superconductor exhibiting the isotope effect, failed to show any anomaly at the superconducting transition.[6] The result of that experiment was

$$|\Delta\psi(0)|^2/|\psi(0)|^2=(-0.9\pm1.0)\times10^{-4}.$$

However, the matrix elements that appear in isomer-shift calculations are diagonal, while the internal conversion process involves matrix elements between bound states and the continuum. The signs of the effect in Nb and Tc are different; this should not be too surprising, as the decay from Tc^{90m} is an $E3$ transition, while from Nb^{90m} it is probably $M2$, so different electronic matrix elements will be involved.

ACKNOWLEDGMENTS

We would like to thank Andy Koehler and Dick Wharton for their help with the cyclotron irradiations.

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[6] N. Snider, Harvard University thesis, 1968 (unpublished).

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Superconducting Isotope Effect in Molybdenum Boride and Tungsten Boride*

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The isotope effect on the superconducting transition temperature was measured for the compounds Mo_2B and W_2B. Both the heavy masses and the B mass were varied independently in each compound. The compounds have isomorphous crystal structures with nearly identical lattice parameters. The effect of changing the boron mass appeared to be small in both compounds. The Mo and W isotope effects were much larger, and indicated either a linear or an exponential relation between transition temperature and heavy-element mass. With the approximation that the Mo_2B lattice was made up of only the Mo mass, the Mo isotope effect was found to be roughly the same as that found in elemental Mo. By considering the W isotope effect in W_2B analogously, the elemental W isotope effect is predicted to be the same as that found in nontransition-element superconductors.

I. INTRODUCTION

THE unusual superconducting behavior of the transition elements around column VIB (Cr, Mo, W) in the Periodic Table has prompted a number of investigations of the isotope effect on those superconductors. Many of the elements in that region having stable isotopes have had their isotope effects measured with Ti, Hf, W, and Ir remaining to be done. Two different problems have discouraged measurements on these elements: sensitivity to impurities, especially oxides and nitrides, in Ti and Hf, and low transition temperatures with associated small isotope shifts in W and Ir. With the hope of avoiding these problems and yet gaining some information about the isotope effect in the transition elements, a search was made for superconducting compounds whose isotope effect could be measured. Two promising compounds were found in the borides Mo_2B ($T_c=5.86$°K) and W_2B ($T_c=3.18$°K). The transition temperatures are relatively high and isotopes are available for molybdenum, tungsten, and boron. Both compounds crystallize in the body centered tetragonal (bct) ($CuAl_2$ type) structure with almost equal lattice parameters, a and c, of 5.543 and 4.735 Å for Mo_2B and 5.564 and 4.740 Å for W_2B.[1] To the extent that the phase diagrams are known the homogeneity ranges are very narrow. The principal metallurgical difference between the two compounds is that W_2B melts congruently at 2800°C while Mo_2B decomposes peritectically at 2000°C.[2,3]

As with the borides, the crystal structures of elemental Mo and W are isomorphous, bcc, with nearly equal lattice parameters. The possibility thus arises that an analogy can be made between the transition elements and their borides. If this analogy is realistic, the relationship between the known Mo isotope effect and the Mo in Mo_2B effect could be carried over to elemental W and to W in W_2B. In this way the isotope effect in elemental tungsten could be estimated. The validity of this analogy would depend upon the role played by boron in the compounds. Evidence of this would be found in two ways: (a) by comparing the molybdenum isotope effects in the element and in the boride, and (b) by measuring the boron isotope effect in both compounds.

The large mass ratio between the constituents some-

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* Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Grant No. AF-AFOSR-631-67.

[1] R. Kiessling, Acta Chem. Scand. **1**, 893 (1947).

[2] P. Schwarzkopf and R. Kieffer, *Refractory Hard Metals* (The Macmillan Co., New York, 1953), p. 301.

[3] J. J. English, Defense Metals Information Center Report No. 183, 1963, Battelle Memorial Institute, Columbus, Ohio, p. (80)-63 (unpublished).

what simplifies interpretation of the results since it would allow, ideally, a distinct separation to be made between the optical and acoustical branches of the phonon spectrum. Thus, to the extent that this approximation is valid, the effect of the change in boron mass would involve the interaction between the conduction electrons and the optical phonons via an electric polarization. The heavy transition-element mass, on the other hand, would dominate the acoustical phonon frequencies and its isotope effect would reflect a situation similar to that in a pure transition-metal lattice.

