Superconductivity enhanced by $d$-band filling in $\text{La}Tr_2\text{Al}_{20}$ with $Tr = \text{Mo}$ and $W$

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Abstract

Electrical resistivity, magnetic susceptibility, and specific heat measurements on single crystals of $\text{La}Tr_2\text{Al}_{20}$ with $Tr = \text{Mo}$ and $W$ revealed that these compounds exhibit superconductivity with transition temperatures $T_c = 3.22$ and $1.81$ K, respectively, achieving the highest values in the reported $\text{La}Tr_2\text{Al}_{20}$ compounds. There appears a positive correlation between $T_c$ and the electronic specific heat coefficient, which increases with increasing the number of 4$d$- and 5$d$-electrons. This finding indicates that filling of the upper $e_g$ orbitals in the 4$d$ and 5$d$ bands plays an essential role for the significant enhancement of the superconducting condensation energy. Possible roles played by the $d$ electrons in the strongly correlated electron phenomena appearing in $RTr_2\text{Al}_{20}$ are discussed.
I. INTRODUCTION

Ternary intermetallic compounds containing rare-earth ions are the subject of continuous interest in the fields of strongly correlated electron physics. Among them, a family of $RTr_2X_{20}$ ($R$: rare earths, $Tr$: transition metals, $X$: Al, Zn, and Cd), which crystallize in the cubic CeCr$_2$Al$_{20}$-type structure ($Fd\bar{3}m$, #227), have attracted considerable attention in recent years, because a wide variety of exotic electron states caused by strong hybridization of $f$-electrons with non-$f$-ligands have been observed. A heavy fermion (HF) behavior appears in YbCo$_2$Zn$_{20}$ with an electronic specific heat coefficient of 8 J/(mol K$^2$), which is the largest among Yb compounds [1–3]. In a HF state of YbIr$_2$Zn$_{20}$, a metamagnetic anomaly occurs at around 10 T [4]. Sm$Tr_2$Al$_{20}$ ($Tr$ = Ti, V, Nb, and Ta) exhibit rare Sm-based HF behaviors, which are anomalously field-insensitive [5–8]. Many of Pr$Tr_2X_{20}$ compounds have a non-Kramers $\Gamma_3$ doublet crystalline-electric-field ground state of Pr ions, and exhibit quadrupole Kondo lattice behaviors [9–14]. Therefore, the superconductivity (SC) appearing in the Pr$Tr_2X_{20}$ compounds is presumed to be induced by quadrupolar fluctuations [15–19]. In Ce- and U-based compounds, strongly correlated electron behaviors have also been reported [20–22].

The SC appearing in $RTr_2X_{20}$ with nonmagnetic $R$ ions has been discussed in terms of the cage structure, which is one of the characteristic features of the CeCr$_2$Al$_{20}$-type crystal structure. The $R$ ions at the $8a$ site with cubic $T_d$ symmetry are located at the center of an $X_{16}$ cage. In $R$V$_2$Al$_{20}$ with $R$ = Al and Ga (the SC transition temperatures $T_c$ are 1.49 and 1.66 K, respectively), the cage-center $R$ ions show anharmonic large-amplitude oscillations as observed in filled skutterudites [23], which are considered to enhance $T_c$ through the electron-phonon coupling [24–27]. Superconductors of $R$ = Sc, Y, and Lu seems to have similar features [28]. For recently-found superconductors of La$Tr_2$Al$_{20}$ with $Tr$ = Ti, V, Nb, and Ta ($T_c$ ranging from 0.15 to 1.05 K) [29], however, the cage does not have enough space for such anharmonic large-amplitude oscillations and the reason for the largely distributed $T_c$ remains to be clarified.

