Probing the electronic properties of ternary \( A_nM_{3n-1}B_{2n} \) (\( n = 1 \): \( A = \text{Ca, Sr} \); \( M = \text{Rh, Ir} \) and \( n = 3 \): \( A = \text{Ca, Sr} \); \( M = \text{Rh} \)) phases: observation of superconductivity

Hiroyuki Takeya\(^1\), Mohammed ElMassalami\(^2\), Luis A Terrazos\(^3\), Raul E Rapp\(^2\), Rodrigo B Capaz\(^2\), Hiroki Fujii\(^1\), Yoshihiko Takano\(^1\), Mathias Doerr\(^4\) and Sergey A Granovsky\(^4,5\)

\(^1\)National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
\(^2\)Instituto de Física, Universidade Federal do Rio de Janeiro, Caixa Postal 68528, 21945-970 Rio de Janeiro, Brazil
\(^3\)Centro de Educação e Saúde, Universidade Federal de Campina Grande, Cuité, PB 58175-000, Brazil
\(^4\)Institut für Festkörperphysik, Technische Universität Dresden, D-01062 Dresden, Germany
\(^5\)Faculty of Physics, M V Lomonossov Moscow State University, 119991 Leninskiye Gory, Moscow, Russia

E-mail: takeya.hiroyuki@nims.go.jp

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Abstract

We follow the evolution of the electronic properties of the titled homologous series when \( n \) as well as the atomic type of \( A \) and \( M \) are varied where for \( n = 1 \), \( A = \text{Ca, Sr} \) and \( M = \text{Rh, Ir} \) while for \( n = 3 \), \( A = \text{Ca, Sr} \) and \( M = \text{Rh} \). The crystal structure of \( n = 1 \) members is known to be \( \text{CaRh}_2\text{B}_2 \)-type (\( Fddd \)), while that of \( n = 3 \) is \( \text{Ca}_3\text{Rh}_8\text{B}_6 \)-type (\( Fmmm \)); the latter can be visualized as a stacking of structural fragments from \( \text{AM}_3\text{B}_2 \) (\( P6/mmm \)) and \( \text{AM}_2\text{B}_2 \). The metallic properties of the \( n = 1 \) and 3 members are distinctly different: on the one hand, the \( n = 1 \) members are characterized by a linear coefficient of the electronic specific heat \( \gamma \approx 3 \text{ mJ mol}^{-1} \text{ K}^{-2} \), a Debye temperature \( \theta_D \approx 300 \text{ K} \), a normal conductivity down to 2 K and a relatively strong linear magnetoresistivity for fields up to 150 kOe. The \( n = 3 \) family, on the other hand, exhibits \( \gamma \approx 18 \text{ mJ mol}^{-1} \text{ K}^{-2} \), \( \theta_D \approx 330 \text{ K} \), a weak linear magnetoresistivity and an onset of superconductivity (for \( \text{Ca}_3\text{Rh}_8\text{B}_6 \), \( T_c = 4.0 \text{ K} \) and \( H_{c2} = 14.5 \text{ kOe} \), while for \( \text{Sr}_3\text{Rh}_8\text{B}_6 \), \( T_c = 3.4 \text{ K} \) and \( H_{c2} \approx 4.0 \text{ kOe} \)). These remarkable differences are consistent with the findings of the electronic band structures and density of state (DOS) calculations. In particular, satisfactory agreement between the measured and calculated \( \gamma \) was obtained. Furthermore, the Fermi level, \( E_F \), of \( \text{Ca}_3\text{Rh}_8\text{B}_6 \) lies at almost the top of a pronounced local DOS peak, while that of \( \text{CaRh}_2\text{B}_2 \) lies at a local valley: this is the main reason behind the differences between the, e.g., superconducting properties. Finally, although all atoms contribute to the DOS at \( E_F \), the contribution of the Rh atoms is the strongest.

Keywords: ternary superconductors, \( \text{CaRh}_2\text{B}_2 \)-type structures, \( A_nM_{3n-1}B_{2n} \) (\( A = \text{Ca, Sr} \), \( M = \text{Rh, Ir} \)), band structure, heat capacity

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1. Introduction

Recently, we observed superconductivity in a number of new non-centrosymmetric ternary Li–Rh–B phases with $T_c$ ranging from 2 to 3 K [1]. In an attempt to raise such $T_c$, we investigated the A–M–B system wherein Li was replaced by alkaline earth atoms, Rh by another noble platinium atom while B was maintained since such a light-mass metalloid may be conducive to higher frequency modes. Traces of superconductivity were observed in compositions wherein the majority phase belongs to the $A_nM_{3n-1}B_{2n}$ series ($A = Ca, Sr; M = Rh, Ir; n$ is an integer) [2].

