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Superconductivity at 9 K in Mo$_5$PB$_2$ with evidence for multiple gaps

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Superconductivity is observed with critical temperatures near 9 K in the tetragonal compound Mo$_5$PB$_2$. This material adopts the Cr$_5$B$_3$ structure type common to superconducting Nb$_5$Si$_3$-type, Mo$_5$SiB$_2$, and W$_5$SiB$_2$, which have critical temperatures ranging from 5.8−7.8 K. We have synthesized polycrystalline samples of the compound, made measurements of electrical resistivity, magnetic susceptibility, and heat capacity, and performed first principles electronic structure calculations. The highest $T_c$ value (9.2 K) occurs in slightly phosphorus rich samples, with composition near Mo$_5$P$_{1.1}$B$_{1.9}$, and the upper critical field $H_{c2}$ at $T=0$ is estimated to be $\approx 17$ kOe. Together, the measurements and band structure calculations indicate intermediate coupling ($\lambda=1.0$), phonon mediated superconductivity. The temperature dependence of the heat capacity and upper critical field $H_{c2}$ below $T_c$ suggest multiple superconducting gaps may be present.

I. INTRODUCTION

The tetragonal Cr$_5$B$_3$ structure type is adopted by a wide variety of binary and ternary compounds with examples incorporating at least 47 different elements spanning the main group, transitions metals, and rare-earth metals [1]. One of the more interesting subsets of these compounds is the ternary borides with stoichiometries $MF_XB_2$, with $X=\text{P},\text{Si}$. These are reported to form with many transition metals ($M$) including the 3$d$ transition metals from V to Co, the 4$d$ transition metals Nb and Mo, and the 5$d$ transition metal W. Mn$_5$SiB$_2$ and Mn$_5$PB$_2$ are ferromagnets with Curie temperatures near room temperature and are of interest for magnetocaloric applications [2, 3]. Fe$_2$SiB$_2$ and Fe$_2$PB$_2$ are uniaxial ferromagnets with high Curie temperatures, and a low temperature spin-reorientation in the case of the silicide, and have been studied as potential permanent magnet materials [4–7]. In striking contrast to these high temperature ferromagnets, the 4$d$ and 5$d$ compounds Nb$_5$SiB$_2$, Mo$_5$SiB$_2$, and W$_5$SiB$_2$ are superconductors with transition temperatures of 7.2, 5.8, and 5.8 K, respectively [8–10]. The occurrence of superconductivity in these borosilicide compounds brings to mind other well known boron-containing, phonon-mediated superconductors, including the borocarbides $RT_2B_2C$ ($R=\text{rare-earth element}$, $T=\text{Ni, Pd, Pt}$) [11] and magnesium diboride MgB$_2$ [12].

The observation of superconductivity in several examples of Cr$_5$B$_3$-type compounds with the 512 stoichiometry suggests that further examination may produce more examples in this relatively new group of superconductors [9]. In the present work, we have studied the analogous Mo$_5$PB$_2$, and find that it too is a superconductor. The superconducting critical temperature ($T_c$) is determined to be as high as 9.2 K. This is the highest $T_c$ yet reported for superconductors in this structure type. In addition to measurements of resistivity, magnetic susceptibility, and heat capacity, we report results of first principles calculations that reveal the presence of multiple bands crossing the Fermi level in this borophosphide and the related borosilicides, as seen in, for example, the iron-based superconductors including the phosphide LaFePO [13], as well as MgB$_2$ [14]. Calculations indicate the coupling in Mo$_5$PB$_2$ is in the intermediate limit (i.e. the electron-phonon coupling $\lambda \approx 1$). Analysis of the heat capacity and upper critical field data suggests the presence of two distinct energy gaps. Together the experimental and theoretical results indicate that Mo$_5$PB$_2$ may be a multiband superconductor.

