$, and Re 5$S$ are in good quantitative agreement. Re 2$P$ exhibits an over-all behavior which is similar to that of the other Re samples, but the minimum in $T_c$ occurs at a slightly higher pressure. This is possibly due to contamination with tungsten (50 ppm atomic would be sufficient) during arc melting. This explanation would be consistent with its slightly higher zero pressure $T_c$.

The low-pressure ice-bomb measurement of Olsen *et al.*[13] is also indicated in Figs. 2 and 3. In view of the large uncertainty given in this previous determination their result is not inconsistent with the initial slope of $(-2.3\pm0.1)\times10^{-6}$ °K bar$^{-1}$ obtained from the present measurements.

### Rhenium Alloys

The zero-pressure superconducting transition temperature as a function of concentration for the solid solutions of Os, W, and Mo in Re is shown in Fig. 4. The $T_c$ increases slightly over the limited range of Re-W and Re-Mo alloys examined, but in the case of

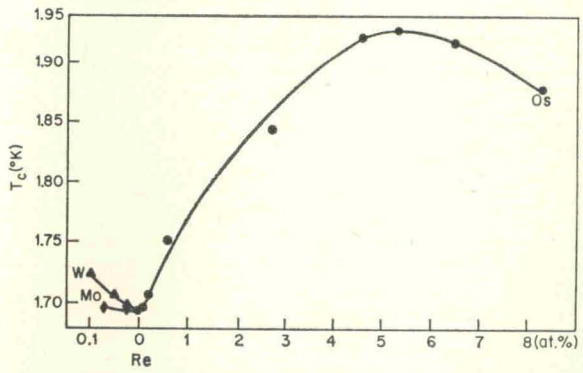


FIG. 4. $T_c$ for Re alloys. ●, Re-Os; ▲, Re-W; ♦, Re-Mo (note change of scale from left to right of Re).

[10] J. K. Hulm and B. B. Goodman, Phys. Rev. **106**, 659 (1957).
[11] B. Blanpain, Bull. Acad. Roy. Belg. Class Sci. **47**, 750 (1961).
[12] E. Maxwell, M. Strongin, and T. B. Reed, Phys. Rev. **166**, 557 (1968).
[13] J. L. Olsen, K. Andres, H. Meir, and H. de Salaberry, Z. Naturforsch. **18a**, 125 (1963).

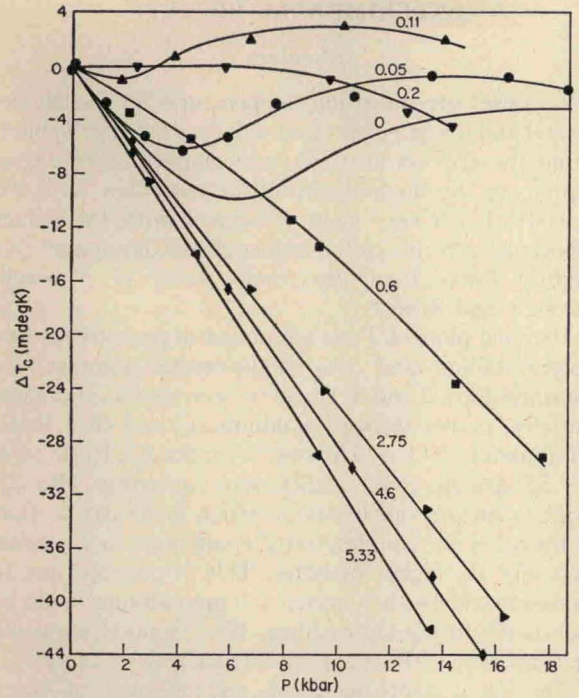


FIG. 5. $\Delta T_c$ as a function of pressure for Re-Os alloys. The number associated with each curve represents the at.% concentration of Os.