The results of this experiment have been previously reported[4] in brief along with conclusions drawn from the estimated tungsten isotope effect.

II. SAMPLE PREPARATION

The starting materials used for the samples are listed in Table I. All of the enriched isotopes and the elements of natural isotopic abundance were received in elemental powdered form. The analyses of impurities listed in Table I were provided by the suppliers and no further chemical analyses were made during the course of this experiment.

The criteria for sample quality was that they be single phase as measured by x-ray diffraction and that they have narrow and reproducible transitions. The best samples were those made by vacuum sintering as used by Kiessling[1] in his investigation of transition metal borides. Arc melting was tried initially, producing W_2B samples with quite narrow superconducting transitions, but the Mo_2B transitions were extremely erratic and broad. Subsequent annealing below the peritectic temperature did not adequately sharpen them. For Mo_2B, sintering was the best method of raising the temperature of the sample high enough for the elements to completely react together while keeping in the single-phase region below the peritectic temperature.

TABLE I. Mass analyses and purity of the isotopes. Analyses provided by suppliers.[a] Impurities determined by spectrographic analyses are semiquantitative estimates. "(nat)" means naturally occuring isotopic abundance.

Isotope	Isotopic enrichment (at. %)	Average mass (amu)	Major impurities Element	%
B-10	96.5	10.04	Si	0.02
B-(nat)		10.81	(purity 99.9995%)	
B-11	98.0	10.98	Si	0.11
Mo-92	97.6	92.12	Fe, Na, V	0.02
Mo-94	93.97	94.12	Ni	0.1
			Ca, Mg, Na, V	0.02
			Sn	<0.1
Mo-(nat)		95.94	(purity 99.9+%)	
Mo-96	96.8	96.01	Na, Ca	0.03
			Ba, Si, V	0.02
			B	0.01
Mo-98	98.3	97.97	V	0.02
Mo-100	95.9	99.84	V	0.05
			Ca	0.01
W-182	94.4	182.19	Ca	<0.02
W-183	83.0	183.12	Si	0.05
			Ca	<0.02
			Na	<0.01
W-(nat)		183.85	(purity 99.9+%)	
W-184	95.1	184.0	Si	0.05
W-186	97.23	185.93	Zr, Ta	<0.1
			Si	<0.02

[a] Suppliers: Mo, W, and B isotopes—Isotope Development Center, Oak Ridge National Laboratory, Oak Ridge, Tenn.; Mo, W (nat)—General Electric Company, Cleveland, Ohio; B (nat)—Eagle-Pitcher Company, Cincinnati, Ohio.

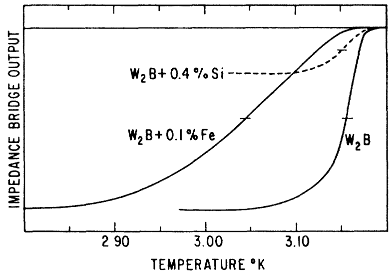

FIG. 1. Effect on the W_2B superconducting transition of the addition of Fe and Si. The percentage impurity is the amount added by weight before sintering.

Investigations were carried out to determine the effects on T_c of impurities, deviations from stoichiometry, sintering time and temperature, sample size, treatment of elemental powders, and other such considerations. Fortunately, because of the narrow homogeniety ranges, the transition temperatures were found to be independent of small deviations (few percent) from stoichiometry. Also sintering times and temperatures were found such that their influence on T_c were minimized.

Small amounts of various elements were added to Mo_2B and W_2B to see how they would effect T_c. Two extreme cases are shown in Fig. 1. Transition-element impurities tended to lower and broaden T_c. The greatest effect was found for magnetic elements such as iron, even though much of it was observed to boil off the sample during sintering. In contrast, as much as 0.4% Si in W_2B did not shift T_c appreciably, but reduced the amount of sample that became superconducting. This insensitivity of T_c to Si is fortunate because of the large (0.11%) silicon impurity in the B^{11} isotope. The impurity effects were found to be roughly twice as large in Mo_2B as in W_2B.

