Superconductivity at 1 K in Y-Au-Si quasicrystal approximants

Takayuki Shiino^{1,*}, Girma Hailu Gebresenbut², Fernand Denoel¹, Roland Mathieu¹, Ulrich Häussermann³, and Andreas Rydh⁴

¹*Department of Materials Science and Engineering, Uppsala University, Box 35, 751 03 Uppsala, Sweden*

²*Department of Chemistry, Ångström Laboratory, Uppsala University, 751 21 Uppsala, Sweden*

³*Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden*

⁴*Department of Physics, Stockholm University, 106 91 Stockholm, Sweden*

(Received 24 November 2020; revised 5 February 2021; accepted 8 February 2021; published 22 February 2021)

We report the structural and physical properties of two Y-Au-Si (YAS) compounds, $\text{Y}_{14.1}\text{Au}_{69.2}\text{Si}_{16.7}$ and $\text{Y}_{15.4}\text{Au}_{68.6}\text{Si}_{16.1}$, which are 1/1 approximant crystals of a Tsai-type quasicrystal without intrinsic magnetic moments. The compounds differ by the presence of either a tetrahedron (Au,Si)₄ or a single Y atom at the center of their characteristic structural building unit consisting of concentric polyhedral shells. Both compounds exhibit bulk superconductivity, which seems to be of a conventional type-II BCS type. The compound with Y atoms at the cluster center has a slightly higher transition temperature with a sharper step in the specific heat than the compound with tetrahedral units. We discuss the occurrence of this superconducting state in the light of the specific structural and physical properties of these quasicrystal approximants.

DOI: [10.1103/PhysRevB.103.054510](https://doi.org/10.1103/PhysRevB.103.054510)

Quasicrystals (QCs) are unique crystals that possess long-range aperiodic order with diffraction symmetries forbidden in conventional crystals [1]. The formation conditions of QCs and their stability with respect to their related periodic and compositionally similar approximant crystals (ACs) have been intensely investigated but are still not well understood. Likewise, a complete understanding of the effects of quasiperiodic long-range order on physical properties can be challenging [2]. In this context, ACs have played a pivotal role in the analysis of atomic structure of QCs by providing the common local structural information [3–5]. They are also crucial as reference systems in efforts to extract the potential unique physical properties emerging from quasiperiodicity. The recent discovery of bulk superconductivity in the Al-Zn-Mg QC [6] (together with its related 1/1 and 2/1 ACs) has attracted a great deal of attention as this was a convincing report on the emergence of long-range order in the physical properties of QCs. Surprisingly, to the best of our knowledge, there is only one other report of superconductivity for periodic AC: Yb-Au-Ge (YAG) AC [7]. In that report, the relationship between superconductivity and magnetism is discussed; our current Y-Au-Si (YAS) system has similar structures as YAG while having no intrinsic magnetic moments, which enables us to investigate superconductivity in the absence of magnetism. There also exist intriguing theoretical predictions for

superconductivity on a quasiperiodic lattice [8,9], which have not been clarified in experiments yet.

The most prolific group of QCs are the icosahedral Tsai-type QCs, which are frequently accompanied by cubic 1/1 and 2/1 AC phases. Tsai-type QCs and their ACs can be described locally by the same atomic cluster building unit [3]. The conventional Tsai cluster, as shown in Fig. 1(a), is made up of four concentric polyhedral shells. The first shell is a dodecahedron, which is followed by an icosahedron. The third and fourth shell are an icosidodecahedron and a rhombic triacontahedron, respectively [3]. The clusters are arranged periodically in ACs and aperiodically in QCs. There is a tetrahedral unit at the cluster center [see Fig. 1(b)], which is orientationally disordered for the QCs and the cubic ACs. Recently, it has been shown that RE-Au-Si systems (RE = Gd, Tb, Ho) contain a second type of Tsai-type 1/1 approximant in which the orientationally disordered (Au/Si)₄ central tetrahedron is replaced by a single RE atom [10]; see Fig. 1(c). In the following, we refer to the former as IT phase (for inner-tetrahedron) and to the latter as CC phase (for cluster-center atom). The CC approximant phases, built from orientationally identical units that locally exhibit perfect icosahedral symmetry, provide additional opportunity to explore the ways in which aperiodicity may influence physical properties.