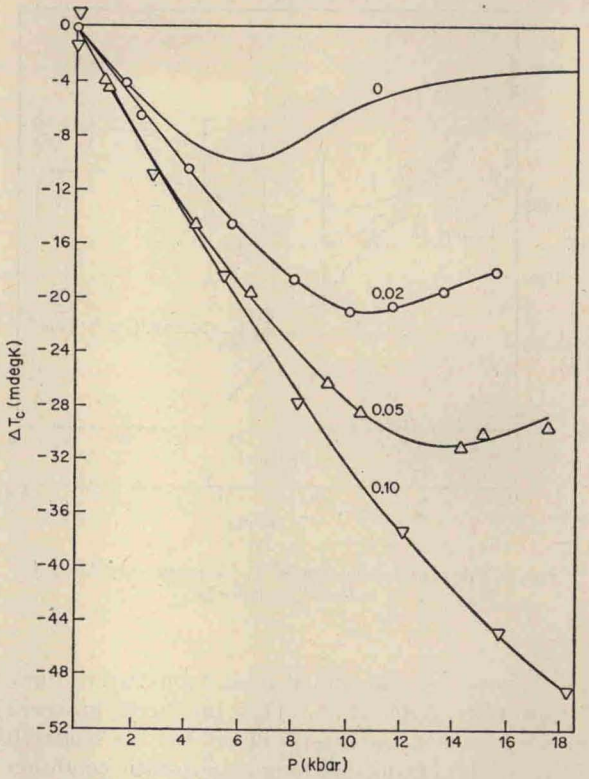


FIG. 6. $\Delta T_c$ as a function of pressure for Re-W alloys. The number associated with each curve represents the at.% concentration of W.

the Re-Os alloys, $T_c$ passes through a maximum at ~5.5-at.% Os. This behavior of $T_c$ for the Os alloys is in contrast to that of the density of states, which decreases continuously over this composition range.[14]

The pressure induced change in $T_c$, $\Delta T_c$, for the alloy systems is plotted as a function of pressure for several compositions in Figs. 5–7. With the addition of Os, the pressure $P_m$ at which the minimum of the $\Delta T_c(P)$ curve occurs was found to move towards lower pressure and disappear when the Os concentration reaches 0.2 at.%. For concentrations greater than 2.75-at.% Os, $T_c$ decreases almost linearly with pressure. It is of interest to note that the sensitivity to pressure inhomogeneity observed for the transition for pure Re was found to be absent in alloys with Os concentrations in excess of 0.6 at.%. The addition of $W$ causes $P_m$ to move rapidly to higher pressures. Thus, the addition of 0.1-at.% W raises $P_m$ from 6 kbar to a value in excess of 18 kbar. Mo is less effective in raising $P_m$, and $P_m$ shows very little change between 0.02 and 0.07-at.% Mo.

## DISCUSSION

We propose to adopt the approach of Lazarev and co-workers[5] and regard the anomaly in the behavior of $T_c$ as a function of pressure as being composed of two parts, one of which is the normal linear variation of $T_c$ with pressure, and the other, a nonlinear contribution which is associated with an abrupt change in the Fermi-surface topology.

Abrupt changes in Fermi-surface topology are related to critical points in the $E(\mathbf{k})$ spectrum.[15] Such critical

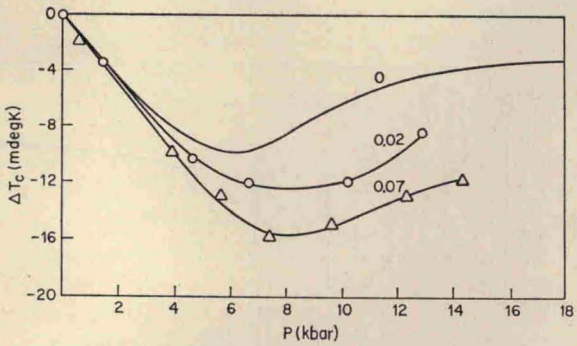


FIG. 7. $\Delta T_c$ as a function of pressure for Re-Mo alloys. The number associated with each curve represents the at.% concentration of Mo.

[14] E. Bucher, F. Heiniger, and J. Muller, in *Proceedings of the Ninth International Low-Temperature Conference, Columbus, Ohio,* edited by J. G. Daunt *et al.* (Plenum Press, New York, 1965), p. 1059; J. P. Maita (private communication).