In this paper, we study La$Tr_2$Al$_{20}$ with $Tr$ = Mo and W using single crystals. The results reveal that these compounds are new superconductors with the highest $T_c$ values among La$Tr_2$Al$_{20}$ compounds. Comparison among all these compounds suggests that the $d$-band filling plays an essential role for determining the superconducting properties in La$Tr_2$Al$_{20}$.
TABLE I. Crystallographic parameters of LaTr$_2$Al$_{20}$ ($Tr = \text{Mo and W}$) at room temperature. $R$ and $wR$ are reliability factors. $B_{eq}$ is the equivalent isotropic atomic displacement parameter. Occ. is the site occupancy. Standard deviations in the positions of the least significant digits are given in parentheses.

| Atom | Site | $x$  | $y$  | $z$  | $B_{eq}$(Å$^2$) | Occ. |
|------|------|------|------|------|-----------------|------|
| La   | 8$a$ | 1/8  | 1/8  | 1/8  | 0.738(17)       | 1    |
| Mo   | 16$d$| 1/2  | 1/2  | 1/2  | 0.54(2)         | 0.928(4) |
| Al(1)| 96$g$| 0.05870(5) | 0.05870(5) | 0.32549(7) | 0.82(3) | 1 |
| Al(2)| 48$f$| 0.48694(10) | 1/8 | 1/8  | 0.82(3) | 1 |
| Al(3)| 16$c$| 0    | 0    | 0    | 1.79(5) | 1 |

LaMo$_2$Al$_{20}$ \[ R = 1.94\%, \ wR = 3.67\% \quad Fd\overline{3}m \ (\#227) \ (\text{origin choice 2}) \ a = 14.6631(13) \ \text{Å}, \ V = 3152.7(5) \ \text{Å}^3 \]

| Atom | Site | $x$  | $y$  | $z$  | $B_{eq}$(Å$^2$) | Occ. |
|------|------|------|------|------|-----------------|------|
| La   | 8$a$ | 1/8  | 1/8  | 1/8  | 0.667(15)       | 1    |
| W    | 16$d$| 1/2  | 1/2  | 1/2  | 0.437(12)       | 0.848(2) |
| Al(1)| 96$g$| 0.05872(4) | 0.05872(4) | 0.32575(6) | 0.89(2) | 1 |
| Al(2)| 48$f$| 0.48720(9) | 1/8 | 1/8  | 0.91(2) | 1 |
| Al(3)| 16$c$| 0    | 0    | 0    | 1.74(5) | 1 |

LaW$_2$Al$_{20}$ \[ R = 1.04\%, \ wR = 2.76\% \quad Fd\overline{3}m \ (\#227) \ (\text{origin choice 2}) \ a = 14.6813(11) \ \text{Å}, \ V = 3164.4(4) \ \text{Å}^3 \]

II. EXPERIMENTAL DETAILS

Single crystals of LaTr$_2$Al$_{20}$ ($Tr = \text{Mo and W}$) were grown by the Al self-flux method. The starting materials were La chips (99.9%), Al grains (99.99%) and powders of Mo (99.99%) and W (99.99%). With an atomic ratio of La:Mo:Al = 1:2:50 and La:W:Al = 1:2:90, the starting materials were put in an alumina crucible and sealed in a quartz tube. The quartz tube was heated up to 1050
°C and then slowly cooled. Single crystals were obtained by spinning the ampoule in a centrifuge in order to remove the excess Al flux.

The electrical resistivity \( \rho \) and specific heat \( C \) were measured using a Quantum Design (QD) Physical Property Measurement System (PPMS) equipped with a Helium-3 cryostat. The magnetic susceptibility \( \chi \) was measured down to 2 K using a QD Magnetic Property Measurement System (MPMS).