II. PROCEDURES

Polycrystalline samples with nominal compositions Mo$_5$P$_{0.9}$B$_{2.1}$, Mo$_5$PB$_2$, and Mo$_5$P$_{1.1}$B$_{1.9}$ were prepared from hydrogen-reduced molybdenum powder (99.999%), phosphorus pieces (99.999%), and boron powder (99.5%). The elements were reacted together at 1050°C for 16–24 hours, and the resulting powders were pressed into cylindrical pellets and heated at 1100−1150°C for a total duration of up to eight days, with intermediate grinding and re-pelletizing. Crystals of the isostructural Fe$_5$PB$_2$ have been grown from an Fe-P melt [7]; however, there is no liquid region on the Mo-rich side of the Mo-P phase diagram below about 1700°C. The optical floating zone method has been used to grow crystals of Mo$_5$SiB$_2$ [15]; however, arc-melting experiments in our lab indicate that Mo$_5$PB$_2$ does not melt congruently, and the volatility of phosphorus may preclude this type of crystal growth. The most likely route to single crystal Mo$_5$PB$_2$ may be the molten metal flux technique [16, 17], if a suitable flux can be identified.

Powder X-ray diffraction was performed using monochromatic Cu K$_{\alpha1}$ radiation with a PANalytical X’Pert Pro diffractometer and analyzed using the Rietveld technique with the Fullprof software package [18]. Magnetization measurements were performed with a Quantum Design Magnetic Property Measurement System (MPMS) and Physical Property Mea-

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measurements of electrical resistivity and heat capacity. The heat capacity data were analyzed using both the conventional relaxation method employing small heat pulses (temperature rise of 2% of the sample temperature) and slope-analysis [19] of large heat pulse data (temperature rise of 30% of the sample temperature).

First principles density functional theory calculations of the electronic structure of Mo$_5$PB$_2$ were performed using the linearized augmented plane-wave (LAPW) code WIEN2K [20], employing the generalized gradient approximation of Perdew, Burke and Ernzerhof [21]. LAPW sphere radii of 2.41, 2.08 and 1.7 Bohr, respectively for Mo, P, and B were chosen with an RK$_{max}$ of 7.0, where RK$_{max}$ is the product of the smallest sphere radius and the largest plane-wave expansion vector. Internal coordinates were relaxed until forces on the ions were less than 2 mRyd/Bohr.

III. RESULTS AND DISCUSSION

Rietveld analysis showed the resulting purity of the samples to be 92, 89, and 92% by weight for samples with nominal compositions Mo$_5$P$_0.9$B$_{2.1}$, Mo$_5$PB$_2$, and Mo$_5$P$_1.1$B$_{1.9}$, respectively. Mo$_5$P and MoB were observed as impurity phases in all samples. Refinement results are shown for Mo$_5$P$_1.1$B$_{1.9}$ in Figure 1a, where the crystal structure is shown in the inset. Table I contains the refined crystallographic properties of the Mo$_5$PB$_2$ phase in each sample. Allowing mixed occupation of P and B on their respective sites suggested some P may reside on the B site, but did not indicate any mixing of B onto the P site. The compositions determined from the refined occupancies are listed in the Table. Adding excess P (relative to Mo$_5$PB$_2$) appears to significantly increase the P content of the main phase, as indicated by both the refined composition as well as the increase in the unit cell volume. Addition of excess B had no detectable effect on the atomic site occupancies (relative to Mo$_5$PB$_2$) and produced only a small decrease in the unit cell volume. These observations indicate that there is some phase width in Mo$_5$PB$_2$ with respect to the P and B ratio, a common feature in this structure-type [7, 8, 22–24], and that in this case excess P is favorable.