Following this lead, we carried out a systematic magnetoresistivity characterization of this series [2]: the obtained results revealed distinct differences among the electronic properties of the $n = 1$ (AM$_2$B$_2$ where A = Ca, Sr; M = Rh, Ir) and the $n = 3$ (AM$_3$B$_6$; A = Ca, Sr) phases. In the present work, further investigations were carried out to study their electronic properties (in particular, the superconductivity, the main concern of this work). For this purpose, various preparation routes and differing heat treatments as well as different starting compositions were applied. The structural, elemental, magnetic, thermal and electric transport properties were extensively investigated. The results confirm the strong difference in electronic properties of these two series; as an example, all of the studied $n = 1$ phases are normal conductors, while the studied $n = 3$ ones are superconductors. The experimental results are satisfactorily interpreted in terms of the theoretically calculated band structures and density of state (DOS) curves.

The crystal structures of the $n = 1$ and 3 families, together with those of the related AM$_3$B$_2$, are shown in figure 1 [3]. All these structures can be visualized as a sequence of stacked layers: taking AM$_3$B$_2$ as a reference, the M-layers of AM$_3$B$_2$ contain only 2/3 of the M atoms and are shifted by $b/2$ along the $y$-direction. On the other hand, the structure of AM$_3$M$_6$B$_6$, (AM$_3$-B$_2$, $\delta = 1/3$) can be visualized as a stacking of the structural fragments of AM$_3$B$_2$ (AM$_3$-B$_2$, $\delta = 0$) and AM$_2$B$_2$ (AM$_3$-B$_2$, $\delta = 1$); there are six Rh layers in the unit cell of AM$_3$M$_6$B$_6$ but only two of these exhibit 1/3 vacant Rh-sites (for further structure details see [3, 4]).

2. Experiment

2.1. Instruments

Powder diffractograms were collected on an x-ray diffractometer equipped with a Si detector and employing Cu $K_{\alpha}$ radiation. Structural analyses (using the Rietveld method and the structural models shown in figure 1) were carried out on all synthesized samples to evaluate the sample homogeneity, phase content and structural parameters. Elemental analyses were carried out with the help of an energy-dispersive x-ray (EDAX) analyzer. Magnetizations, $M(T, H)$, were measured on a superconducting quantum interference device magnetometer, while magnetoresistivities, $\rho_H(T)$, were measured on a conventional collinear four-point technique. Specific heats were measured on a relaxation-type calorimeter.

2.2. Calculation method and procedure

To solve the scalar-relativistic Kohn–Sham equations, calculations based on the density-functional theory were performed. We used the augmented plane wave plus local orbital method [5–7] as embodied in the WIEN2K code [8]; here, the wave functions are expanded in terms of spherical harmonics inside non-overlapping atomic spheres of radius $R_{MT}$, while in the remaining space of the unit cell (the interstitial region), plane waves were used. The exchange and correlation effects were treated within the recently proposed generalized gradient approximation of Perdew et al [9].

Reasonable values were used for the atomic spherical radius ($r_{atom}$) as well as the smallest muffin tin radius ($R$) and the largest wave number of the basis set ($K_{MAX}$). As an example, for CaRh$_2$B$_2$, $r_{Ca}$ is 1.32 Å and both $r_{Rh}$ and $r_{B}$ are fixed at 0.95 Å, while for Ca$_3$Rh$_2$B$_6$, $r_{Ca}$ is 1.32 Å, $r_{Rh}$ is 1.11 Å and $r_{B}$ is 0.95 Å. On the other hand, the product $R \times K_{MAX}$ (which controls the size of the basis set) is fixed at 7.0 for both CaRh$_2$B$_2$ and Ca$_3$Rh$_2$B$_6$ phases.

Integration in the reciprocal space was performed using the tetrahedron method taking up to 512 $k$-points in the first irreducible Brillouin zone. Once self-consistency of the potential was achieved, quantum mechanically derived forces were obtained and the ions were displaced according to a rank-one multiscat method, and then the relaxed atomic positions were obtained. The tolerance for ionic forces was 1 mRyd au$^{-1}$. For all the studied phases, the unit cell dimensions were fully relaxed (see below in table 2).