III. RESULTS AND DISCUSSION

Single crystal X-ray diffraction analysis was performed using a Rigaku XtaLABmini with graphite monochromated Mo-K\(\alpha\) radiation. The structural parameters refined using the program SHELX-97 [30] are shown in Table I. The lattice parameters \( a \) are close to those in the previous report [33]. The equivalent isotropic atomic displacement parameter \( B_{eq} \) of Al(3) at the 16c site has relatively large values: \( B_{eq} = 1.74 - 1.79 \, \text{Å}^2 \). This feature is characteristic to \( RTr_2X_{20} \) compounds; see Refs. [29, 34, 35] for \( X = \text{Al} \) and Refs. [15, 31, 32] for \( X = \text{Zn} \). The cage-center La ions at the 8a site have normal values, in contrast to \( R_xV_2\text{Al}_{20} \) \((R = \text{Al} \text{ and Ga})\), in which the cage-center \( R \) ions are suggested to have anharmonic rattling modes [24-27]. The occupancy of Mo and W sites was found to be less than one. Similar feature was also observed for CeMo\(_2\)Al\(_{20}\) [33]. This could mean that these \( Tr \) sites are partially substituted by Al atoms because of the similarity in the metallic radii [36].

The temperature dependence of resistivity \( \rho(T) \) divided by \( \rho(300 \, \text{K}) \) is shown in Fig. 1. The residual resistivity ratio \( RRR \equiv \rho(300 \, \text{K})/\rho_{\text{res}} \) (\( \rho_{\text{res}} \): the residual resistivity) is 1.8 for W and 9.1 for Mo. Figures 2(a-d) show the low-temperature expansion of \( \rho(T, H) \) data. In zero field, both compounds show SC transitions with the onset at 3.4 K for Mo and 2.6 K for W. In the applied fields, the transition temperature shifts to lower temperatures. The details are discussed below.

The temperature dependence of specific heat \( C \) divided by temperature as a function of \( T^2 \) is shown in Fig. 3. The normal-state \( C/T \) data can be well described by \( C/T = \gamma + \beta T^2 \), where \( \gamma \) and \( \beta \) are the electronic and phonon specific heat coefficients, respectively. The Debye temperature \( \Theta_D \) is obtained from \( \Theta_D = \frac{3}{\sqrt{12/5}}\pi^4 n R / \beta \), where \( n = 23 \) is the number of atoms per formula unit and \( R \) is the gas constant. The obtained parameters are summarized in Table II.

The temperature dependence of the electronic contribution to the specific heat \( C_{el}/T \equiv C/T - \beta T^2 \) is shown in Fig. 4. A clear specific heat jump appears at 3.22 K (Mo) and 1.81 K (W), which
FIG. 1. (a) Temperature dependence of electrical resistivity $\rho$ for La$\text{Tr}_2\text{Al}_{20}$ ($\text{Tr} = \text{Mo}$ and $\text{W}$) with the current along the $\langle 110 \rangle$ direction.

FIG. 2. Temperature and magnetic field dependences of electrical resistivity $\rho$ for La$\text{Tr}_2\text{Al}_{20}$ ($\text{Tr} = \text{Mo}$ and $\text{W}$) measured at low temperatures with the current along the $[1\bar{1}0]$ direction in the fields along the $[111]$ direction.
FIG. 3. Temperature dependence of specific heat $C$ divided by temperature as a function of $T^2$ for La$Tr_2$Al$_{20}$ ($Tr = Mo$ and $W$).

is referred to as the bulk SC transition temperature $T_c$ hereinafter. The fitting of the $C_{el}(T)$ data by the $\alpha$ model [37, 38] is shown by the solid curve. The obtained $\alpha$ value is 1.74 and 1.75 for Mo and W, respectively, which is close to 1.764 expected from the BCS theory, suggesting that they are weak-coupling superconductors.

The bulk nature of the superconductivity in LaMo$_2$Al$_{20}$ has been confirmed by magnetic-susceptibility ($\chi$) measurements. The temperature dependence of $\chi$ measured in 10 Oe is shown in Fig. 5. The diamagnetic signal develops below $T_c$. The $4\pi\chi$ values of the order of -1 far below $T_c$ suggest that the SC volume fraction reaches approximately 100%.

The $H$-vs-$T$ SC phase diagram constructed using the $\rho$, $C_{el}$, and $\chi$ data is shown in Fig. 6.
FIG. 4. Temperature dependence of the electronic contribution to the specific heat $C_{el}/T$ (the upper panel) and $H_{c2}(0)$ (the lower panel) for La$T_2Al_{20}$ ($T = Mo$ and $W$). The solid curves represent the fitting by the $\alpha$ model [37, 38].