Figure 1b and 1c show the ac magnetic susceptibility and resistivity measured below 10 K. All of the samples are superconducting. Values of $T_c$ are determined by the onset of diamagnetism (Fig. 1b) and the temperature at which the resistivity reaches zero (Fig. 1c). These are listed for each sample in Table I. Similar values of $T_c$ = 8.7–8.9 K are seen in the Mo$_5$P$_0.9$B$_{2.1}$ and Mo$_5$PB$_2$ samples, which have similar stoichiometries as discussed above. A higher value of $T_c$ = 9.2 K is seen in Mo$_5$P$_1.1$B$_{1.9}$. This demonstrates the sensitivity of the superconductivity to the chemical composition of the Mo$_5$PB$_2$ phase. Further experimental analysis presented here will focus primarily on the Mo$_5$P$_1.1$B$_{1.9}$ sample. The $T_c$ values seen in these materials are the highest yet reported in this class of ternary superconductors, which include Mo$_5$SiB$_2$ ($T_c$ = 5.8 K)[9], Nb$_5$SiB$_2$ ($T_c$ = 7.2 K)[9], W$_5$SiB$_2$ ($T_c$ = 5.8 K)[10], W$_7$Sn$_{1-x}$Si$_2$B$_2$ ($T_c$ = 6.5 K)[25], and the closely related Nb$_5$Si$_2.4$B$_{0.6}$ ($T_c$ = 7.8 K)[22].

Figure 2 shows the results of magnetization measurements on Mo$_5$P$_1.1$B$_{1.9}$. The dc measurements were conducted in 10 Oe field, and the ac magnetization measurements were conducted in a dc field of 10 Oe using a frequency of 1 kHz and an ac excitation field of 5 Oe. The superconducting transition is marked by the onset of diamagnetism in the dc susceptibility ($\chi_{dc}$) and the real part of the ac susceptibility ($\chi'$), while the imaginary part ($\chi''$) peaks just below $T_c$. The large diamagnetic signal in both field-cooled (fc) and zero field cooled (zfc) measurements demonstrates the bulk nature of the superconductivity. Complete magnetic flux exclusion corresponds to a volume susceptibility of $-1/4\pi$ in the units used here. This corresponds to a mass susceptibility of 0.0089 cm$^3$/g using the single crystal density of 8.97 g/cm$^3$ determined from the structure refinements presented above. Thus, the shielding
TABLE I. Results of room temperature x-ray diffraction analysis [space group $I4/mcm$, Mo1 at (0,0,0), Mo2 at $(x_{Mo2}, x_{Mo2} + \frac{1}{2}, z_{Mo2})$, P at (0,0,1), B at $(x_B, x_B - \frac{1}{2}, 0)$] and measured superconducting transition temperatures.

| Nominal comp. | Mo$_5$P$_2$A$_{2.1}$ | Mo$_5$P$_2$B$_{2.1}$ | Mo$_5$P$_2$B$_{2.1}$ | Mo$_5$P$_2$B$_{2.1}$ |
|---------------|----------------------|----------------------|----------------------|----------------------|
| Reﬁned comp. | $a$ ($\AA$)          | $c$ ($\AA$)          | $V$ ($\AA^3$)        | $\chi'$ ($cm^3/g$) |
|               | 5.9726(1)            | 11.074(3)            | 395.04(2)            | 0.000                |
|               | 5.9730(7)            | 11.076(1)            | 395.142(7)           | 0.000                |
|               | 5.9763(6)            | 11.0813(2)           | 395.784(8)           | 0.000                |
|               | $x_{Mo2}$            | 0.1663(3)            | 0.1659(3)            | 0.000                |
|               | 0.1409(2)            | 0.1410(2)            | 0.1409(2)            | 0.000                |
|               | $T_{c,0}$ (K)        | 8.7(1)               | 8.8(2)               | 9.2(1)               |
|               | $T_{c,sat}$ (K)      | 8.9(1)               | 8.7(2)               | 9.2(1)               |

FIG. 2. Results from (a) dc and (b) ac magnetization measurements on Mo$_5$P$_{1.1}$B$_{1.9}$. The dc data show both zero-field-cooled (zfc) and field-cooled (fc) results. The ac data were collected in zfc mode and both the real ($\chi'$) and imaginary ($\chi''$) parts of the ac susceptibility are shown. The superconducting transition temperature $T_c$ determined by the onset of diamagnetism is indicated by the dashed line.