The following process was found to produce samples with the narrowest and most reproducible transition temperatures. The Mo (or W) and boron powders in the molecular weight ratio 2:1 were mixed and compressed in a hardened steel die into cylindrical samples of approximately 1.5 mm in diam by 4 mm in height. The samples weighed about 75 mg for the Mo_2B and 100 mg for the W_2B. The pressed powder was then sintered in a quartz tube with a vacuum of better than 5×10^{-6} mm Hg. While sintering, the sample was suspended away

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[4] J. J. Engelhardt, G. W. Webb, and B. T. Matthias, Science **155**, 191 (1967).

from the quartz tube by molybdenum wires for the Mo_2B and tungsten wires for the W_2B. The sample was heated inductively from a coil outside the quartz tube and the temperature determined with an optical pyrometer. Generally the W_2B samples shrank about 20% during sintering while the Mo_2B samples expanded slightly. In both cases, the sintered samples were quite porous with a density considerably below the x-ray density. A very large evolution of gas was observed during the initial heating of the pressed powder samples up to about 1700°C. Also, high vapor-pressure metallic impurities were observed to boil off and condense on the quartz tube.

For the Mo_2B samples, the best results were obtained for a sintering temperature sequence of 1 h at about 1850°C followed by 3 h at 1550°C. The transition temperature of these samples was found, by magnetic measurements, to be 5.8°K, with a transition width of 30 mdeg. This result disagrees with that of previous investigators. Matthias and Hulm[5] had found a broad transition at 4.74°K for arc melted Mo_2B samples. This low T_c was probably due to the arc melting, as we found, along with starting materials that were less pure than those available today. Gaulé *et al.*[6] concluded that Mo_2B was not superconducting above 1.5°K, but this may be due to their not annealing below the peritectic. We found very little correlation between the transition temperature and the amount of the correct crystal structure phase present, as determined by x-ray diffraction. Presumably, because of the very low x-ray scattering of boron, an inhomogeneous distribution of boron would not be seen, yet would have a strong effect on T_c.

Because of the conflicting results the possibility arises that the 5.8°K transition might be associated with only a small part of the sample in some unknown phase. Since magnetic measurements of T_c are ambiguous, a specific-heat measurement was performed by Maita[7] at Bell Telephone Laboratories, on a 5-g Mo_2B amples. The result of this measurement, revealed a sharp transition at 5.74°K, in agreement with the magnetic measurements on the same sample. The size of the specific-heat anomaly at 5.74°K indicates that a large fraction of the sample becomes superconducting there. The BCS theory predicts that the ratio of the superconducting to normal electronic specific heats at T_c, $(C_{es}/\gamma T)_{T_c}$, to be 2.43 and many elements have ratios near this value or larger.[8] For Mo_2B this ratio was 2.3. This is large enough to indicate that the 5.8°K transition is characteristic of bulk Mo_2B. Also, from the specific-heat measurement the Debye temperature was found to be 413°K and the electron specific-heat coefficient 18.4×10^{-4} cal deg^{-2} mole^{-1}. The specific heat of a W_2B sample was also measured by Maita. The superconducting transition occured at 3.06°K and $(C_{es}/\gamma T_c)_{T_c}$ was 2.2,[7] indicating bulk superconductivity. This transition was broader and lower than that for the W_2B isotope samples because the sample was so large (5 g) that it was difficult to remove all absorbed gases during sintering. The Debye temperature was 365°K and the electron specific-heat coefficient was 11.8×10^{-4} cal deg^{-2} mole^{-1}.