The values of $H_{c2}(0)$ are much lower than the Pauli-limiting field $H_P = (1.84 \times 10^4 \text{ Oe/K}) T_c$ [39], suggesting that $H_{c2}(0)$ is determined by the orbital depairing effect. The temperature dependence of $H_{c2}$ can be well described by the Werthamer-Helfand-Hohenberg (WHH) clean-limit expression [40, 41], as shown by the solid curves in Fig. 6. In this model, $H_{c2}(0)$ can be expressed as

$$H_{c2}(0) = -0.73 \times \left. \frac{dH_{c2}}{dT} \right|_{T = T_c} T_c = \frac{\phi_0}{2\pi\xi_{GL}^2},$$

(1)

where $\phi_0$ and $\xi_{GL}$ are the quantum magnetic flux and the Ginzburg-Landau (GL) coherence length, respectively. The GL parameter $\kappa_{GL}$, which is equal to the Maki parameter [42] $\kappa_2(T \rightarrow T_c)$, is
FIG. 5. Temperature dependence of magnetic susceptibility $\chi$ for LaMo$_2$Al$_{20}$. The zero-field-cooled (ZFC) warming data and the field-cooled (FC) data for the applied magnetic field of 10 Oe are shown.

determined using the thermodynamic relation [43]:

$$\frac{\Delta C_{\text{vol}}}{T} \bigg|_{T=T_c} = \left( \frac{dH_c}{dT} \bigg|_{T=T_c} \right)^2 \frac{1}{4\pi(2\kappa^2 - 1)\beta_A},$$

where $\Delta C_{\text{vol}}$ is measured per unit volume [unit: erg/(K cm$^3$)], and $\beta_A = 1.16$ for a triangular vortex lattice. The thermodynamic critical field $H_c(0) = \alpha \sqrt{6/\pi} \gamma_{\text{vol}} T_c$ [38], the London penetration depth $\lambda_L = \kappa_G \xi_G$, and the lower critical field $H_{c1} = H_c(0) \ln \kappa_G / (\sqrt{2}\kappa_G)$ are also calculated. The obtained characteristic parameters are summarized in Table II.

The electron-phonon coupling constant $\lambda_{\text{e-ph}}$ is obtained using McMillan’s formula

$$\lambda_{\text{e-ph}} = \frac{1.04 + \mu^* \ln(\frac{\theta_D}{1.45T_c})}{(1 - 0.62\mu^*) \ln(\frac{\theta_D}{1.45T_c}) - 1.04},$$

where the Coulomb coupling constant $\mu^*$ is assumed to be 0.13 [44]. The fact that $\lambda_{\text{e-ph}} = 0.48 - 0.50$ is consistent with the above-mentioned weak-coupling nature of the superconductivity.

In the crystal structure of $RTr_2Al_{20}$, the Al$_{16}$ cage includes a guest $R$ ion at the center ($8a$ site) as shown in the inset of Fig. 7. In Ref. [29], we have introduced a parameter to quantify the “guest free space” as $d_{\text{GFS}} \equiv d_{R-Al} - (r_R + r_{Al})$, where $d_{R-Al} \equiv (12d_{R-Al}(96g) + 4d_{R-Al(16c)})/16$ is the average distance between $R$ and Al in the cage, and $r_R$ and $r_{Al}$ are the covalent radii for $R$ and Al ions, respectively [45]. $d_{R-Al}$ is calculated using the results of the single-crystal X-ray diffraction
FIG. 6. $H$-$T$ phase diagram of La$\mathrm{Tr}_2\mathrm{Al}_{20}$ with $\mathrm{Tr} = \mathrm{Mo}$ and $\mathrm{W}$ in comparison with $\mathrm{Tr} = \mathrm{Nb}$ and $\mathrm{Ta}$ [29]. Filled circles represent the bulk SC transition points obtained from the $C(T, H)$ data, which can be well described by the Werthamer-Helfand-Hohenberg (WHH) clean-limit model (solid curves) [40, 41]. The “cross” and “plus” symbols designate resistive transition points defined at 75% and 0% of the normal-state resistance, respectively. These points obtained from the $\rho(T, H)$ data provide higher values of $T_c$ and $H_{c2}$ compared to those from the $C(T, H)$ data, more significantly for $\mathrm{Tr} = \mathrm{W}$. This observation indicates that a minor part of the single crystal has higher $T_c$’s and $H_{c2}$’s, which are detected by the $\rho$ measurements.