Fraction indicated by the data in Figure 2a exceeds unity by almost a factor of two. This may be attributed to geometrical and demagnetization effects in these samples, which were loosely compacted powders in irregular shapes. A shielding volume fraction of 120% was observed (with no demagnetization correction) for a denser sample that was cold pressed at high pressure between tungsten carbide anvils.

Resistivity data for polycrystalline Mo$_5$P$_{1.1}$B$_{1.9}$ are shown in Figure 3. The residual resistivity ratio is $\rho_{20K}/\rho_{300K} = 11$, relatively high considering the polycrystalline nature of the sample. The resistivity varies like $T^{2.4}$ above $T_c$ up to about 60 K. Above about 100 K, $\rho(T)$ displays a negative curvature rather than the linear behavior expected for most metals. The normal state temperature dependence is similar to that reported for Mo$_5$SiB$_2$ [9] and W$_5$SiB$_2$ [10], and the negative curvature at higher temperatures has been observed as a common feature in a variety of chemically related compounds, based on Mo$_5$X$_3$ (X=Si, B, C) [26]. This behavior is also seen in the A15-type superconductors, where Fisk and Webb concluded that resistivity saturation results from the approach to the Mott-Ioffe-Regel limit [27]. This occurs when the electron mean free path reaches a minimum value defined by the lattice constant [28, 29]. Gurvitch [30] cast the resulting relationship between the saturation resistivity $\rho_{sat}$ in $\mu\Omega$cm, the carrier concentration $n$ in cm$^{-3}$, and lattice parameter $a$ in Å (assuming cubic symmetry) into the following useful form: $\rho_{sat} = 1.29 \times 10^{18}/(n^{7/3}a)\mu\Omega$cm. Hall effect measurements on Mo$_5$P$_{1.1}$B$_{1.9}$ give a Hall coefficient of $R_H \approx -3.1 \times 10^{-4}$ cm/V. From this, in a simple one band model, a carrier concentration of $2 \times 10^{22}$ electrons per cm$^3$ is inferred. Using this value of $n$ and the average lattice constant of $(2a + c)/3 = 7.7\AA$ gives $\rho_{sat} = 230 \mu\Omega$cm. The resistivity data in Figure 3 exceed this value by about 60% at room temperature, which may be attributed to the polycrystalline nature of the sample with resistive grain boundaries. However, this estimated $\rho_{sat}$ does compare well with data reported for several isostructural $M_5SiB_2$ compounds that have been measured up to 1000 K [26].

Resistivity data collected in applied magnetic fields are shown in the upper inset of Figure 3. In zero field the resistive transition is very sharp, with a width of $\Delta T < 0.1$ K. The transition broadens as magnetic field is applied, with the width increasing to 0.7 K at 12.5 kOe. This is typical behavior of a type II superconductor. From the resistivity data, the field dependence of $T_c$ is obtained, where $T_c$ is defined as the temperature at which $\rho \rightarrow 0$. The results are shown in the lower inset of Fig. 3, which also include results from the same analysis applied to the sample of nominal composition Mo$_5$PB$_2$. From this data, an upper critical field $H_{c2}(0)$ of $\approx 17$ kOe can be estimated. This is significantly larger than in the closely related superconductors Mo$_5$SiB$_2$ and W$_5$SiB$_2$, for which val-
FIG. 3. Resistivity of Mo$_2$P$_{1.1}$B$_{1.9}$ in zero applied magnetic field is shown in the main panel. The upper inset shows the effect of magnetic field on $T_c$, which is plotted in the lower inset. The lower inset also includes data from the Mo$_2$PB$_2$ sample for comparison.