The T_c of elemental molybdenum[9] at 0.92°K was used to check the purity of the natural Mo, and some of the Mo isotopes, before being made into the borides. The natural GE Mo powder was measured and yielded a T_c of 0.79°K, which indicated reasonable purity for a fine powder. Also, the Mo_2B made from natural Mo had a sharp transition at 5.8°K. However, the isotope Mo^{98} was measured and found not superconducting down to 0.35°K, and $Mo^{98}{}_2B$, made from this, had two broad transitions at 5.6°K and 7.3°K. Geballe *et al.*[9] found that arc melting for long periods purified Mo sufficiently to yield samples with a sharp transition at 0.92°K. Following this procedure, the Mo^{98} was melted in the arc furnace in high-purity argon for 6 min, producing a shiny, ductile button. It was then necessary to reduce this button to a fine powder in order to make the boride. Crushing or filing caused excessive contamination, so another means had to be found that was not only clean, but practical for very small samples. This was accomplished by dissolving the Mo^{98} button in dilute electronic grade nitric acid, which was then slowly boiled away leaving a high-purity, finely powdered MoO_3 precipitate. The oxide was then reduced in ultra pure hydrogen at 1050°C for more than 3 h. The resulting finely divided Mo powder was found to have a $T_c=0.83$°K, indicating an appreciable purification. A $Mo^{98}{}_2B$ sample, made from Mo^{98} treated in this way, was found to have a sharp transition at $\sim$5.8° similar to the boride of Mo^{nat}. On a number of borides made with treated and untreated natural Mo, the treated samples consistently had a slightly lower T_c. However, the difference was quite small (about 20 mdeg) and reproducible.

For the set of Mo_2B samples with Mo isotopes, the arc melt-oxidation-reduction procedure was carried out on all the Mo isotopes and the natural Mo before making the borides. Since the natural Mo was sufficiently pure, this process was not used on the Mo^{nat} in the B isotope set of Mo_2B samples.

The production of W_2B was considerably less complicated. Stoichiometric proportions of W and B were mixed together, compacted into cylindrical pellets, and sintered in a vacuum at about 2150°C for 2 h. The

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[5] B. T. Matthias and J. K. Hulm, Phys. Rev. **87**, 799 (1952).

[6] G. K. Gaulé, O. Adlhart, and R. L. Ross, in *Proceedings of the Eighth International Conference on Low-Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 162.

[7] J. P. Maita (private communication).

[8] J. Bardeen and J. R. Schrieffer, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1961), Vol. 3, p. 170.

[9] T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. Letters **8**, 313 (1962).

vacuum-sintering apparatus was the same for Mo_2B. These samples were found to have superconducting transitions at 3.18°K with a width of 15 mdeg, in reasonable agreement with results found previously by Hardy and Hulm.[10]

The crystal-structure parameters determined by x-ray diffraction for Mo_2B and W_2B samples fabricated in the manner described above were found to be in agreement with previous measurements. Most of the lines associated with the bct structure were very prominant with little Mo or W in evidence.

III. MEASUREMENT

For the measurement of the superconducting transitions, an apparatus was constructed similar to that used by Hake *et al.*[11] for their isotope-effect measurements in Pb. There are six pickup coils for measuring the permeability of the samples mounted in a massive copper block which is, in turn, suspended inside a vacuum can. The temperature of the assembly was sensed by a 0.1-W 100-Ω Allen-Bradley carbon resistor cemented in the center of the block.

Superconductivity was detected by means of a standard ac-impedance-bridge technique with an ac magnetic field on the samples below 0.02 G and a bridge frequency of 1000 cps. There was no change in T_c or the size of the transition for finely powdered samples or lower bridge frequencies. The superconducting transitions were plotted during both cooling and heating of the samples with a temperature difference between these transitions of less than 1 mdeg.

For the W_2B transitions at 3.18°K, the carbon resistance thermometer was calibrated directly against the vapor pressure of the helium bath. Since the isotope shifts in T_c were found by a simultaneous measurement of a number of samples, the error in these shifts is dependent on the inaccuracy of $\Delta T/\Delta P$ of the He bath which is a weak function of T. Therefore, an estimated measurement error in T_c of 10 mdeg would result in an error in the isotope effect of about 1%.

For the transition-temperature measurements of the Mo_2B samples at 5.8°K, the carbon thermometer resistance was interpolated by means of the three-parameter equation of Clement and Quinnell.[12] Calibration of the thermometer was carried out during each run with two points taken in the liquid-He range and one at the transition of a Pb sample at 7.193°K.[13] In addition, a check on this calibration was made with points in the liquid-H_2 range. An estimate of error in T_c of the Mo_2B samples of about 30 mdeg leads to an error in the isotope effect of about 2%.