[15] I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **38**, 1569 (1960) [English transl.: Soviet Phys.—JETP **11**, 1130 (1960)]; I. M. Lifshitz and M. I. Kaganov, Usp. Fiz. Nauk **69**, 419 (1959) [English transl.: Soviet Phys.—Usp. **2**, 831 (1960)]; Usp. Fiz. Nauk **78**, 411 (1962) [English transl.: Soviet Phys.—Usp. **5**, 878 (1963)]; Usp. Fiz. Nauk **87**, 389 (1965) [English transl.: Soviet Phys.—Usp. **8**, 805 (1966)].

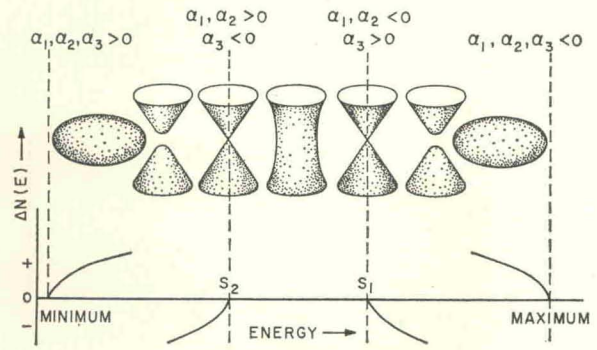


FIG. 8. Density of states contribution and energy surfaces associated with critical points in the $E(\mathbf{k})$ spectrum.

points[16] will occur when $\nabla(E(\mathbf{k}))=0$. Thus, the critical points in $k$ space will be found where the energy bands are very flat. Since $E(\mathbf{k})$ is a continuous function, we may expand the energy about the critical energy $E_c(\mathbf{k})$ as a Taylor series, where the linear terms are zero since $\nabla(E(\mathbf{k}))=0$. Thus, we have

$$E(\mathbf{k})=E_c(\mathbf{k})+\alpha_1 q_1^2+\alpha_2 q_2^2+\alpha_3 q_3^2+\cdots, \qquad (1)$$

where $\mathbf{q}=\mathbf{k}-\mathbf{k}_c$ and $\alpha_i=\partial^2 E(\mathbf{k})/\partial k_i^2$.

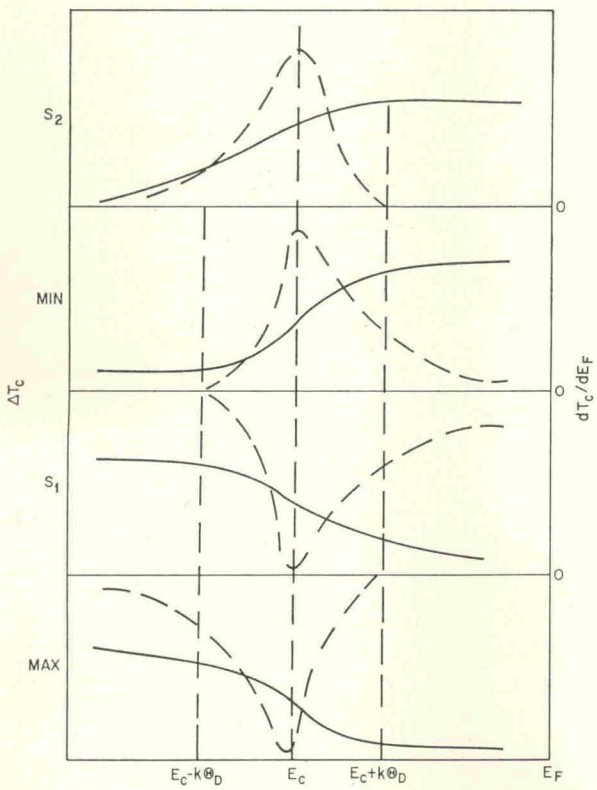


FIG. 9. Energy dependences of $\Delta T_c$ (solid line) and $\partial T_c/\partial E_F$ (broken line) as $E_F$ passes through a critical point in the $E(\mathbf{k})$ spectrum. $S_1$, $S_2$, min., and max. refer to the critical points illustrated in Fig. 8.

[16] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, New York, 1964), p. 48.