In Fig. 7, we show $T_c$ vs. $d_{\mathrm{GFS}}$ for $R\mathrm{Tr}_2\mathrm{Al}_{20}$ with nonmagnetic $R$ ions; this is a revised one of Fig. 5 in Ref. [29]. Nonmagnetic $R\mathrm{Tr}_2\mathrm{Al}_{20}$ superconductors are classified into two groups, i.e., (A) $d_{\mathrm{GFS}} \neq 0$ and $T_c$ correlates with $d_{\mathrm{GFS}}$, and (B) $d_{\mathrm{GFS}} \approx 0$ and $T_c$ seems to be governed by other factors. For group (A), it is thought that $T_c$ is enhanced by the “rattling” anharmonic vibration modes of Ga, Al, Sc, and Lu ions due to the coupling with conduction electrons [24–28]. In contrast, all the data points in group (B) fall almost into a vertical line with $d_{\mathrm{GFS}} \approx 0$, indicating that these La$\mathrm{Tr}_2\mathrm{Al}_{20}$ compounds do not have guest free space and the large $T_c$ distribution is not associated with the La ion oscillations.

The distribution of $T_c$ among La$\mathrm{Tr}_2\mathrm{Al}_{20}$ is remarkably large; $T_c(\mathrm{Tr} = \mathrm{Mo})/T_c(\mathrm{Tr} = \mathrm{V}) = 3.22/0.15 \approx 22$. Figure 8 shows $T_c$ vs. the electronic specific heat coefficient $\gamma$ for all La$\mathrm{Tr}_2\mathrm{Al}_{20}$ superconductors. This figure clearly demonstrates that there is a positive correlation between $T_c$ and $\gamma$. $\mathrm{Tr}$ ions are located at sites with trigonal point symmetry $D_{3d}$. Due to the crystalline-electric field effect, the fivefold degenerate $d$ orbitals of a $\mathrm{Tr}$ ion split into a low-energy singlet ($a_{1g}$) and
FIG. 7. $T_c$ vs $d_{\text{GFS}} \equiv d_{R-\text{Al}} - (r_R + r_{\text{Al}})$ quantifying the “guest free space” of nonmagnetic cage-center $R$ ions for $RTr_2\text{Al}_{20}$ (see text for details). The data except for LaMo$_2$Al$_{20}$ and LaW$_2$Al$_{20}$ are taken from Fig. 5 in Ref. [29]. This figure demonstrates that nonmagnetic $RTr_2\text{Al}_{20}$ superconductors are classified into two groups, i.e., (A) $d_{\text{GFS}} \neq 0$ and $T_c$ correlates with $d_{\text{GFS}}$, and (B) $d_{\text{GFS}} \approx 0$ and $T_c$ seems to be governed by other factors. Note that superconductors PrTi$_2$Al$_{20}$ [16] and PrV$_2$Al$_{20}$ [18], and field-insensitive HF compounds Sm$Tr_2\text{Al}_{20}$ ($Tr=\text{Ti, V, Cr, and Ta}$) [5–7] also have $d_{\text{GFS}} \approx 0$. The inset picture shows the structure of a $R(8a)$-$\text{Al}_{16}(96g, 16c)$ cage; $\text{Al}_{16}$ forms a CN 16 Frank-Kasper polyhedron.