These measurement errors were found to be much smaller than the scatter in T_c due to nonuniformity in the sample making process.

During the transition-temperature measurements, the earth's magnetic field at the samples was nulled to 0.02 G by two pairs of Helmholtz coils outside of the Dewar. A rough measurement was made of the effect on T_c of a small dc magnetic field parallel to the axis of the pickup coils. For fields of 0.02–10 G the results were as follows: for Mo_2B, $dT_c/dH = -0.0022$°K/G, and for W_2B, $dT_c/dH = -0.0018$°K/G. The dependence of transition width on magnetic field found by Fassnacht and Dillinger[14] in their investigation of the isotope effect in zinc was not observed for magnetic fields in the range 0.02–10 G.

IV. RESULTS

The superconducting transitions of four sets of samples are shown in Figs. 2–5 corresponding to variations of the four masses; Mo and B in Mo_2B, and W and B in W_2B. In each set, the samples consist of the different enriched isotopes of one of the constituent masses with the naturally occurring mass for the other. The abscissa is the temperature and the ordinate is the impedance-bridge unbalance, which is a measure of the effective permeability of the samples. The same samples are listed in Table II, along with the average mass of the particular element varied, and transition temperatures. Within each isotope set the sample preparation

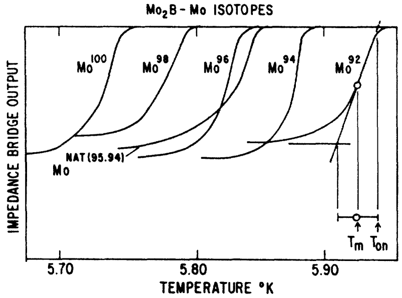

FIG. 2. Superconducting transitions of Mo_2B made with different molybdenum isotopes and with boron of natural isotopic abundance.

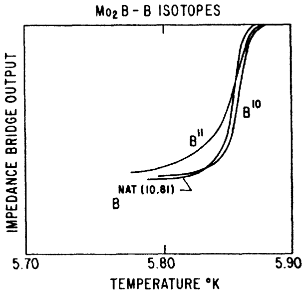

FIG. 3. Superconducting transitions of Mo_2B made with different boron isotopes and with molybdenum of natural isotopic abundance.

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[10] G. F. Hardy and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).

[11] R. R. Hake, D. E. Mapother, and D. L. Decker, Phys. Rev. **112**, 1522 (1958).

[12] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[13] B. W. Roberts, in *Progress in Cryogenics*, edited by K. Mendelsohn (Academic Press Inc., New York, 1964), Vol. 4, p. 159.

[14] R. E. Fassnacht and J. R. Dillinger, Phys. Rev. **164**, 565 (1967).

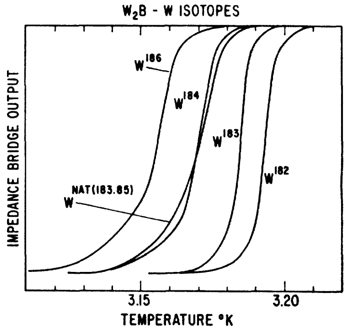

FIG. 4. Superconducting transitions of W_2B made with different tungsten isotopes and with boron of natural isotopic abundance.

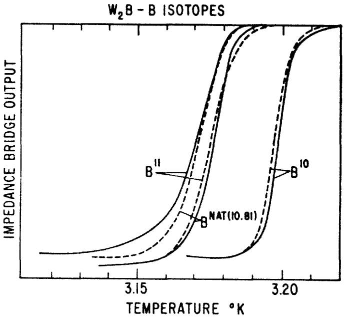

FIG. 5. Superconducting transitions of W_2B made with different boron isotopes and with tungsten of natural isotopic abundance. Two sets of samples are shown.

and measuring conditions were kept as uniform as possible to minimize systematic errors. The samples were made and measured in a random sequence, with regard to the isotopic mass, for the same reason.