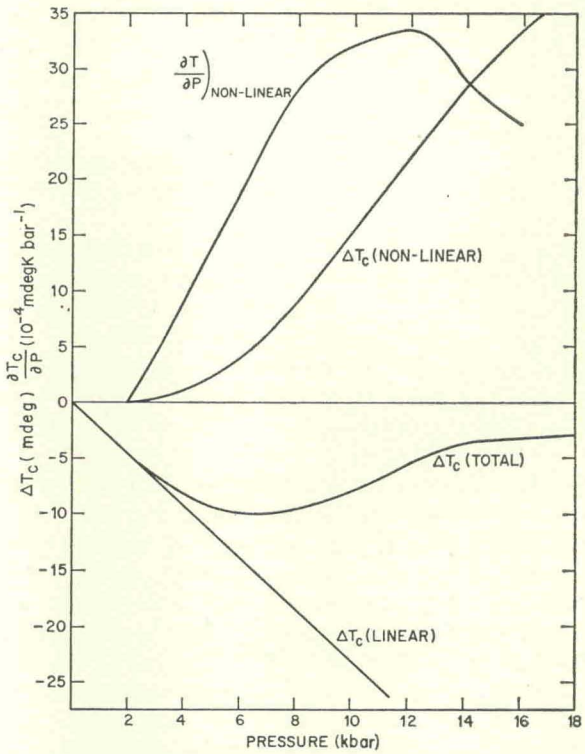


FIG. 10. Breakdown for Re of $\Delta T_c$ as a function of pressure into its linear and nonlinear contributions.

If, for example, all the $\alpha_i$ were positive, then there would be a local minimum in $E(\mathbf{k})$, and the additional contribution to the density of states would be

$$\begin{aligned} \Delta N(E)&=0, && E<E_c, \\ &\propto (E-E_c)^{1/2}, && E>E_c. \end{aligned} \qquad (2)$$

The energy dependence of $\Delta N(E)$ for this and the other three possible types of critical points is shown in Fig. 8, where $S_1$ and $S_2$ denote saddle points of indices 1 and 2. The shapes of the constant energy surfaces represented by Eq. (1) with all possible combinations of signs for $\alpha_i$ are also shown. Thus, as the energy passes through the critical energy corresponding to a local minimum in $E(\mathbf{k})$, a new surface is formed; or, conversely, on passing through a local maxima, a surface is destroyed. A transition through a saddle point results in the formation (or disruption) of a "neck," i.e., the transition from an open to a closed section of Fermi surface (or vice versa).

In the nearly free-electron approximation of a metal with pressure-independent potentials, the topology of the Fermi surface remains unchanged under an isotropic compression, but changes may occur if there is distortion. However, calculations based on the pseudopotential approximation to the nearly free-electron model show that the form factor depends upon volume and thus the connectivity of the Fermi surface at boundary points can change under isotropic compres-

sion.[17] In metals containing non-$s$ electrons, flat regions in $E(\mathbf{k})$ curves may also occur at $k$ values other than boundary points. If these regions are associated with strong hybridization, then changes in the lattice parameter can produce significant energy shifts relative to the Fermi energy. Thus, when these regions lie close to the Fermi surface, abrupt changes in topology can occur.

The first systematic study of the effects of such abrupt changes in topology on the thermodynamic and kinetic properties of a metal was undertaken by Lifshitz.[15] Markarov and Bar'yakhtar[4] extended this study to include the effects on the superconducting properties by introducing the change in the density of states into the energy-gap equation of the Bordeen-Cooper-Schrieffer (BCS) model.[18] They investigated the behavior of $T_c$ and $\partial T_c/\partial E_F$ as functions of $E_F$ (the Fermi energy) at energies close to $E_c$; their results are summarized in Fig. 9. Over the energy range $(E_c-k\Theta_D)\leq E_F\leq(E_c+k\Theta_D)$, where $\Theta_D$ is the Debye temperature, $T_c$ increases sharply at the critical points corresponding to $S_2$ or a minimum, whereas $T_c$ decreases sharply at $S_1$ or a maximum. In all cases, $\partial T_c/\partial E_F$ exhibits an extremum at $E_F=E_c$. From an experimental point of view, we are concerned with $\partial T_c/\partial P$, but since we may consider $\partial T_c/\partial P=(\partial T_c/\partial E_F)(\partial E_F/\partial P)$ and since we may reasonably assume that $\partial E_F/\partial P$ will vary slowly with pressure, any rapid variation of $\partial T_c/\partial E_F$ will also appear as a rapid variation of $\partial T_c/\partial P$.