2.3. Synthesis of $A_nM_{3n-1}B_{2n}$ ($n = 1, 3$)

It was found difficult to synthesize stable, single-phase samples of these seemingly incongruent $A_nM_{3n-1}B_{2n}$ phases directly from stoichiometric starting compositions (such a difficulty might have been the barrier that hampered the search for superconductivity in this series). Instead, these
compounds were precipitated, via peritectic reactions, from A-rich compositions\(^6\). Dozens of samples were synthesized by two preparation routes: (i) the conventional argon arc-melt procedure, which was found to produce heavy losses in the easily evaporating alkaline earth elements, and (ii) the standard solid-state method in which pure elements were reacted in BN or Ta crucibles: this route (used throughout this work) was found to produce the best stoichiometric composition. For all compositions, a significant improvement in sample quality was obtained when as-prepared A–M–B samples were annealed in a Ta crucible for 18–20 h at 850 °C (used for all samples in this work).

After various adjustments and optimizations of the above-mentioned procedures, we managed to prepare various almost single-phase samples. In general, it is relatively easier to prepare a single-phase AM\(_2\)B\(_2\) sample than that of A\(_2\)Rh\(_6\)B\(_6\) (cf figures 2 and 3): the latter are fragile, deteriorate easily if left exposed to air and are often contaminated with weak impurity phases (such a contamination was also reported in other A\(_3\)M\(_6\)B\(_6\) isomorphs such as La\(_3\)Ru\(_6\)B\(_6\) and Y\(_3\)Os\(_6\)B\(_6\) [4]). For most A\(_3\)M\(_6\)B\(_6\) samples, the following impurity traces (<8%) were identified: AM\(_2\)B\(_2\), AM\(_3\)B\(_2\) or AM\(_2\). Some of these contaminants (<6%) are superconductors: for example, ARh\(_2\) (e.g. CaRh\(_2\), \(T_c = 6.4\) K; CaIr\(_2\), \(T_c = 4–6.15\) K; SrRh\(_2\), \(T_c = 6.2\) K; SrIr\(_2\), \(T_c = 5.7\) K) [10] or an unidentified superconducting contaminant with \(T_c \approx 9\) K. The superconductivity of these contaminants should not be confused with the superconductivity of the main A\(_3\)M\(_6\)B\(_6\) phase: the latter is manifested at a similar \(T_c\), independent of the type of the contaminations, and is well correlated with the pronounced peak in DOS calculations (see below). Accordingly, it is emphasized that the conclusions reached in this work are independent of the presence of these contaminations since their features can be easily identified.

For the purpose of improving the phase purity of these A\(_2\)Rh\(_6\)B\(_6\) samples, various starting compositions were tested. As an illustration, we discuss below the structural and magnetic properties of three different Ca-rich starting compositions: namely Ca : Rh : B = 14 : 8 : 6 (S1), Ca : Rh : B = 10 : 8 : 6 (S2) and Ca:Rh:B = 6 : 8 : 6 (S3). Note the differences in intensities of the main and contaminating phases.

3. Results

3.1. Structural and EDAX characterization

Representative diffractograms of AM\(_2\)B\(_2\) samples are shown in figure 2 and those of A\(_2\)Rh\(_6\)B\(_6\) samples in figure 3. Both XRD and EDAX analyses (table 1) indicate a single-phase character for the AM\(_2\)B\(_2\) samples and a major-phase character for the A\(_3\)M\(_6\)B\(_6\) samples.

The crystal structures of the studied A\(_n\)M\(_{3n−1}\)B\(_{2n}\) samples are shown in figure 1. The experimentally determined structural parameters are given in table 2; evidently, the lattice parameters of both series are in excellent agreement with the reported values as well as with those obtained from our theoretical calculations (see below). The ratios of these orthorhombic lattice parameters (see table 2) emphasize the similarity of their bonding character: it is remarkable that the \(b/a\) ratios of the ARh\(_2\)B\(_2\) (similarly A\(_2\)Rh\(_6\)B\(_6\)) family are equal even though A and M are widely varied. Similar arguments hold for the \(c/a\) ratios; however, due to the
difference in their stacking arrangements, the evolution of the c/a ratio with n is much stronger than that of the b/a ratio.