FIG. 8. $T_c$ vs the electronic specific heat coefficient $\gamma$ for La$Tr_2\text{Al}_{20}$. 
TABLE II. Characteristic parameters of LaTr$_2$Al$_{20}$ superconductors (see text for definitions). The errors in the last significant digit(s) are indicated in parentheses.

| compounds | LaMo$_2$Al$_{20}$ | LaW$_2$Al$_{20}$ |
|-----------|------------------|------------------|
| $T_c$ (K) | 3.22             | 1.81             |
| $\gamma$ (mJ/mol K$^2$) | 33.1 | 26.7 |
| $\alpha$ | 1.74             | 1.75             |
| $\Delta C/\gamma T_c$ | 1.32 | 1.37 |
| $\Theta_D$ (K) | 511 | 383 |
| $\lambda_{e-ph}$ | 0.504 | 0.476 |
| $H_c(0)$ (Oe) | 219 | 111 |
| $dH_{c2}/dT |_{T=T_c}$ (Oe/K) | -3240 | -2860 |
| $H_{c2}(0)$ (Oe) | 7620 | 3770 |
| $\xi_{GL}$ (Å) | 207 | 295 |
| $\kappa_{GL} = \kappa_2(T \rightarrow T_c)$ | 14.0 | 13.5 |
| $\lambda_L = \kappa_{GL} \xi_{GL}$ (Å) | 2900 | 3980 |
| $H_{c1}(0)$ (Oe) | 29 | 15 |

Two high-energy doublets ($e_g$) \[46\]. Electronic band structure calculations for Tr = Ti, V, and Cr \[46\] suggest that there is a ferromagnetic instability, which becomes more dominant with 3d-electron filling into the upper $e_g$ orbitals approaching Cr; the calculated Stoner factor of LaCr$_2$Al$_{20}$ is relatively high although no ferromagnetic ordering has been observed experimentally. This instability may be one of the possible reasons for the suppressed $T_c$ values for those 3d compounds. On the contrary, for the 4d and 5d compounds, Fig. 8 demonstrates that the 4d(5d) electron filling with Nb→Mo (Ta→W) boosts up the $T_c$ value. The increased $\gamma$ values with the electron filling indicate enhancements in the density of states at the Fermi energy and/or in the effective mass of conduction electrons for Tr = Mo and W. Actually, as shown in Fig. 8 $dH_{c2}/dT |_{T=T_c}$ increases as Nb→Mo (Ta→W), providing evidence for the mass enhancement. With these features, we speculate that the filling of the upper $e_g$ orbitals in the 4d(5d) bands significantly enhances the SC condensation energy.
IV. SUMMARY

We have studied the electrical resistivity, magnetic susceptibility, and specific heat of single crystalline LaMo$_2$Al$_{20}$ and LaW$_2$Al$_{20}$. It has been revealed that these compounds exhibit superconductivity with transition temperatures $T_c = 3.22$ and 1.81 K, respectively, achieving the highest values in the reported La$Tr_2$Al$_{20}$ compounds. The values of $T_c$ exhibit a positive correlation with the electronic specific heat coefficient $\gamma$, which increases with the 4$d$ and 5$d$ electron filling. This finding indicates that the upper $e_g$ orbitals in the 4$d$ and 5$d$ bands play an essential role for the significant enhancement of the SC condensation energy.

In the realization of the several types of strongly correlated electron phenomena in $RTr_2$Al$_{20}$, the roles played by $d$ electrons have not been clarified yet. According to the calculated band structures \[46\], the Fermi surface structures change drastically with the $d$ band filling. Therefore, the strength of hybridization with the $f$ electrons of $R$ ions is expected to change depending on the $Tr$ elements. Further studies on the features of $d$ electron orbitals in $RTr_2$Al$_{20}$ may help to understand the unsolved problems in Sm-based field-insensitive heavy-fermion behaviors and Pr-based quadrupole Kondo lattice behaviors accompanied by superconductivity induced by quadrupolar fluctuations.