In both the Mo_2B (B isotope) and W_2B (B isotope) sets, two independent sets of samples were made. These indicate the transition-temperature reproducibility. Samples 188, 203, and 218 in Table II should all have the same transition temperatures within the reproducibility limits, since they all have the same constituent masses, Mo^{nat} and B^{nat}. The slightly lower T_c of 218 is due to the arc melt-oxidation-reduction process having been performed on the Mo, for that sample.

In Table II two temperatures, T_m and T_{on}, are given for the transitions. T_m is the usual midpoint temperature. T_{on} is the temperature of the onset of bulk superconductivity, and will be considered to be the critical transition temperature T_c. The reason for choosing this part of the transition to define T_c is because it was found in preliminary experiments that the addition of impurities, or inhomogeneity of the structure, invariably reduced the temperature of the transition and broadened it. The midpoint of the transition was usually changed drastically compared with the onset. This can be seen in Fig. 1 for two W_2B samples that are identical except that one has been doped with 0.1% of iron. Similar behavior was observed for the addition of other elements as small impurities. It was also noted that in most transitions the first (high-temperature) half often was sharp, while the lower-temperature half was broader and generally varied from sample to sample. The onset temperature, then, appears to best represent the T_c of the ideal, pure compound. The onset temperature T_{on} was determined as follows: A line was drawn through the midpoint of the transition, tangent to the adjoining high-temperature half, as shown for $Mo^{92}{}_2B$ in Fig. 2. The intersection of this line with the horizontal normal-state line is designated as T_{on}. The other intersection of this line with the horizontal superconducting-state line then gives a measure of the width of the transition. These points are designated by the ends of the error bars in Figs. 6 and 7, where the transitions in Figs. 2–5 are plotted versus the average isotopic mass in atomic mass units of the element varied.

The dependence of T_c on mass appears to be linear, at least for the Mo and W isotopes. Straight lines fitted to the four isotope effects in Figs. 6 and 7 yield the slopes $\Delta T_c/\Delta M$, which are compiled in Table III. Included also in Table III for comparison are the isotope effects that have been previously measured in Nb_3Sn,[15] Mo_3Ir,[16] and $Be_{22}Mo$.[17] In each case M is the mass varied only

TABLE II. Molybdenum boride and tungsten boride superconducting transition temperatures. T_{on} and T_m are onset and midpoint of transition, respectively.

Sample no.	Isotope	Mo or W mass	B mass	T_{on} °K	T_m °K
		Mo_2B—molybdenum isotopes			
207	Mo-92	92.12	10.81 (nat)	5.945	5.927
221	Mo-94	94.12	10.81 (nat)	5.885	5.876
218	Mo-nat	95.94	10.81 (nat)	5.847	5.829
220	Mo-96	96.01	10.81 (nat)	5.834	5.822
228	Mo-98	97.97	10.81 (nat)	5.794	5.778
219	Mo-100	99.84	10.81 (nat)	5.747	5.733
		Mo_2B—Boron isotopes			
189	B-10	95.94 (nat)	10.04	5.870	5.859
204	B-10	95.94 (nat)	10.04	5.868	5.859
188	B-nat	95.94 (nat)	10.81	5.871	5.862
203	B-nat	95.94 (nat)	10.81	5.862	5.854
190	B-11	95.94 (nat)	10.98	5.869	5.860
205	B-11	95.94 (nat)	10.98	5.867	5.851
		W_2B—Tungsten isotopes			
213	W-182	182.19	10.81 (nat)	3.197	3.192
215	W-183	183.12	10.81 (nat)	3.188	3.183
217	W-nat	183.85	10.81 (nat)	3.180	3.170
216	W-184	184.0	10.81 (nat)	3.176	3.169
214	W-186	185.93	10.81 (nat)	3.163	3.153
		W_2B—Boron isotopes			
191	B-10	183.85 (nat)	10.04	3.205	3.199
225	B-10	183.85 (nat)	10.04	3.204	3.196
192	B-nat	183.85 (nat)	10.81	3.182	3.175
223	B-nat	183.85 (nat)	10.81	3.180	3.172
193	B-11	183.85 (nat)	10.98	3.179	3.169
224	B-11	183.85 (nat)	10.98	3.182	3.175

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[15] G. E. Devlin and E. Corenzwit, Phys. Rev. **120**, 1964 (1960).