3.2. Magnetic, thermal and magnetoresistive characterization

3.2.1. SrM$_2$B$_2$ and Sr$_3$Rh$_6$B$_6$ (M = Rh, Ir). Magnetization (figure 4), magnetoresistivity [2], and specific heat (figure 5) curves of SrRh$_2$B$_2$ and SrIr$_2$B$_2$ show no superconducting signal down to 1.8 K. By contrast, magnetization (figure 4), magnetoresistivity (inset of figure 4) [2] and specific heat (figures 5 and 6) of Sr$_3$Rh$_6$B$_6$ show a relatively large, bulk superconducting signal with an onset at $T_c = 3.4(2)$ K. In addition to such a difference in their superconducting properties, Sr$_3$Rh$_6$B$_6$ and Sr$_3$Ir$_6$B$_6$ exhibit two other differences: (i) based on figures 5 and 6 and table 3, the Sommerfeld coefficient, $\gamma$, of Sr$_3$Ir$_6$B$_6$ is six times lower than that of Sr$_3$Rh$_6$B$_6$, but, on the other hand, $\theta_D$ of the former is only 10% lower than that of the latter. (ii) Based

| Compound        | Space group | Parameters from experiments | Parameters from theory | Parameters from reference |
|-----------------|-------------|------------------------------|------------------------|---------------------------|
| CaRb$_2$B$_2$   | Fddd 8      | a (Å) 5.8396(21) b (Å) 9.2555(24) c (Å) 10.6071(18) b/a 1.58 | a (Å) 5.8185 b (Å) 9.2225 c (Å) 10.5674 | 5.832 a 9.24 b 10.606 c [11] |
| CaIr$_2$B$_2$   | Fddd 8      | a (Å) 5.8741(12) b (Å) 9.5244(17) c (Å) 10.7267(13) b/a 1.58 | a (Å) 5.8550 b (Å) 9.2240 c (Å) 10.6906 | 5.877 a 9.257 b 10.727 c [11] |
| SrRb$_2$B$_2$   | Fddd 8      | a (Å) 5.9826(12) b (Å) 9.3906(9) c (Å) 10.6682(9) b/a 1.57 | a (Å) 5.9626 b (Å) 9.3592 c (Å) 10.6325 | 5.989 a 9.399 b 10.672 c [12] |
| SrIr$_2$B$_2$   | Fddd 8      | a (Å) 6.0221(7) b (Å) 9.3983(13) c (Å) 10.7123(76) b/a 1.56 | a (Å) 6.0020 b (Å) 9.3660 c (Å) 10.6765 | 5.989 a 9.404 b 10.723 c [12] |
| CaRh$_3$B$_6$   | Fmmm 4      | a (Å) 5.4872(46) b (Å) 9.7035(56) c (Å) 16.9683(24) b/a 1.77 | a (Å) 5.4816 b (Å) 9.6656 c (Å) 16.9900 | 5.500 a 9.698 b 17.047 c [3] |
| SrRh$_3$B$_6$   | Fmmm 4      | a (Å) 5.5655(40) b (Å) 9.9042(40) c (Å) 17.1186(20) b/a 1.78 | a (Å) 5.5534 b (Å) 9.8878 c (Å) 17.0607 | 5.572 a 9.921 b 17.118 c [3] |
and 8 and (3) is confirmed, independently, in the specific heat curves of

$$H_{C2}(0) = 3.85 \, \text{kOe},$$ which is higher than the calculated $H_{C2}(0) = -0.693 T_c (\alpha H_{C2}/\beta T_c) T_c = 2.7 \, \text{kOe}$. (ii) The Werthamer–Helfand–Hohenberg (WHH) expression [13, 14], which is usually parameterized in terms of $\alpha$ (a measure of the Pauli spin paramagnetism) and $\lambda_{so}$ (a measure of the spin–orbit scattering). As usual [13, 14], $\alpha$ was calculated as follows: $\alpha_{cal}^{\text{bare}} = 5.33 \times 10^{-3} \alpha H_{C2}/\beta T_c$. $\lambda_{so} = 0.06$ and $\rho = \text{low-} T$ normal resistivity; among these, $\alpha_{cal}^{\text{bare}}$ was found to give a better description of the measured $H_{C2}(T)$ curve. Furthermore, it was found that, in spite of the higher-Z value of Rh atom, the calculated WHH curve with finite $\lambda_{so}$ does not differ from that with $\lambda_{so} \to \infty$ (see figure 7): this coupled with the lower value of $H_{C2}(0)$ suggests that spin effects in Sr$_3$Rh$_2$B$_6$ have no strong influence on the evolution of $H_{C2}$.
and table 3 shows the thermal evolution of CaRh particular, the non-superconductivity) were observed for normal conductor down to 1.8 K. Similar features (in

Figure 8. (a) Mass dc susceptibilities of CaRh$_2$B$_2$, CaIr$_2$B$_2$ and CaRh$_3$B$_6$. Inset: an expansion of the $\chi_{dc}(T)$ curves of S1, S2 and S3 samples of Ca$_3$Rh$_8$B$_6$ (see figures 3 and 6). The vertical arrows mark the onset of $T_c$. One notes two very weak additional superconducting signals: one at $T_c = 6.4(2)$ K (related to CaRh$_3$B$_2$) and another, unidentified, at $T_c = 8.7(2)$ (currently under further investigation); the thermal evolutions of $H_{c2}$ of both contaminants are shown in figure 10.