In this paper, we show that IT- and CC-type Y-Au-Si (YAS) 1/1 AC can be selectively synthesized, as has been demonstrated for the RE-Au-Si (RE = Gd, Tb, Ho) in Ref. [10]. We observe zero-resistance behavior at $T \sim 1$ K for YAS(IT) and YAS(CC). We checked the bulk nature of the superconductivity from their specific heat. The effect of a magnetic field on the resistivity and specific heat was also studied. The result indicates type-II Bardeen-Cooper-Schrieffer (BCS) superconductivity for both phases. We discuss the effect of the presence/absence of the disordered tetrahedral unit on the emergence of superconductivity.

*takayuki.shiino@angstrom.uu.se

FIG. 1. Atomic structure plots and calculated electron density obtained from single crystal x-ray diffraction refinement. (a) The four concentric shells of a Tsai-type cluster unit (as present in the Y-Au-Si phases) are as follows: dodecahedron, icosahedron, icosidodecahedron, and rhombic-triacontahedron (from left to right). The icosahedron (second) shell is exclusively constituted of Y atoms, while the other shells are built commonly from Au and Si atoms. The Si position at the cubic interstitial site with cartesian coordinates $(1/4, 1/4, 1/4)$ is indicated with a red arrow at the third shell. All atomic sites are represented by thermal ellipsoids with 70% probability. (b) Cluster center of the IT phase. The space group of the Y-Au-Si is $Im\bar{3}$ for both phases and cluster units are centered at the Wyckoff position 2a which yields a bcc packing of clusters where the triacontahedral shells interpenetrate [3]. (c) Cluster center of the CC phase. The cluster centers in (b) and (c) are presented as electron density isosurfaces (isosurface level is set at $13 \text{ e}/\text{\AA}^3$), revealing either an orientationally disordered M4 tetrahedral unit ($M \approx 55\% \text{ Au}$, $45\% \text{ Si}$) or a single Y atoms for the IT and CC phase, respectively. The diameter of the surrounding dodecahedral shell reduces from 7.3 to 6.8 Å. The orientational disorder of M4 is modeled as a twelve-vertex cuboctahedron (i.e., averaging three orientations) using the space group $Im\bar{3}$ position 24g and constraining the occupancy to $1/3$ [5].

The samples were synthesized by a self-flux method as described in detail in Ref. [10]. The starting nominal compositions were $\text{Y}_8(\text{Au}_{0.79}\text{Si}_{0.21})_{92}$ for YAS(IT) and $\text{Y}_{11}(\text{Au}_{0.79}\text{Si}_{0.21})_{89}$ for YAS(CC). More details about synthesis conditions and pictures of crystal specimens are presented in the Supplemental Material [11], which include Ref. [12].

Sample characterization was performed using powder-x-ray diffraction (PXRD), single-crystal-X-ray diffraction (SCXRD), differential scanning calorimetry, scanning electron microscopy (SEM) coupled with energy-dispersive x-ray spectroscopy (EDX). We refined the structure of the two phases from SCXRD data [see Figs. 1(a)–1(c), and crystallographic supporting information (cif files) [11]]. The determined mass density is $13.88 \text{ g}/\text{cm}^3$ for YAS(IT) and $13.70 \text{ g}/\text{cm}^3$ for YAS(CC). Figure 2 shows and compares their PXRD patterns. The shift of the peak positions manifests the significant change in lattice parameter, $a =$

FIG. 2. PXRD patterns (Cu-K α) and backscattered SEM image (upper left inset) of YAS(IT) and YAS(CC). The cross-section polished samples were glued together and investigated simultaneously. The lighter grey contrast indicates a lower concentration of Y atoms in the YAS(IT) phase. The inset to the right is a close up of the PXRD patterns, emphasizing the $40 \leq 2\theta \leq 48$ degree region. Polycrystalline silicon powder (marked as “Si”) was added as internal standard to correct for possible shifts of Bragg peaks due to experimental conditions. Diffraction background, Bragg peaks from Cu-K α 2 and off-centering contributions have been corrected in the plots.

$14.6525(17) \text{ \AA}$ and $14.549(3) \text{ \AA}$ for YAS(IT) and YAS(CC), respectively. The compositions were determined from EDX analysis: $\text{Y}_{14.1(3)}\text{Au}_{69.2(4)}\text{Si}_{16.7(3)}$ and $\text{Y}_{15.4(4)}\text{Au}_{68.6(3)}\text{Si}_{16.1(4)}$ for YAS(IT) and YAS(CC), respectively. The compositional difference was also confirmed from a contrast difference in the backscattered SEM image (see the left inset in Fig. 2).