ues of 6 kOe and 5 kOe, respectively, are reported [9, 10]. Nearly linear behavior, with a slight positive curvature near $H = 0$, is observed up to fields of 12.5 kOe in Figure 3. Fitting this range gives a slope of -2.1 kOe/T. From this value, the WHH expression $H_{c2}(0) = -0.693T_c(dH_{c2}/dT)|_{T=T_c}$ gives $H_{c2}(0) = 13$ kOe. This is not compatible with the resistivity data collected at $H = 15$ kOe (Fig. 3), for which $T_c \approx 1.5$ K can be estimated (Fig. 3). This discrepancy is a direct result of the nearly linear relationship between magnetic field and $T_c$ over a wide range of fields. A similar shape of $H_{c2}$ vs $T_c$ is seen in W$_5$SiB$_2$ [10], but reports for Mo$_5$SiB$_2$ show clear negative curvature over most of the temperature range [9], more consistent with expectations based on the WHH theory. The observed temperature dependence of the upper critical field $H_{c2}$ in polycrystalline Mo$_2$PB$_2$ may be an indication of contributions from multiple superconducting gaps arising from underlying crystalline anisotropy or from multiple superconducting bands. Similar shapes have been observed in several multigap superconductors including polycrystalline MgB$_2$ [31] and LaFeAsO$_{0.85}$F$_{0.11}$ [32], and single crystals of borocarbides [33], dichalcogenides [34, 35], and more recently TiNi$_2$Se$_2$ [36].

Results of heat capacity measurements on Mo$_2$P$_{1.1}$B$_{1.9}$ are shown in Figure 4. Rietveld refinement of the powder x-ray diffraction data shows that this sample contains 7 wt. % of Mo$_2$P, which is a superconductor with $T_c$ reported of 5–7 K [37–39]. For this study, an Mo$_2$P sample was synthesized and its heat capacity was measured and subtracted from the total heat capacity measured for the Mo$_2$P$_{1.1}$B$_{1.9}$ sample after scaling by the x-ray diffraction determined concentration. The measured $T_c$ for the Mo$_2$P sample was 5.5 K. See Appendix for additional data and information.

At 300 K the heat capacity of Mo$_2$P$_{1.1}$B$_{1.9}$ reaches 86% of the Dulong-Petit limit (Fig. 4a, inset). The increase in heat capacity upon cooling into the superconducting state is centered at $T_c = 9.2$ K. The magnitude of the heat capacity jump is determined to be 43.2 mJ/mol-at/K. Data collected at 30 kOe show that this field is sufficient to suppress the superconductivity to below 2 K, consistent with the resistivity results above that show $H_{c2}(0) \approx 17$ kOe. Figure 4b shows the electronic portion of the heat capacity, determined by subtracting the data collected at 30 kOe. The 30 kOe data is well described up to 9 K by $c_p(T) = \gamma T + \beta T^3$, as shown by the black line through the data in Figure 4a. This fit gives a normal state Sommerfeld coefficient of $\gamma = 3.16(1)$ mJ/mol-at/K$^2$ and a Debye temperature of 492(2) K. Similar values were obtained from the same analysis of heat capacity data (not shown) for the Mo$_2$PB$_2$ sample. These values are compared with other isostructural superconductors in Table II.

Results of electronic band structure calculations are shown in Figure 5a. Six bands are observed to cross the Fermi level,
with several bands contributing strongly to the total density of states (DOS). The partial Fermi-level DOS in these bands (per unit cell per eV, both spins) is found to be 2.06, 4.66, 1.90, 1.10, 0.96, and 0.04, for a total Fermi level DOS \(N(E_F)\) of 10.7 eV/unit cell. With 10 Mo per unit cell and the majority of the DOS being Mo (Fig. 5b), \(N(E_F)\) is somewhat enhanced relative to elemental Mo itself, which has \(N(E_F)\) of 0.65 eV [40], but not to a degree that would suggest a magnetic instability. This argues in favor of a phononic pairing mechanism.