3.2.2. CaM$_2$B$_2$ and Ca$_3$Rh$_8$B$_6$(M = Rh, Ir). The susceptibility (figure 8), magnetoresistivity (figure 9) and specific heat (figure 5) indicate that CaRh$_2$B$_2$ is a normal conductor down to 1.8 K. Similar features (in particular, the non-superconductivity) were observed for CaRh$_3$B$_2$ [2]. On the other hand, the magnetization (figure 8) and magnetoresistivity (figure 9) of Ca$_3$Rh$_8$B$_6$ reveal a superconducting state, $T_c = 4.0(2)$ K, with its bulk character being reflected in: (i) a high degree of screening (figure 8), (ii) a small valued $H_{c2}$ which is well below the usual observed values of $H_{c1}$ and (iii) a satisfactory success of the WHH analysis in describing the thermal evolution of $H_{c2}(T)$. Nevertheless, there are two anomalous features regarding the manifestation of this superconductivity: (i) the resistivity (figure 9) reaches its lowest value at $T_c$; however, it does not attain zero below $T_c$ (this is evident also in Sr$_2$Rh$_6$B$_6$—figure 4—and is attributed to contamination or loosely compacted superconducting grains, which in turn is reflected in the high fragility of these samples), (ii) the specific heat curves (figures 5 and 6) does not show any event at the onset of superconductivity. Such an absence of signature is well known in, e.g., the Fe-based high-$T_c$ pnictides (namely Ba$_2$K$_2$Fe$_2$As$_2$ [16], Na$_2$FeAs [17] and Sr$_2$VO$_3$FeAs [18]) and is usually attributed to sample quality, a scenario which, for Ca$_3$Rh$_8$B$_6$, is demonstrated in figure 8: the diamagnetic response of S1, S2 and S3 is sample dependent (see also the XRD analysis in the inset of figure 3). Similarly, the specific heat curves of S2 and S3, shown in figure 6 and table 3, are found to be sample dependent (due to accidental deterioration, not all of samples S1, S2 and S3 were measured by specific heat, EDAX or magnetoresistivity. Nonetheless, their features are expected to manifest the same trend that is evident from the magnetization (figure 8) and XRD (figure 3).

Figure 10 shows the thermal evolution of $H_{c2}(T)$ of Ca$_3$Rh$_8$B$_6$, as obtained from the analysis of the $\rho_0(T)$ curves (such as in figure 9). Similar to the case of Sr$_2$Rh$_6$B$_6$, the above-mentioned analysis was applied to $H_{c2}(T)$ of Ca$_3$Rh$_8$B$_6$: the quadratic expression (dashed line in figure 10) gave $T_c = 4 K$ and $H_{c2}(0) = 12 kOe (> H_{c2}^{WHH}(0))$, while the WHH analysis (solid line in figure 10) gave $T_c = 4 K$ and $H_{c2}^{WHH}(0) = 10.1 kOe$. During the latter analysis, $\alpha^{2\rho_0} = 0.19$ was fixed by experiment while $\lambda_{iso} \to \infty$ (as the $\rho_0$ of Ca$_3$Rh$_8$B$_6$ is reduced by the onset of superconductivity in the contaminating phases, the calculated $\alpha^{2\rho_0} = 0.015$ is smaller than that calculated using the superconducting parameters). Evidently, this WHH analysis suggests, similar to the case of...
Figure 10. Thermal evolution of $H_{c2}(T)$ of Ca$_3$Rh$_8$B$_6$ as obtained from the magnetoresistivity curves. Inset: the thermal evolution of the two contaminating superconducting phases: namely CaRh$_2$ ($T_c = 6.4(3)$ K) and an unidentified phase ($T_c = 8.7(3)$ K) (see figure 8). The lines indicate the calculated $H_{c2}(T)$ using the WHH [13, 14] expression (solid line: $\alpha = 0.19$ and $\lambda_{so} \to \infty$) and the quadratic expression (dashed line: $H_{c2}(t) = H_{c2}(1 - t^2)/(1 + t^2)$; $H_{c2}(0) = 12$ kOe and $T_c = 4$ K). A dotted line expressing the WHH calculation for $\alpha = 0.19$ and $\lambda_{so} \approx 0$ can hardly be separated from the solid line.