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[1] M. S. Torikachvili, S. Jia, E. D. Mun, S. T. Hannahs, R. C. Black, W. K. Neils, D. Martien, S. L. Bud'ko, and P. C. Canfield, Proc. Natl. Acad. Sci. U.S.A. 104, 9960 (2007).
[2] F. Honda, Y. Taga, Y. Hirose, S. Yoshiuchi, Y. Tomooka, M. Ohya, J. Sakaguchi, T. Takeuchi, R. Settai, Y. Shimura, T. Sakakibara, I. Sheikin, T. Tanaka, Y. Kubo, and Y. Ōnuki, J. Phys. Soc. Jpn. 83, 044703 (2014).
[3] T. Kong, V. Taufour, S.L. Bud’ko, and P. Canfield, Phys. Rev. B 95, 155103 (2017).
[4] T. Takeuchi, S. Yasui, M. Toda, M. Matsushita, S. Yoshiuchi, M. Ohya, K. Katayama, Y. Hirose, N.
Yoshitani, F. Honda, K. Sugiyama, M. Hagiwara, K. Kindo, E. Yamamoto, Y. Haga, T. Tanaka, Y. Kubo, R. Settai, and Y. Ōnuki, J. Phys. Soc. Jpn. 79, 064609 (2010).

[5] R. Higashinaka, T. Maruyama, A. Nakama, R. Miyazaki, Y. Aoki, and H. Sato, J. Phys. Soc. Jpn. 80, 093703 (2011).

[6] A. Sakai and S. Nakatsuji, Phys. Rev. B 84, 201106(R) (2011).

[7] A. Yamada, R. Higashinaka, R. Miyazaki, K. Fushiya, T. D. Matsuda, Y. Aoki, W. Fujita, H. Harima, and H. Sato, J. Phys. Soc. Jpn. 82, 123710 (2013).

[8] R. Higashinaka, A. Yamada, T. D. Matsuda, Y. Aoki, AIP Advances 8, 125017 (2018).

[9] D. L. Cox, Phys. Rev. Lett. 59, 1240 (1987).

[10] A. Tsuruta and K. Miyake, J. Phys. Soc. Jpn. 84, 114714 (2015).

[11] A. Sakai and S. Nakatsuji, J. Phys. Soc. Jpn. 80, 063701 (2011).

[12] T. Onimaru and H. Kusunose, J. Phys. Soc. Jpn. 85, 082002 (2016).

[13] T. Yoshida, Y. Machida, K. Izawa, Y. Shimada, N. Nagasawa, T. Onimaru, T. Takabatake, A. Gourgout, A. Pourret, G. Knebel, and J.-P. Brison, J. Phys. Soc. Jpn. 86, 044711 (2017).

[14] R. Higashinaka, A. Nakama, R. Miyazaki, J. Yamaura, H. Sato, and Y. Aoki, J. Phys. Soc. Jpn. 86, 103703 (2017).

[15] T. Onimaru, K. T. Matsumoto, Y. F. Inoue, K. Umeo, T. Sakakibara, Y. Karaki, M. Kubota, and T. Takabatake, Phys. Rev. Lett. 106, 177001 (2011).

[16] A. Sakai, K. Kuga, and S. Nakatsuji, J. Phys. Soc. Jpn. 81, 083702 (2012).

[17] K. Matsubayashi, T. Tanaka, A. Sakai, S. Nakatsuji, Y. Kubo, and Y. Uwatoko, Phys. Rev. Lett. 109, 187004 (2012).

[18] M. Tsujimoto, Y. Matsumoto, T. Tomita, A. Sakai, and S. Nakatsuji, Phys. Rev. Lett. 113, 267001 (2014).

[19] K. Wakiya, T. Onimaru, K. Matsumoto, Y. Yamane, N. Nagasawa, K. Umeo, S. Kittaka, T. Sakakibara, Y. Matsushita, and T. Takabatake, J. Phys. Soc. Jpn. 86, 034707 (2017).

[20] B.D. White, D. Yazici, P.C. Ho, N. Kanchanavatee, N. Pouse, Y. Fang, A.J. Breindel, A.J. Friedman, and M.B. Maple, J. Phys.: Condens. Matter 27, 315602 (2015).