The electrical resistivity and specific heat measurements were performed using a Bluefors dilution refrigerator equipped with a superconducting magnet. The electrical resistivity was measured using the conventional four-probe method. The specific heat data was collected using a differential membrane-based nanocalorimeter [13] down to $\sim 100 \text{ mK}$. The size of samples for specific heat measurement was approximately $50 \times 50 \times 20 \text{ }\mu\text{m}^3$ for YAS(IT) and $50 \times 50 \times 10 \text{ }\mu\text{m}^3$ for YAS(CC). The sample weight could not be measured due to the small sample sizes. For the dc magnetization measurements, we used a Physical Property Measurement System with the VSM option and an MPMS XL superconducting quantum interference device magnetometer (both from Quantum Design Inc.). We used polycrystalline samples for physical property measurements in this study.

Figure 3(a) shows the M - H curve for YAS(IT) and YAS(CC) measured at $T = 2 \text{ K}$. We observe a diamagnetic behavior which should be of bulk origin. Note that there is a paramagnetic contribution of magnetic impurities probably contained in the starting materials. Figure 3(b) shows the temperature dependence of magnetization M with the external field $H = 10 \text{ kOe}$. We observe a nearly constant diamagnetic behavior down to $\sim 80 \text{ K}$. The increase of M at low temperature should be due to a paramagnetic contribution of magnetic impurities detected also in the M - H measurement.

Figure 4(a) shows the temperature dependence of electrical resistivity of both phases. The value is normalized with the

FIG. 3. (a) M - H curve measured at $T = 2$ K. (b) Temperature dependence of M/H ($H = 300$ Oe and 10 kOe) in the temperature range of $2 \leq T \leq 300$ K. The peak at ~ 50 K is attributed to a parasitic contribution of oxygen [14] in the measurement system.

resistivity at 280 K ($\rho_{280\text{K}}$). The resistivity only shows a very weak temperature dependence down to low temperatures in both systems. This characteristic behavior is not uncommon in ACs. We observe the zero resistance drop for both YAS(IT) and YAS(CC) at ~ 1 K, indicating the emergence of superconductivity. Here we define the transition temperature T_c as the midpoint of the resistivity drop, and obtain $T_c = 0.95$ and 1.1 K for YAS(IT) and YAS(CC), respectively. Figures 4(b) and 4(c) show the magnetic-field dependence of electrical resistivity below T_c .

Figures 5(a) and 5(b) show the temperature dependence of specific heat divided by temperature (C/T). We determined the value normalized by mole of atoms (denoted mol) by comparing the high-temperature part (for $T \gtrsim 100$ K) with the summation of the Debye model (C_D/T) and electronic

FIG. 4. (a) Temperature dependence of the normalized electrical resistivity ($\rho/\rho_{280\text{K}}$) under zero field; note that $\rho_{280\text{K}} = 260$ and $310 \mu\Omega\text{cm}$ for YAS(IT) and YAS(CC), respectively. The inset shows a close-up view for the resistivity near T_c with the resistivity data under $H = 2.5$ kOe. (b), (c) Magnetic-field dependence of electrical resistivity for (b) YAS(IT) and (c) YAS(CC).

FIG. 5. (a), (b) Temperature dependence of C/T (blue curves) for YAS(IT) and YAS(CC), respectively. The green curve indicates the summation of the Sommerfeld coefficient (γ_n) and the Debye model (C_D/T), while the red curve indicates the deviation of C/T (blue) from the model (green): i.e., $C_{ND}/T = C/T - (\gamma_n + C_D/T)$. For the model curves, we set the Debye temperature to $\theta_D = 220$ K for both YAS(IT) and YAS(CC). (c), (d) Temperature dependence of C_{el}/T under magnetic fields for YAS(IT) and YAS(CC), respectively. (e) Plot of C_{el}^*/γ_n^*T as a function of T/T_c . (f) Plot of the upper critical field H_{c2} as a function of temperature. The filled-symbol points were obtained from specific heat data, while the open-symbol points were obtained from electrical resistivity data.

specific heat coefficient in the normal state (γ_n); see below for γ_n . See also the Supplemental Material [11]. We find that C/T deviates from the model ($\gamma_n + C_D/T$) below $T \sim 50$ K; see the deviation curve defined as the non-Debye contribution $C_{ND}/T \equiv C/T - (\gamma_n + C_D/T)$ in Figs. 5(a) and 5(b). This deviation should not be attributed to the disordered tetrahedra, since it appears in both systems; YAS(CC) does not have the tetrahedral unit. Our open question is whether C_{ND} is associated with acoustic excitations (characterized by $\omega \sim q^4$ dispersion) mentioned in Ref. [15] and/or possible soft phonons speculated from the ellipsoidal distribution of atoms (see Fig. 1).