Figure 11. The band structure of Ca$_3$Rh$_8$B$_6$. Most of the Rh 4d bands are found between $-1$ and $-6$ eV. Fewer bands cross the Fermi surface but two of these have extrema that almost touch $E_F$, leading to a local peak in the DOS curve (see figure 13) and an increased $N(E_F)$ value.

Sr$_3$Rh$_6$B$_6$, that the paramagnetic and spin–orbit effects have no discernible influence on $H_{c2}$.

3.3. Band structure and DOS calculations

The band structure and DOS curves of all the studied AM$_2$B$_2$ and A$_3$Rh$_8$B$_6$ compounds were calculated; below we show two representative examples, namely Ca$_3$Rh$_8$B$_6$ and CaRh$_2$B$_2$: their band structures are given, respectively, in figures 11 and 12 while their corresponding DOS curves are shown in figures 13 and 14. The calculated band structure and DOS curves of the other AM$_2$B$_2$ and A$_3$Rh$_8$B$_6$ phases show similar, corresponding features.

Figure 12. The band structure of CaRh$_2$B$_2$. In contrast to the case of Ca$_3$Rh$_8$B$_6$ and within the displayed $k$-region, there are fewer bands located around $E_F$ and, furthermore, only two of these bands cross $E_F$. This leads to the situation where $E_F$ is positioned at a valley of the $N(E_F)$ curve (see figure 14).

Figure 13. The calculated total and partial DOS of Ca$_3$Rh$_8$B$_6$ (in units of states per eV per primitive unit cell). Different atoms (as well as different sites of the same type of atom) contribute differently to $N(E_F)$. The Rh atoms are the major contributors to $N(E_F)$: the Rh atomic partial contributions are such that $N_{E_F}(16j) > N_{E_F}(8i) > N_{E_F}(16m)$. Similarly, the partial contribution of B is such that $N_{E_F}(16m) > N_{E_F}(8h)$, while for Ca one finds that $N_{E_F}(8i) > N_{E_F}(4b)$. 

Figure 14. The total DOS curve.
Table 4. Total and partial DOS (in units of states per eV per primitive cell) of AM$_2$B$_2$ and A$_2$Rh$_6$B$_6$ (A = Ca, Sr, Ba; M = Rh, Ir). See figures 13 and 14. The contributions of the s, p and d bands of each atom in Ca$_3$Rh$_6$B$_6$ and CaRh$_2$B$_2$ are also given (in units of states per eV per formula unit).

| ARh$_2$B$_2$ | Partial/Total | $N_s(E_F)$ | $N_p(E_F)$ | $N_d(E_F)$ | $N_l(E_F)$ |
|--------------|---------------|------------|------------|------------|------------|
| CaIr$_2$B$_2$ | Total         | 0.09       | 0.24       | 0.06       | 0.72       |
| SrRh$_2$B$_2$ | Total         | 0.13       | 0.29       | 0.05       | 0.89       |
| SrIr$_2$B$_2$ | $s$ band      | 0.007      | 0.003      | 0.002      |            |
|               | $p$ band      | 0.046      | 0.010      | 0.008      |            |
|               | $d$ band      | 0.003      | 0.124      | 0.054      |            |
|               | Total         | 0.11       | 0.27       | 0.07       | 0.83       |
| A$_3$Rh$_6$B$_6$ | 8h 16m 8f 8i 16j 4b 8i |            |            |            |            |
| Sr$_2$Rh$_6$B$_6$ | $s$ band      | 0.003 0.007 | 0.008 0.009 | 0.004 0.011 | 0.011 0.011 |
| Ca$_3$Rh$_6$B$_6$ | $p$ band      | 0.110 0.080 | 0.032 0.029 | 0.029 0.011 | 0.011 0.015 |
|               | $d$ band      | 0.004 0.004 | 0.157 0.354 | 0.309 0.030 | 0.054      |
|               | Total         | 0.12 0.19  | 0.20 0.40  | 0.69 0.03  | 0.09 5.13  |

These curves as well as the results shown in table 4 indicate that $N_l(E_F)$ of each composition is substantial and that there is no band gap: these findings are consistent with the observed good metallic character. Furthermore, each $N_l(E_F)$ receives contributions from all atoms but the dominant contribution is from the Rh atoms (this is best illustrated in figure 13 of Ca$_3$Rh$_6$B$_6$). Decomposing this Rh-atoms contribution, one notes that the main contribution is from the d orbitals (although there is a weak contribution from both s- and p-states). Furthermore, the d contribution at, say, the symmetry points $\Gamma$ and X is dominated by the d$_{xy}$ orbitals ($l = 2$, $m_l = \pm 2$) of the Rh$_1$ (8i) atoms. On the other hand, the contribution of the Rh$_2$ (16j) and Rh$_3$ (8f) atoms is dominantly from the $x^2 - y^2$ ($l = 2$, $m_l = \pm 2$) and $z^2 - 1$ ($l = 2$, $m_l = 0$) orbitals. The above arguments are valid also for the case of Sr$_2$Rh$_6$B$_6$. Similar features are also observed in CaRh$_2$B$_2$ (see figure 14): e.g. the stronger contributors are the Rh atoms, followed by B and then Ca atoms.