The value of \(\gamma\) determined from the calculated band structure (Fig. 5a) is 1.57 mJ/mol-at./K\(^2\). This is significantly lower than the observed value of 3.16 mJ/mol-at./K\(^2\). This enhancement by a factor of 2.01 \((= 1 + \lambda)\) gives an electron-phonon coupling constant \(\lambda\) of approximately 1, indicating intermediate coupling. For a single-band s-wave scenario, Eliashberg theory [41] gives a reduced specific heat jump of approximately 2 for elemental Nb, which has a similar \(\lambda\). The observed value of \(\Delta c/\gamma T_c\) in Mo\(_2\)PB\(_2\) is 1.49, close to the weak-coupling BCS value, but only 75\% of the value expected based on the estimated electron-phonon coupling strength for this compound.

In general, such a reduced specific heat jump can result from two factors. The first of these is gap anisotropy, including nodal behavior as observed in the superconducting cuprates [42] or more recently in LaFePO, a structural relative of the high \(T_c\) iron-based superconductors [43, 44]. For example, the BCS weak-coupling theory, applied to a single band two dimensional d-wave material [45], predicts a reduced specific heat jump \(\Delta c/\gamma T_c\) of 0.95. However, there is little evidence for nodal superconductivity in Mo\(_2\)PB\(_2\). For example, the electronic specific heat in the superconducting state in Figure 4b at 1.9 K, or approximately 20 \% of \(T_c\), is only 2 \% of the normal state value at \(T_c\), consistent with BCS predictions for a gapped s-wave superconductor.

The second possibility for such a reduced specific heat jump is multiband superconductivity, as observed in MgB\(_2\) [46]. Strictly speaking this can be considered a form of anisotropy, but here we follow the historical context and treat it separately from the Fermi surface gap anisotropy described above. In MgB\(_2\), well established to be an intermediate coupling multiband s-wave superconductor [47], the largest specific heat jump \(\Delta c/\gamma T_c\) was observed [48] to be 1.32, less than the BCS s-wave value. The band structure calculations for Mo\(_2\)PB\(_2\) support the possibility of multiband superconductivity, since several bands contribute significant DOS at the Fermi level.

Further evidence suggesting potential multiband behavior is seen in the temperature dependence of the heat capacity mea-

| Composition      | \(T_c\) (K) | \(\gamma\) (mJ/mol-at./K\(^2\)) | \(\Theta_D\) (K) | \(\Delta c\) (mJ/mol-at./K) | \(\Delta c/\gamma T_c\) |
|------------------|-------------|---------------------------------|-----------------|-----------------------------|------------------------|
| Mo\(_2\)P\(_1\),B\(_1\).9 | 9.2         | 3.12                            | 494             | 39.9                        | 1.39                   |
| Mo\(_2\)PB\(_2\) | 8.8         | 3.07                            | 501             | 35                          | 1.30                   |
| Mo\(_2\)SiB\(_2\) [9] | 5.8         | 2.12                            | 515             | 17.1                        | 1.39                   |
| W\(_2\)SiB\(_2\) [10] | 5.8         | 1.60                            | 470             | 13.8                        | 1.49                   |