In Fig. 10, we demonstrate the breakdown of $\Delta T_c$ for Re into its linear and nonlinear components. The variation of $(\partial T_c/\partial P)_{\text{nonlinear}}$ as a function of pressure, derived from $\Delta T_c$(nonlinear) is also plotted. The similarity between the pressure dependence of $\Delta T_c$ and $\partial T_c/\partial P$ for the nonlinear contribution and the energy dependence curves at the points $S_2$ and minimum shown in Fig. 9 is evident. Similar plots were made for the Re-Os alloys containing less than 0.2-at.% Os and, in particular, we show the plot for the 0.11-at.% Os in Fig. 11.

In the case of pure Re, the nonlinear contribution was estimated to start at pressures above $\sim$2 kbar and a maximum occurs in $(\partial T_c/\partial P)_{\text{nonlinear}}$ at a pressure $P_c\sim$12 kbar. On alloying with osmium, the pressure at which the nonlinear contribution commences rapidly falls to zero, as shown for example, by the curve for the addition of 0.11-at.% Os. In addition, it is found that the curve for $(\partial T_c/\partial P)_{\text{nonlinear}}$ does not fall smoothly above $P_c$, but has a step approximately 6 kbar wide. This behavior was not observed for pure Re, but this may well be due to the limitations of our pressure range. This form of the curve for the Os alloys suggests the possibility that more than one critical

[17] W. A. Harrison, *Physics of Solids at High Pressure* (Academic Press Inc., New York, 1965), p. 3; L. M. Falicov, *ibid.* p. 30.

[18] J. Bardeen, L. Cooper, and J. Schrieffer, Phys. Rev. **108**, 1175 (1957).

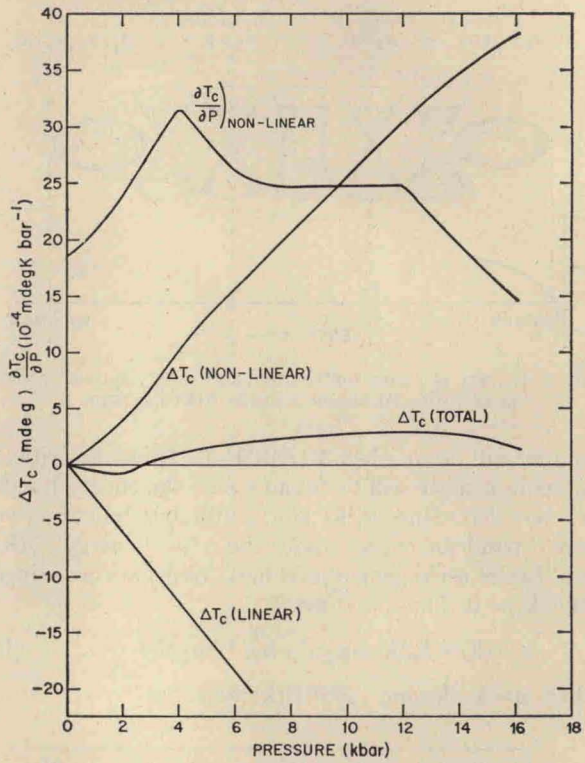


FIG. 11. Breakdown for Re 0.11-at.% Os of $\Delta T_c$ as a function of pressure into its linear and nonlinear contributions.

point may be involved. Furthermore, $P_c$ decreases roughly linearly with the addition of Os and goes to zero at the critical composition $\sim$0.14 at.% (see Fig. 12). It is evident from Figs. 6 and 7 that $P_c$ increases with concentration in the Re-W and Re-Mo systems, but, unfortunately, our pressure range was insufficient to reach $P_c$ for these systems.