The bulk nature of superconductivity was checked by measuring the specific heat. Figures 5(c) and 5(d) show the temperature dependence of C_{el}/T , where C_{el} indicates the electronic contribution to the specific heat. To obtain C_{el} , we

TABLE I. Specific heat coefficients and superconducting parameters of YAS(IT) and YAS(CC). The value of T_c is determined from the midpoint of the resistivity drop. The lower critical field $H_{c1}(0)$ at absolute zero is estimated from the following equation, which is valid for large κ value [16,18]: $H_{c1} = H_c \ln(\kappa)/\sqrt{2}\kappa$. The coherence length $\xi(0)$ and penetration depth $\lambda(0)$ at absolute zero are estimated using the following relations: $H_{c2}(0) = \Phi_0/2\pi\xi(0)^2$ [16] and $\kappa = \lambda/\xi$ (the definition of κ) where Φ_0 is the magnetic flux quanta.

Parameter	YAS(IT)	YAS(CC)
T_c (K)	0.95	1.1
γ_n [γ_n^*] (mJ/K ² mol)	1.14 [0.86]	0.96 [0.96]
β (mJ/K ⁴ mol)	0.137	0.157
$H_{c2}(0)$ (kOe)	5.6	6.6
$H_c(0)$ (Oe)	67	87
$H_{c1}(0)$ (Oe)	3.3	4.6
κ	59	53
$\xi(0)$ (nm)	24.2	22.3
$\lambda(0)$ (nm)	1420	1190

employed linear fitting to the C/T vs T^2 curve above T_c (see the Supplemental Material [11]). From the fitting of the zero-field data, we estimate the electronic (γ_n) and phonon (β) specific heat coefficients in the normal state. The values of specific-heat coefficients are listed in Table I. To extract the electronic part (C_{el}), we subtracted phonon contribution (i.e., βT^3) from the measured specific heat (C): i.e., $C_{el} = C - \beta T^3$. Our YAS(CC) sample exhibits a sharper step in C than the YAS(IT) sample. We observe a residual Sommerfeld term (denoted as $\gamma_0 = 0.28$ mJ/K² mol) for YAS(IT), which gives an offset in the C_{el}/T vs T plot as shown in Fig. 5(a); this could indicate the presence of disorder/inhomogeneity in the system. In order to compare these two systems, we define $C_{el}^* \equiv C_{el} - \gamma_0 T$ and $\gamma_n^* \equiv \gamma_n - \gamma_0$; note that in this approach, $\gamma_0 = 0$ (thus $C_{el}^* = C_{el}$ and $\gamma_n^* = \gamma_n$) for YAS(CC). In Fig. 5(e), we plot $C_{el}^*/\gamma_n^* T$ against T/T_c (for $H = 0$) to compare with the weak-coupling BCS theory. We set $T_c = 0.87$ and 1.1 K for YAS(IT) and YAS(CC), respectively. For YAS(IT), we used a T_c value that is $\sim 8\%$ smaller than one estimated from the midpoint of resistivity drop. The solid line indicates the theoretical curve expected from the weak-coupling BCS model. There seems to be only a slight deviation from the model, suggesting that the superconductivity of YAS(IT) and YAS(CC) is of a conventional (phonon-mediated) BCS type. The normalized specific heat step at T_c is estimated to be $\Delta C_{el}^*/\gamma_n^* T_c = 1.11$ and 1.36 for YAS(IT) and YAS(CC), respectively. The value of YAS(CC) is close to 1.43, as expected from the weak-coupling theory [16].