FIG. 5. Results of DFT calculations. (a) The calculated band structure of Mo\(_2\)PB\(_2\). The six bands crossing the Fermi level are indicated by various symbols and labeled by numbers that enumerate the bands at each k-point with respect to energy. (b) The calculated density-of-states of Mo\(_2\)PB\(_2\), with an inset comparing the total density-of-states of Mo\(_2\)PB\(_2\) with Mo\(_2\)SiB\(_2\). The energy zero is set to the Fermi energies of the respective compounds.
which is itself a superconductor with a somewhat lower $T_c$ results for Mo
ponentially in
Often the specific heat at low temperature is taken to vary ex-
sult from having one gap much smaller than the BCS value.
the specific heat was found, in the case of MgB$_2$
value, as indicated in the inset. The low-T enhancement of
fit significantly improves upon the BCS fit, generating bet-
strating excitations across at least two gaps. The two band
in the inset of Fig. 6 show a substantial curvature demon-
changed values from the band structure calculations.
rough agreement with the highest two Fermi-level DOS val-
level DOS. We note that this DOS reduction from 10.7/eV-
maximum lower value of $\lambda$ for the Si com-
E is a single band superconductor, as Nb is known
stated below $T_c$. In Fig. 6 we depict the heat capacity data
of Mo$_5$PB$_2$, along with two calculated curves: a single band
BCS fit where the $T=0$ gap value has been taken as the canoni
cal BCS weak-coupling value, 1.76 $k_B T_c$, and a two band
The smaller gap is weighted at one third the weight of the larger and the two gap fitting yields one gap of
0.65 times the BCS value and the other gap 1.12 times the
BCS value. The relative weighting of the two band fit is in
rough agreement with the highest two Fermi-level DOS val-
ues from the band structure calculations.
Experimental data from Nb, which has a similar electron-
phonon coupling $\lambda$ as well as similar $T_c$, is included in in
Fig. 6 for comparison. The data was taken from Ref. 49.
If Mo$_5$PB$_2$ is a single band superconductor, as Nb is known
to be, one would expect a similar electronic specific heat curve.
Instead, one finds a specific heat jump $\Delta c/\gamma T_c$ only
slightly above the weak coupling BCS value. In addition, the
low-temperature specific heat is enhanced relative to the BCS
value, as indicated in the inset. The low-T enhancement of
the specific heat was found, in the case of MgB$_2$ [48], to re-
result from having one gap much smaller than the BCS value.
Often the specific heat at low temperature is taken to vary ex-
ponentially in $-\Delta / T$, where $\Delta$ is the smallest energy gap in
the system, but the data (red diamonds) in the logarithmic plot
in the inset of Fig. 6 show a substantial curvature demon-
strating excitations across at least two gaps. The two band
fit significantly improves upon the BCS fit, generating bet-
er agreement at both low temperatures and temperatures near
$T_c$, though measurements on single crystals would be de-
sirable to support this. This is consistent with the electronic
structure calculations, finding multiple bands crossing $E_F$.

It is of interest to compare the experimental and theoretical
results for Mo$_5$PB$_2$ to the isostructural compound Mo$_5$SiB$_2$, which is itself a superconductor with a somewhat lower $T_c$ of
5.8 K [9]. From a comparison of our calculated $\gamma$ of 1.22
mJ/mol-atom-K$^2$ for the Si compound with the $\gamma$ of 2.12
mJ/mol-atom-K$^2$ measured in Ref. 9, an electron-phonon
coupling constant $\lambda_{Mo_5SiB_2}$ of 0.73 is determined, signifi-
cantly lower than the value of 1.0 we infer for the P com-

Our calculations also provide insight into the source of this
change in $\lambda$. Presented in the inset of Figure 5b are the cal-
culated total densities-of-states of the two compounds in a win-
dow of width approximately 4 eV, centered on $E_F$. It is ap-
parent that the densities-of-states can nearly be superimposed
upon each other in a “rigid-band” manner, with a shift of
approximately 0.2 eV corresponding directly to the 2 fewer
valence electrons of the Si compound. Since the calculated
densities-of-states both generally increase with energy around
the respective Fermi energies, the effective hole doping as-
signed with the substitution of Si for P lowers the Fermi
level DOS. We note that this DOS reduction from 10.7/eV-
c.u. to 8.30/eV-u.c., or 22 percent, parallels the inferred 27
percent $\lambda$ reduction from the P compound to the Si compound.
This suggests that the electron phonon matrix element $V$ (re-
calling that in BCS theory $\lambda = N(E_F) V$) is similar in the
two compounds, as is reasonable. In addition, the calcula-
tions are consistent with the observation that the P-rich sample
Mo$_5$P$_{1.1}$B$_{1.9}$ has a higher $T_c$ than the Mo$_5$PB$_2$ sample (Table
I), since the DOS at $E_F$ (Fig. 5b) would be increased by the
substitution of P for B.