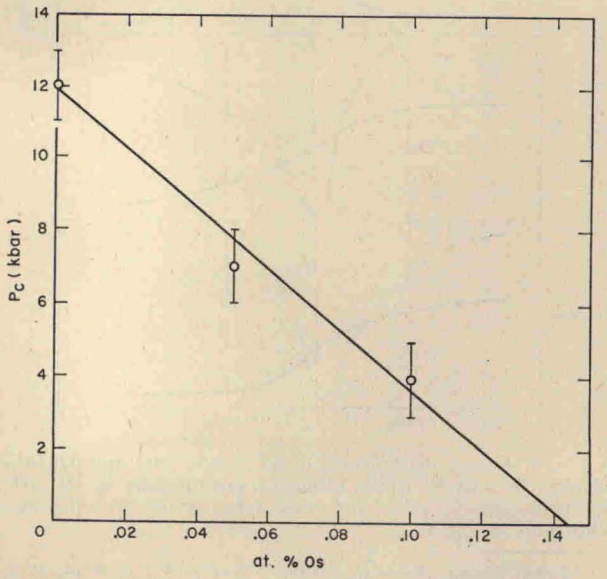


FIG. 12. Variation of $P_c$ with Os concentration.

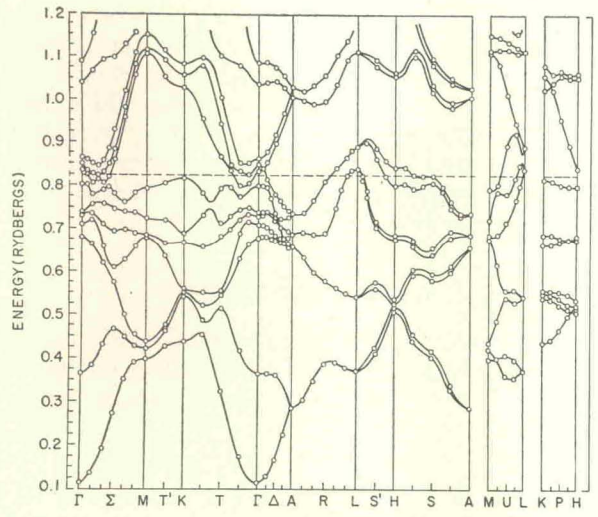


FIG. 13. The relativistic energy bands for rhenium, including the effects of spin-orbit coupling (from Ref. 19).

In principle, we should be able to distinguish between the two possible critical points ($S_2$ or minimum) from the shape of the pressure dependence of $(\partial T/\partial P)_{\text{nonlinear}}$. However, in the present case of rhenium and its alloys, the shape is too ill-defined to make any such distinction. Fortunately, it is possible to make at least a rough qualitative comparison with the height and width of the curves calculated by Makarow and Bar'yakhtar.[4] These authors showed that

$$\Delta T/T_c \sim (k\Theta_D/E_F)^{1/2}, \tag{3}$$

and that the minimum half-width of $(\partial T_c/\partial E_F)_{\text{nonlinear}}$ as a function of energy, is $\sim k\Theta_D$ (see Fig. 10). In Table II, we compare the estimated values of these quantities with the observed values both for rhenium and thallium. The estimate of the half-width energy of the maximum in $(\partial T_c/\partial E_F)_{\text{nonlinear}}$ was obtained from the relationship

$$\Delta E \sim c\Delta z/2N_b(E), \tag{4}$$

where $N_b(E)$ is the band density of states and $c$ is the alloying addition of valence difference $\Delta z$ required to move $P_c$ by a half-width of the maximum in $(\partial T_c/\partial P)_{\text{nonlinear}}$. It can be seen that the contribution to $T_c$ is of the correct order of magnitude in both cases. Reasonable agreement is obtained for the estimate of the energy spread of $(\partial T_c/\partial E_F)_{\text{nonlinear}}$ from alloying and that obtained from $\Theta_D$ for Tl, but a serious discrepancy is found for Re.