[16] B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. **129**, 1025 (1963).

[17] E. Bucher and C. Palmy, Phys. Letters **24A**, 340 (1967).

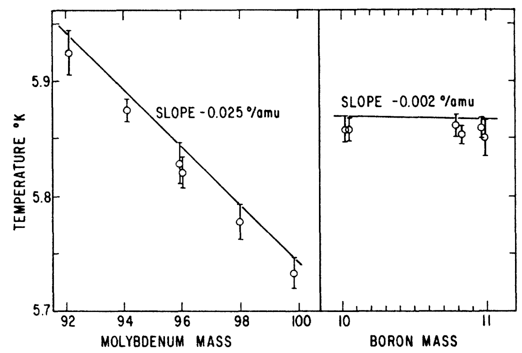

FIG. 6. Isotope effects on the superconducting transition of Mo_2B. The error bars indicate the widths of the transitions in Figs. 2 and 3 and the circles are the midpoints.

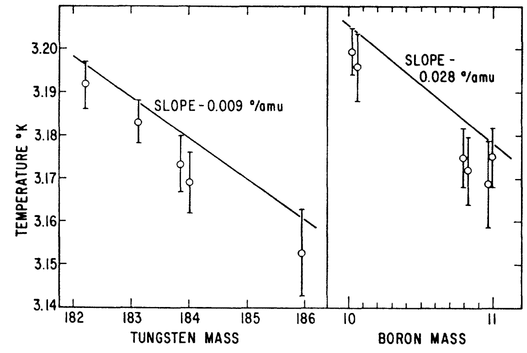

FIG. 7. Isotope effects on the superconducting transition of W_2B. The error bars indicate the widths of the transitions in Figs. 4 and 5 and the circles are the midpoints.

and not the molecular or the average mass. The isotope effect α in the last column of Table III is the fractional change in T_c divided by the fractional change in mass. This α is the same quantity defined in the usual relationship between T_c and mass, $T_c \sim M^{\alpha}$. Because of the limited range in mass covered and the scatter in T_c, the results of Figs. 6 and 7 would also appear linear in a $\ln T_c$-versus-$\ln M$ plot. These measurements then are not sufficiently accurate to reveal the functional relationship between T_c and M but only the slope $\Delta T_c/\Delta M$.

TABLE III. Superconducting isotope effect in Mo_2B and W_2B. Included are previously measured isotope effects in Nb_3Sn (Ref. 15), Mo_3Ir (Ref. 16), and $Be_{22}Mo$ (Ref. 17).

Compound	T_c (°K)	Mass varied (M)	$\Delta T_c/\Delta M$ (°K/amu)	Isotope effect $\alpha=(\Delta T_c/T_c)/(\Delta M/M)$
Mo_2B	5.86	Mo	−0.025 ±0.0014	−0.42 ±0.02
Mo_2B	5.86	B	−0.002 ±0.008	−0.004±0.016
W_2B	3.18	W	−0.009 ±0.001	−0.52 ±0.05
W_2B	3.18	B	−0.028 ±0.005	−0.09 ±0.016
Nb_3Sn	17.9	Sn	−0.0038±0.0009	−0.025±0.006[a]
Mo_3Ir	8.35	Mo	−0.019	−0.22[a]
$Be_{22}Mo$	2.51	Mo	−0.006 ±0.0026	−0.23 ±0.10

[a] Different mass used here to calculate α than in original reports.

The errors assigned in Table III were determined by the scatter of the data as estimated from the reproducibility in the transition temperatures. No account could be taken of the effect of impurities in the isotopes which might cause systematic shifts in T_c. However, such an error would probably be small since the spectrographic analysis of the isotopes (Table I) indicate a random distribution of impurities with respect to isotopic mass.