[21] Y. Hirose, T. Takeuchi, F. Honda, S. Yoshiuchi, M. Hagiwara, E. Yamamoto, Y. Haga, R. Settai, and Y. Ōnuki, J. Phys. Soc. Jpn. 84, 074704 (2015).

[22] E.D. Bauer, C. Wang, V.R. Fanelli1, J.M. Lawrence, E.A. Goremychkin, N.R. de Souza, F. Ronning, J.D. Thompson, A.V. Silhanek, V. Vildosola, A.M. Lobos, A.A. Aligia, S. Bobev, and J.L. Sarrao,
Phys. Rev. B 78, 115120 (2008).

[23] H. Sato, H. Sugawara, Y. Aoki, and H. Harima, Magnetic properties of filled skutterudites, in Handbook of Magnetic Materials, Vol. 18, edited by K.H.J. Buschow (Elsevier, Amsterdam, 2009) Chap. 1. pp. 1-110.

[24] Z. Hiroi, A. Onosaka, Y. Okamoto, J. Yamaura, and H. Harima, J. Phys. Soc. Jpn. 81, 124707 (2012).

[25] D. J. Safarik, T. Klimczuk, A. Llobet, D. D. Byler, J. C. Lashley, J. R. O’Brien, and N. R. Dilley, Phys. Rev. B 85, 014103 (2012).

[26] A. Onosaka, Y. Okamoto, J. Yamaura, and Z. Hiroi, J. Phys. Soc. Jpn. 81, 023703 (2012).

[27] M. M. Koza, A. Leithe-Jasper, E. Sischka, W. Schnelle, H. Borrmann, H. Mutka, and Y. Grin, Phys. Chem. Chem. Phys. 16, 27119 (2014).

[28] M. J. Winiarski, B. Wiendlocha, M. Sternik, P. Wiśniewski, J. R. O’Brien, D. Kaczorowski, and T. Klimczuk, Phys. Rev. B 93, 134507 (2016).

[29] A. Yamada, R. Higashinaka, T. D. Matsuda, and Y. Aoki, J. Phys. Soc. Jpn. 87, 033707 (2018).

[30] G. M. Sheldrick: SHELX-97: Program for the Solution for Crystal Structures, University of Göttingen, Germany, 1997.

[31] T. Hasegawa, N. Ogita, and M. Udagawa: J. Phys. Conf. Ser. 391 (2012) 012016.

[32] K. Wakiya, T. Onimaru, S. Tsutsui, T. Hasegawa, K. T. Matsumoto, N. Nagasawa, A. Q. R. Baron, N. Ogita, M. Udagawa, and T. Takabatake, Phys. Rev. B 93, 064105 (2016).

[33] S. Niemann and W. Jeitschko, J. Solid State Chem. 114, 337 (1995).

[34] T. Nasch, W. Jeitschko, and U. C. Rodewald, Z. Naturforsch. B 52, 1023 (1997).

[35] M. J. Kangas, D. C. Schmitt, A. Sakai, S. Nakatsuji, J. Y. Chan, J. Solid State Chem. 196, 274 (2012).

[36] A. Earnshaw and N. Greenwood, Chemistry of the Elements, Second ed., Butterworth-Heinemann (1997).

[37] H. Padamsee, J. E Neighbor, and C. A. Shiffman, J. Low Temp. Phys. 12, 387 (1973).

[38] D. C. Johnson, Supercond. Sci. Technol. 26, 115011 (2013).

[39] A. M. Clogston, Phys. Rev. Lett. 9, 266 (1962).

[40] E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966).

[41] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. 147, 295 (1966).

[42] K. Maki, Physics (Long Island City, N.Y.) 1, 21 (1964).

[43] B. Serin: in Superconductivity, ed. R. D. Parks (Marcel Dekker, New York, 1969) Vol. 2, Chap. 15.

[44] W. L. McMillan, Phys. Rev. 167, 331 (1968).
[45] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, and S. Alvarez, Dalton Trans. 21, 2832 (2008).

[46] P. Swatek, M. Kleinert, P. Wiśniewski, and D. Kaczorowski, Comput. Mater. Sci. 153, 461 (2018).