TABLE II. A comparison of the calculated and observed parameters associated with a nonlinear contribution to $T_c$ for rhenium and thallium.

| | Half-width of $\left(\frac{\partial T_c}{\partial E_F}\right)_{\text{nonlinear}}$ meV | | $\frac{\Delta T_c}{T_c}$ | $\left(\frac{k\Theta_D}{E_F}\right)^{1/2}$ |
|---|---|---|---|---|
| | $k\Theta_D$ | Measured | | |
| Re | 44 | 2 | 0.03 | 0.06 |
| Tl | 8 | 5 | 0.06 | 0.03 |

Support for our model of a change in Fermi-surface connectivity is found in the band structure and Fermi-surface calculations for rhenium by Mattheiss.[19] The results of his calculation for the relativistic energy bands, including the effects of spin-orbit coupling are shown in Fig. 13. It can be seen that flat regions in the $E(\mathbf{k})$ curves occur close to the Fermi surface in the eigth zone along the direction AH and in the ninth zone along the directions $\Gamma K$ and $\Gamma M$. Mattheiss pointed out that the detailed nature of the Fermi surface in these regions is very sensitive to the value of $E_F$ and he illustrated the changes in topology which would occur if the Fermi energy were increased by $\sim$70 meV. Thus, he showed (Fig. 14) that necks appear in the electron sheets ($e_8$ and $e_9$) in the eighth and ninth zones.

Using the elastic-constant data of Shepard and Smith[20] for rhenium, we calculate that a hydrostatic pressure of 20 kbar does not change $c/a$ by more than 0.05% at 4.2°K. Thus, since the compression is isotropic to obtain the necessary changes in the relative energies of the flat regions of the $E(\mathbf{k})$ curves and the Fermi energy requires strong hybridization of the wave functions. It is therefore of considerable interest to

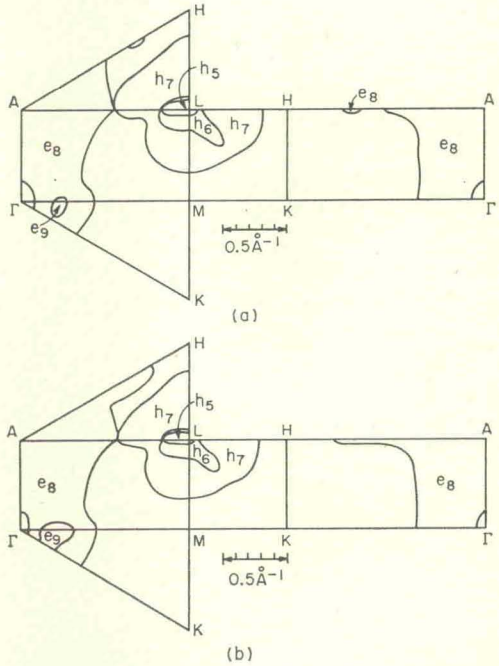


FIG. 14. Intersection of the rhenium Fermi surface with symmetry planes of the hexagonal Brillouin zone. The $e_8$ and $e_9$ represent electron sheets in the eighth and ninth zones. The results in (a) correspond to a Fermi energy of 11.22 eV. The corresponding results in (b) indicate the changes which occur when the Fermi energy is raised by 68 meV (from Ref. 19).

[19] L. F. Mattheiss, Phys. Rev. **151**, 450 (1966).
[20] M. L. Shepard and J. F. Smith, J. Appl. Phys. **36**, 1447 (1965).

examine the degree of admixture in the wave functions in the eighth zone along AH and in the ninth zone along $\Gamma K$ and to calculate the change in energy of these bands with change of volume. It is an interesting aside that these effects would not have occured in the absence of spin orbit coupling in rhenium.

*Note added in proof.* Since this paper was written, an article by Higgins and Kaehn has been published [Phys. Rev. **182**, 649 (1969)] in which the effect of impurity broadening on the singularities in the electron density of states and the superconducting transition temperature, associated with the passage of the Fermi energy through a critical point, was investigated. These authors report that the structure in $T_c$ as a function of Fermi energy is broadened by the order of $kT_c$ for pure metals ($\sim$4°K in the particular case of In which they consider), whereas for In with 2% Cd the impurity broadening is $\sim$50°K. However, since the effect of the electron-phonon interaction is to average the density of states over a region $\pm k\Theta_D$ about the Fermi energy, any structure in $T_c$ as a function of energy must be broadened over an energy of $2\Theta_D$, or $\sim$200°K in the case of In. This is clearly seen in Fig. 9.

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