Figure 5(f) shows the plot of the upper critical field (H_{c2}) vs temperature. Note that the filled-symbol points are obtained from the midpoints of specific heat steps, whereas the open-symbol ones are from the resistivity measurement. From the lowest temperature value of H_{c2} presented in Fig. 5(f), we estimate $H_{c2}(0) \approx 5.6$ and 6.6 kOe for YAS(IT) and YAS(CC), respectively. From the data near T_c , we extract the value of slope [see the solid lines in Fig. 5(f)]: $dH_{c2}/dT = -8.49$ and -8.01 kOe/K for YAS(IT) and YAS(CC), respectively. This

allows us to estimate the orbital critical field at zero temperature using the Werthamer–Helfand–Hohenberg formula (in the dirty limit) [17]: $H_{c2}^{orb}(0) = -0.693T_c dH_{c2}/dT \approx 5.6$ and 6.1 kOe for YAS(IT) and YAS(CC), respectively. The H_{c2}^{orb} value is close to $H_{c2}(0)$ for both phases, and thus the orbital effect mainly contributes to H_{c2} rather than the spin paramagnetic effect [17]. The estimated values of superconducting parameters are listed in Table I. From the zero-field data in Figs. 5(c) and 5(d), we estimate the thermodynamic critical field H_c from the condensation energy $-H_c^2(T)/8\pi$ and the specific heat data (see Supplementary Materials [11] and Ref. [12] therein). The Ginzburg–Landau parameter κ at absolute zero is estimated from the relation $H_{c2} = \sqrt{2}\kappa H_c$ [16]. Since $\kappa \gg 1/\sqrt{2}$, the superconductivity for both phases should be of type II. See the caption of Table I for the other parameters.

According to the weak-coupling BCS theory, T_c can be expressed as $T_c = 1.14 \theta_D \exp[-1/VD(E_F)]$ in the condition $|VD(E_F)| \ll 1$, where V is the effective electron-electron interaction energy and $D(E_F)$ is the density of states at the Fermi energy [6]. Since $\theta_D \propto \beta^{-1/3}$ [18], there should be no significant difference for θ_D between YAS(IT) and YAS(CC). Thus the slightly higher T_c of YAS(CC) indicates that YAS(CC) may have larger $VD(E_F)$ value than YAS(IT). Assuming that $\gamma_n^* \propto D(E_F)$, the magnitude of $VD(E_F)$ should reflect γ_n^* .

We compare the superconductivity of YAS samples with that of YAG analogues [7], which are the only previously reported superconducting ACs having both the IT- and CC-type structures. Note that these structures are named AGY(I) and AGY(II) in Ref. [7] and correspond to IT-type and CC-type, respectively. Interestingly, the cluster-center Yb atoms in the CC-type YAG seems to have a magnetic moment, while the icosahedral Yb atomic shell does not. It is discussed in Ref. [7] that the relationship between the magnetic property and the superconductivity could be important in the YAG system. The CC-type YAG exhibits a lower T_c than the IT-type one. However, in the case of YAG systems it is unclear how the presence/absence of a disordered tetrahedral unit affects the nature of superconductivity in ACs due to the intrinsic magnetic Yb ions in the CC-type YAG. The present YAS system does not have an intrinsic magnetic moment and shows the opposite behavior: YAS(CC) has a slightly higher T_c (with the sharper step in C) than YAS(IT). The difference in the emergence of superconductivity between YAS(IT) and YAS(CC) could be attributed to the existence/absence of the cluster-center disordered-tetrahedral unit. We speculate that the absence of the disordered-tetrahedral unit enhance the homogeneity and atomic order, resulting in the sharper step in C at T_c . Since YAS(IT) and YAS(CC) have nearly the same value of T_c , it is suggested that the superconducting mechanism is common between the IT- and CC-phase. This allows us to conjecture that the superconductivity of the CC-type YAG is destabilized by the Yb magnetism, rather than induced by a Yb-related mechanism. We also note that the resistivity (at $T > T_c$) is higher in YAS samples than in YAG, which could be related to a stronger electron-phonon coupling in the YAS case.

In conclusion, we have synthesized the AC compounds YAS(IT) and YAS(CC) that differ by their cluster center. Both YAS(IT) and YAS(CC) show bulk superconductivity,

confirmed from specific-heat and transport measurements. Note that the observation of the Meissner effect is needed to complete the proof of the superconductivity. Both systems exhibit nearly the same T_c , suggesting that the mechanisms behind superconductivity are the same for IT and CC phases. However, YAS(CC) has a slightly higher T_c with a sharper step in C than YAS(IT), which could be reflecting the absence of disordered tetrahedra breaking the internal icosahedral symmetry in the local Tsai-type cluster. Since both YAS(IT) and YAS(CC) do not have intrinsic magnetic moments, our results could reflect an intrinsic effect of the presence/absence of

disordered tetrahedral units on the emergence of superconductivity in AC. Our results pave the road to further investigation of superconductivity in AC and QC.