V. DISCUSSION

Unfortunately, it is difficult to make a comparison between the results of the present experiment and theoretical calculations. The theory of Morel and Anderson[18] accounts very well for the isotope effects in the nontransition elements, especially in light of the recent measurements of Fassnacht and Dillinger[14] on zinc. However, this theory does not consider the additional complexities inherent in transition elements and compounds. While the theory of Garland[19] does include parameters to describe a more complex electronic structure, it is difficult in this case to choose these parameters such that a meaningful comparison can be made.

In Table III the mass M used to calculate the isotope effect α was the atomic mass of the enriched element only. The total molecular, or, equivalently, the average mass, could also have been used. This arbitrariness is reflected in the interpretation of previous isotope-effect measurements in compounds. For the Mo isotope effect in Mo_3Ir,[16] the molecular mass was chosen to make the result agree with the isotope effect in elemental Mo. On the other hand, for the Mo effect in $Be_{22}Mo$,[17] it was necessary to use the Mo mass in order to get a realistic ($|\alpha|<0.5$) result. The Sn isotope effect in Nb_3Sn [15] was very small either way. For the present experiment, without consideration in detail of the interactions causing superconductivity, the most natural quantity to relate to the fractional change in T_c would be the fractional change in the isotope element mass as in Table III.

Regarding the isotope effect α defined this way, the boron isotope effects in both Mo_2B and W_2B are quite small. The relative insensitivity of T_c to the boron mass might be accounted for by a very small interaction between the conduction electrons and the boron ions. This could come about because of (a) the high energy required to excite a vibration (optical phonon) of the boron ions due to their small mass, (b) a small electron-optical phonon coupling due to a very small charge transfer between the boron and transition metal ions.

Both the Mo in Mo_2B and W in W_2B isotope effects are large and in the range of values of nontransition-metal effects. The use of the Mo and W masses only in calculating these α's are equivalent to neglecting the boron mass entirely and considering the lattice to be

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made up of the transition element only. In this approximation a comparison can be made between the Mo effect in Mo_2B and that of elemental Mo.

The isotope effect in Mo has been measured by Matthias *et al.*[16] and by Bucher and Palmy.[17] Both measurements agree with each other for $\alpha=-0.37\pm0.04$ except for a constant temperature difference which may be due to thermometry. The error quoted is from the latter measurement. This figure is, within error limits, comparable to the Mo in Mo_2B effect found in the present experiment of $\alpha=-0.42\pm0.02$. If we consider then that both Mo in Mo_2B and elemental Mo have isotope effects of about $\alpha=-0.4$, the analogous situation for W_2B and W would be an $\alpha=-0.5$. This predicted isotope effect in tungsten would then be the same as in the nontransition elements.

A large isotope effect in tungsten is consistant with what appears to be a systematic variation of α across the transition elements symmetrical around column VI. Thus α is small for Zr ($\alpha=0$),[20] Ru ($\alpha=0$),[21] and Os ($\alpha=0.21$)[22]; then rising at Re ($\alpha=-0.36$)[23] to a large value at Mo and W. This behavior is in line with other physical quantities such as T_c, cohesive energy and melting points that are roughly symmetrical around column VI.[4,24]

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Pressure Dependence of the Superconducting Transition Temperature

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A theory of the superconducting transition temperature using a simple model for the electron-phonon interaction has been used to calculate the pressure dependence of the transition temperature for nontransition metals. The pressure dependence of the Debye temperature and phonon frequencies is included by using a Grüneisen model. The theory is compared to experiment for aluminum, lead, zinc, cadmium, indium, and tin, and the agreement is generally quite good. The results have been used to predict the critical pressures at which $T_c=0$; and for the cases of zinc, cadmium, and possibly aluminum, it should be possible to carry out experiments where T_c is pushed below presently measurable temperatures. The empirical $T_c=f(P)$ relations published in the literature are discussed and compared with the present results.

In roughly the last ten years, there has been a great deal of work on the effect of pressure on superconductors. There have been various experimental investigations[1–17] of the behavior of the superconducting transition temperature (T_c) as well as a number of phenomenological analyses[4,5,12,13,16,18] which have tried to describe the systematics of the behavior of T_c with pressure. There has, however, been no serious attempt to try to understand the pressure dependence from a detailed consideration of the interactions involved. In this paper the pressure dependence of T_c for nontransi-

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