It is noted that the Rh 8i and 16j sites (located within the structural fragment of CaRh$_2$B$_2$) contribute almost twice as much as that from the 8f site (associated with the fragments of CaRh$_2$B$_2$). This may suggest that the observed superconductivity is related to the fragments of the CaRh$_2$B$_2$ phase; contrary to such an expectation, no superconductivity was observed in preliminary magnetization curves of CaRh$_2$B$_2$, measured down to 2 K [19].

Figures 11 and 12 indicate that the Ca$_3$Rh$_6$B$_6$ bands seem to form both electron and hole pockets near $E_F$, whereas for CaRh$_2$B$_2$ only electron pockets are noticeable; furthermore, for Ca$_3$Rh$_6$B$_6$ (in contrast to CaRh$_2$B$_2$) there are more levels crossing $E_F$; these features lead to the situation wherein $E_F$ of Ca$_3$Rh$_6$B$_6$ is at almost the top of a local peak while $E_F$ of CaRh$_2$B$_2$ is positioned at a DOS local valley. As a consequence, $N_l(E_F)$ of Ca$_3$Rh$_6$B$_6$ is almost fourfold higher than that of CaRh$_2$B$_2$; these features are taken to be the major reasons behind the observed differences among the transport and thermal properties of AM$_2$B$_2$ and A$_2$Rh$_6$B$_6$ compounds. As an example, (i) the pronounced peak in the bare Sommerfeld coefficient $\gamma_{\text{bare}} = \frac{\pi^2}{3} k_B^2 \cdot N_l(E_F)$ (see e.g. figures 13 and 14), the bare Sommerfeld coefficient

\[ \gamma_{\text{bare}} = \frac{\pi^2}{3} k_B^2 \cdot N_l(E_F) \]  

(1)

gives values (shown in table 3) which are surprisingly close to the measured ones (denoted, in the same table, as $\gamma_l$); the small discrepancy is attributed to normalization effects and these are characterized by the $(1 + \lambda)$ factor

\[ \gamma_l = (1 + \lambda) \gamma_{\text{bare}}. \]  

(2)

where $\lambda$ is the interaction (electron–phonon or electron–electron) parameter. Apparently, the calculated $\lambda$ (table 3) for the superconducting A$_2$Rh$_6$B$_6$ are smaller.
than those of the normal conducting \(\text{AM}_2\text{B}_2\). This apparent contradiction is removed if we take into consideration the product \(\lambda N_c(E_F)\) (the last column of table 3): indeed this product is much higher for \(\text{AM}_2\text{B}_2\) than for \(\text{AM}_2\text{B}_2\). The presence of high-Z atoms (Rh and Ir with their higher partial contribution to \(N(E_F)\)) may introduce a spin–orbit interaction which, in the absence of inversion symmetry \([20, 21]\), would have a strong influence on the electronic properties: e.g. a split of the energy bands, a reduction of \(N(E_F)\)—a lowering of \(\gamma\)—or acting as a pair-breaking potential. To investigate this scenario, spin–orbit interactions were introduced into the band structure calculations. As far as \(N_c(E_F)\) is concerned, no perceptible changes were observed. This is attributed to the fact that the space groups of all compounds, in contradiction to our earlier claim \([2]\), are centrosymmetric.

4. Discussion and conclusions

Both experiments and theory indicate that the properties of the \(\text{AM}_2\text{B}_6\) compounds are strongly different from those of the \(\text{AM}_2\text{B}_2\) ones. Such differences include: (i) the structure of \(\text{AM}_2\text{B}_6\), in contrast to that of \(\text{AM}_2\text{B}_2\), is a mixture of structural fragments of \(\text{AM}_2\text{B}_2\) and \(\text{AM}_2\text{B}_2\); as the space group of \(\text{AM}_2\text{B}_2\) is \(Fd\dddot{d}dd\) while that of \(\text{AM}_2\text{B}_6\) is \(Fmmm\) \([3]\), then all symmetry-related physical properties are expected to be different, (ii) \(\gamma\) of the \(n = 3\) phases are relatively larger than those of the \(n = 1\) ones (see table 3), (iii) the superconductivity is present in \(\text{AM}_2\text{B}_6\) but not in the \(\text{AM}_2\text{B}_2\) compounds and (iv) the magnetoresistivity of the latter is relatively stronger than that of the former \([2]\). As mentioned above, the differences in the electronic properties can be understood in terms of the band structure and DOS calculations (see figures 11–14). In particular, these calculations give support to the surge of superconductivity in \(\text{Ca}_2\text{Rh}_8\text{B}_6\) (see above).