Our first principles calculations and analysis of the experi-
mental data thus suggest that Mo$_5$PB$_2$ is an intermediate cou-
ping, phonon-mediated, and potentially multiband supercon-
ductor. We note that it is possible that the superconductors
Mo$_5$SiB$_2$ and additionally Nb$_5$SiB$_2$ are also multiband ma-
terials as our calculations (depicted in the Appendix) find each of
these materials to have several bands crossing $E_F$.

IV. SUMMARY AND CONCLUSIONS
We have discovered a new superconductor, Mo$_5$PB$_2$, with
critical temperature $T_c$ as high as 9.2 K. It crystallizes in a
tetragonal Cr$_2$B$_2$ structure shared by a number of supercon-
ductors, such as Mo$_5$SiB$_2$ and Nb$_5$SiB$_2$, and W$_5$SiB$_2$, and has the
highest transition temperature and upper critical field re-
ported for this family of compounds. Electron doping is may
be expected to increase $T_c$ further. Based on analysis of the
specific heat data as well as our first principles calculations,
Mo$_5$PB$_2$ appears to be an intermediate-coupling, multi-gap,
phonon-mediated superconductor.

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FIG. 7. The calculated band structures for (a) \( \text{Mo}_5\text{SiB}_2 \) and (b) \( \text{Nb}_5\text{SiB}_2 \). Note the multiple bands crossing \( E_F \) in each case.

samples with varying stoichiometry, experimental characterization, theory, and analysis. In addition, M.A.M. acknowledges support for the initial synthesis of the material from U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office, Propulsion Materials Program. The authors thank B.C. Sales and J.Q. Yan for helpful discussions throughout the course of this work.

APPENDIX

A. Electronic structure of \( \text{Mo}_5\text{SiB}_2 \) and \( \text{Nb}_5\text{SiB}_2 \)

Figure 7 shows results from first principles calculations for the superconductors \( \text{Mo}_5\text{SiB}_2 \) and \( \text{Nb}_5\text{SiB}_2 \), isostructural to \( \text{Mo}_5\text{PB}_2 \). These calculations were also carried out using the LAPW method, with an \( R_{K_{\text{max}}} \) of 7.0 and all internal coordinates relaxed, and approximately 1000 \( k \)-points in the full Brillouin zone used for all calculations; spin-orbit coupling was not included. As is apparent, both these compounds have multiple bands cutting the Fermi level, with 6 such bands for \( \text{Mo}_5\text{SiB}_2 \) and 4 for \( \text{Nb}_5\text{SiB}_2 \). This is indicative of a potential multiband superconductivity in these materials, although definitive resolution of this issue would require further investigation.

B. Heat capacity of \( \text{Mo}_3\text{P} \)

Results of low temperature heat capacity measurements on a polycrystalline sample of \( \text{Mo}_3\text{P} \) are shown in Figure 8a. The sample was prepared by reacting hydrogen-reduced Mo powder with red phosphorus pieces in an evacuated silica ampoule at 850°C, then pelletizing the product and firing again at 1150°C. This data was used to calculate the \( \text{Mo}_3\text{P} \) contribution to the measured heat capacity of the \( \text{Mo}_5\text{P}_{1,1}\text{B}_{1,9} \) sample. Figure 8b shows the total heat capacity measured from the \( \text{Mo}_5\text{P}_{1,1}\text{B}_{1,9} \) sample with a total mass of 17.2 mg. Using the x-ray diffraction determined concentration of 7 wt. % \( \text{Mo}_3\text{P} \), the heat capacity of the \( \text{Mo}_3\text{P} \) component (1.2 mg), was determined, and is also shown in the Figure. These datasets were subtracted using OriginPro to determine the heat capacity of 15 mg of \( \text{Mo}_5\text{P}_{1,1}\text{B}_{1,9} \), which is shown in Figure 4.

[1] P. Villars and K. Cenzual, Pearson’s Crystal Data - Crystal STructure Database for Inorganic Compounds, Releast