We thank the Knut and Alice Wallenberg Foundation (Grant No. KAW 2018.0019), the Carl Tryggers Stiftelse för Vetenskaplig Forskning (Grant No. CTS 19:235), and the Swedish Research Council (VR) including Dnr 2016-04516. We also thank R. Maddu and J. Panda for their help in lithography to make electrical contact pads on sapphire substrates, which are used in our electrical resistivity measurement.

-
- [1] T. Fujiwara and Y. Ishii, *Quasicrystals*, Vol. 3 (Elsevier Science, Amsterdam, 2007).
 - [2] A. I. Goldman, Magnetism in icosahedral quasicrystals: current status and open questions, *Sci. Technol. Adv. Mater.* **15**, 044801 (2014).
 - [3] H. Takakura, C. P. Gómez, A. Yamamoto, M. De Boissieu, and A. P. Tsai, Atomic structure of the binary icosahedral Yb-Cd quasicrystal, *Nat. Mater.* **6**, 58 (2007).
 - [4] A. I. Goldman and R. F. Kelton, Quasicrystals and crystalline approximants, *Rev. Mod. Phys.* **65**, 213 (1993).
 - [5] C. P. Gómez and S. Lidin, Comparative structural study of the disordered MCd_6 quasicrystal approximants, *Phys. Rev. B* **68**, 024203 (2003).
 - [6] K. Kamiya, T. Takeuchi, N. Kabeya, N. Wada, T. Ishimasa, A. Ochiai, K. Deguchi, K. Imura, and N. K. Sato, Discovery of superconductivity in quasicrystal, *Nat. Commun.* **9**, 154 (2018).
 - [7] K. Deguchi, M. Nakayama, S. Matsukawa, K. Imura, K. Tanaka, T. Ishimasa, and N. K. Sato, Superconductivity of Au-Ge-Yb approximants with Tsai-type clusters, *J. Phys. Soc. Jpn.* **84**, 023705 (2015).
 - [8] S. Sakai, N. Takemori, A. Koga, and R. Arita, Superconductivity on a quasiperiodic lattice: Extended-to-localized crossover of Cooper pairs, *Phys. Rev. B* **95**, 024509 (2017).
 - [9] S. Sakai and R. Arita, Exotic pairing state in quasicrystalline superconductors under a magnetic field, *Phys. Rev. Research* **1**, 022002(R) (2019).
 - [10] G. Gebresenbut, T. Shiino, D. Eklöf, D. C. Joshi, F. Denoel, R. Mathieu, U. Häussermann, and C. Pay Gómez, Atomic-scale tuning of Tsai-Type clusters in RE-Au-Si systems (RE = Gd, Tb, Ho), *Inorg. Chem.* **59**, 9152 (2020).
 - [11] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.103.054510> for crystallographic supporting information (.cif files), details about synthesis conditions, pictures of the samples, additional information about specific heat data, and estimation of the thermodynamic critical field.
 - [12] J. P. Carbotte, Properties of boson-exchange superconductors, *Rev. Mod. Phys.* **62**, 1027 (1990).
 - [13] S. Tagliati, V. M. Krasnov, and A. Rydh, Differential membrane-based nanocalorimeter for high-resolution measurements of low-temperature specific heat, *Rev. Sci. Instrum.* **83**, 055107 (2012).
 - [14] S. Gregory, Magnetic Susceptibility of Oxygen Adsorbed on Graphite, *Phys. Rev. Lett.* **40**, 723 (1978).
 - [15] M. de Boissieu, Phonons and phasons in icosahedral quasicrystals, *Isr. J. Chem.* **51**, 1292 (2011).
 - [16] M. Tinkham, *Introduction to Superconductivity*, Dover Books on Physics Series (Dover, New York, 2004).
 - [17] M. B. Maple and Ø. Fischer, eds., *Superconductivity in Ternary Compounds II*, Topics in Current Physics, Vol. 34 (Springer, Berlin, 1982).
 - [18] Y. Wang, T. Plackowski, and A. Junod, Specific heat in the superconducting and normal state (2–300 K, 0–16 T), and magnetic susceptibility of the 38 K superconductor MgB_2 : evidence for a multicomponent gap, *Physica C Supercond.* **355**, 179 (2001).