A comparison of figures 7 and 10 indicates that while \(T_c\) of \(\text{Ca}_2\text{Rh}_8\text{B}_6\) is only 15% higher than that of \(\text{Sr}_3\text{Rh}_8\text{B}_6\), \(H_c(0)\) of the former is almost four times higher than that of the latter. The similarity in \(T_c\) is consistent with the observation that their \(\gamma\) (also \(\theta_2\) and \(\lambda N_c(E_F)\)) are not strongly different. This is also consistent with the features of figure 13: as the \(\text{Ca}\) contributes very weakly to \(N_c(E_F)\) of \(\text{Ca}_2\text{Rh}_8\text{B}_6\), then a substitution of \(\text{Sr}\) by an isovalent \(\text{Sr}\) would not lead to a very different \(N_c(E_F)\). On the other hand, the observation that \(H_c(0)\) of \(\text{Ca}_2\text{Rh}_8\text{B}_6\) is higher than that of \(\text{Sr}_3\text{Rh}_8\text{B}_6\) is related to the fact that both \(T_c\) and \((\partial H_c/\partial T)_{T_c}\) of the former are higher than those of the latter (recall that \(H_c(0) \propto T_c(\partial H_c/\partial T)_{T_c}\)).

The superconductivity in the studied \(\text{A}_2\text{B}_6\) samples (as well as that of \(\text{Y}_2\text{Os}_8\text{B}_6\): \(T_c = 5.8\) K, \(H_c(0) \approx 20\) kOe \([22]\)) is associated with the \(Fmmm\) \(\text{Ca}_2\text{Rh}_8\text{B}_6\)-type phase, the very same one shown in figure 1(c). It is difficult, at this stage of investigation, to discuss the nature of this superconducting state; however, the observed superconducting features of \(\text{A}_2\text{B}_6\) and \(\text{Y}_2\text{Os}_8\text{B}_6\) \([22]\) suggest a BCS-type superconductivity with a singlet character, a low \(T_c\), a weak \(H_c(0)\) and a relatively smaller Meissner effect (all are strongly sensitive to sample history and impurities).

In summary, the application of a variety of preparation and heat treatment procedures enabled us to synthesize various \(\text{A}_2\text{M}_{3n-1}\text{B}_{2n}\) \((n = 1, 3)\) samples. Extensive structural, elemental and physical characterizations indicate that among the various stabilized compounds, superconductivity is detected only in \(\text{A}_2\text{Rh}_8\text{B}_6\) \((\text{A} = \text{Ca}, \text{Sr})\) samples; all studied \(\text{AM}_2\text{B}_2\) samples are found to be normal conductors. There are additional striking differences among the \(\text{AM}_2\text{B}_2\) and \(\text{A}_2\text{M}_6\text{B}_6\) phases: as compared to the latter, the former exhibits stronger magnetoresistivities and lower \(\gamma\). Such strong differences are also evident in the calculated electronic band structure and DOS curves: as an example, \(E_F\) of \(\text{AM}_2\text{B}_2\) is positioned at a local valley of the DOS curve, while that of an \(\text{A}_2\text{M}_6\text{B}_6\) phase stands at almost the top of a local DOS peak; accordingly, their \(N(E_F)\) and \(\gamma\) are different. Assuringly, the calculated \(\gamma\)’s are found to approximate quite satisfactorily the experimentally determined values.

Finally, these low-\(T_c\) superconducting \(\text{A}_2\text{Rh}_8\text{B}_6\) \((\text{A} = \text{Ca}, \text{Sr})\) phases are members of the homologous \(\text{A}_2\text{M}_{3n-1}\text{B}_{2n}\) series. It is of interest to search for superconductivity in the other members of this series as well as to further explore how the metallic properties of this series are influenced by a variation in the pressure, in the substitution or in the stacking of the structural fragments of \(\text{AM}_2\text{B}_2\) and \(\text{AM}_2\text{B}_2\) \([19]\).

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