Superconductivity in Sm-doped 1,3,5-triphenylbenzene

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We report the discovery of superconductivity at about 4.3 K in samarium-doped 1,3,5-triphenylbenzene. Using a solid-state reaction method, samarium-doped 1,3,5-triphenylbenzene samples are successfully synthesized. These samples are characterized by magnetization, x-ray diffraction, scanning electron microscope, and energydispersive spectroscopy measurements. The x-ray diffractions reveal that the sample crystallizes in the space group P2/m. The magnetization measurements reveal a superconducting transition at about 4.3 K. However, the superconducting shielding fraction is only about 1%, which is similar to previous reports of the superconductivity in other aromatic hydrocarbons. Magnetization hysteresis loops of the sample show that it is a typical type II superconductor. Our results indicate possible superconductivity in this organic material.

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I. INTRODUCTION

Organic superconductors have attracted a lot of attention for two fundamental reasons. First, it was predicted that the superconducting transition temperature may reach a high value [1]; second, the pairing mechanism in many organic superconductors seems to be beyond the Bardeen-Cooper-Schrieffer (BCS) paradigm [2]. The first observation of superconductivity in organic materials can be traced back to the 1980s, when Bechgaard et al. found superconductivity [3] with a transition temperature (T_c) of 0.9 K under a pressure of 12 kbar in (TMTSF)₂PF₆. Here TMTSF represents tetramethyltetraselenafulvalene $(C_{10}H_{12}Se_{14})$ and is an electron donor molecule. Since then, researchers have found a series of superconductors of this type by replacing PF_6 with AsF₆, SbF₆, ClO₄, and so on [4]. They are collectively referred to as $(TMTSF)_2X$, where X represents the electron acceptor molecule, because they all have the same electron donor molecule TMTSF and similar quasi-one-dimensional organic structures. Another major category of superconducting organic salts is $(BEDT-TTF)_2X$, where BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene ($C_{10}H_8S_8$) and X can be I₃, Cu(SCN)₂, Cu[N(CN)₂]Br, Cu[N(CN)₂]Cl, and so on. The highest superconducting transition temperature T_c can be increased to 14.2 K in the form of β' -(BEDT-TTF)₂ICl₂ by applying pressure to 8.2 GPa [5]. Differently from the former $(TMTSF)_2X$, the $(BEDT-TTF)_2X$ family is quasi-twodimensional. There are abundant interesting physical phenomena in these systems, such as the competition between various ground states, including antiferromagnetic order and superconductivity [6].

Concerning the pairing mechanism of these organic superconductors, the widely accepted picture is that the correlation effect may play a role here. For two-dimensional organic tuning the ratio between the Coulomb interaction potential Uand the band width W, one can change the system from a Mott insulator to a superconducting state [2,7,8]. In 1982, experimental data on the specific heat of (TMTSF)₂ClO₄ were explained by the BCS theory with strong superconducting fluctuations due to the low dimensionality [9]. In 2004, study of the compounds $(TMTSF)_2(ClO_4)_{1-x}(ReO_4)_x$ showed a suppressive effect on superconductivity caused by nonmagnetic impurities [10], which suggests that the superconducting order parameter may undergo a sign change with the momentum. Furthermore, a study of the spin lattice relaxation rate $(1/T_1)$ suggests the existence of an anisotropic order parameter with line nodes on the Fermi surface [11]. This goes against the original electron-phonon coupling-based BCS picture. However, a thermal conductivity experiment showed the opposite result; it indicates a nodeless superconducting gap function in the same organic superconductor [12]. Some theoretical investigations show that in the quasi-one-dimensional system $(TMTSF)_2PF_6$, superconductivity possibly has a *p*-wave pairing symmetry with a spin-triplet pairing state [13], while in the quasi-two-dimensional system (BEDT-TTF) $_2X$, it could have a *d*-wave pairing symmetry with a spin-singlet state [14]. In 2012, a refined field-angle-resolved calorimetry measurement on $(TMTSF)_2ClO_4$ supported *d*-wave singlet pairing [15]. However, one year later, an experiment on (TMTSF)₂ClO₄ by muon-spin rotation showed no indication of gap nodes on the Fermi surface and suggested p-wave triplet pairing [16]. Nuclear magnetic resonance (NMR) experiments on κ -(ET)₂Cu[N(CN)₂]Br exclude the BCS electron-phonon mechanism and suggest an unconventional pairing state with possible nodes in the gap function [17–19]. Recent NMR experiments on β -(ET)₂SF₅CH₂CF₂SO₃ also support pair symmetry of the *d* wave and suggest that pairing in this compound is driven by charge fluctuations [20]. In addition to NMR experiments, angle-resolved thermal-conductivity measurements on κ -(ET)₂Cu(NCS)₂ are inconsistent with *d*-wave

superconductors, it is in the vicinity of the Mott insulator. By

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pairing [21]. Numerous scanning tunneling spectroscopy measurements on κ -(ET)₂X have been done; the tunneling conductance curves obtained on the conducting plane and the temperature dependences of the tunneling spectra all indicate *d*-wave pairing [22–27]. In contrast to this conclusion, most experiments on specific heat measurements show the feature of nodeless gaps [28–32]; this creates puzzles in this field. Thus some debate still exists about the pairing symmetry of the superconducting order parameter of organic superconductors, but many more experiments show the existence of gap nodes, which excludes the possibility of phonon-mediated pairing and suggests, rather, another medium, like spin or charge fluctuations.

Beside these organic charge-transfer salts, superconductivity has also been discovered in many other carbon-based materials, such as graphite, molecular crystals of C₆₀, and other aromatic materials. In 1965, researchers first discovered superconductivity in carbon-based compounds [33]. Superconductivity was induced by intercalating alkali-metal potassium into graphite. Along this line, in 1991, researchers found superconductivity with a transition temperature of 18 K in potassium-doped C_{60} [34]. Later it was found that the T_c of Cs_2RbC_{60} can reach 33 K, and for Cs_3C_{60} the T_c is 40 K at 15 kbar [35,36]. Since the spin relaxation rate $1/T_1$ of Rb_3C_{60} shows a clear Hebel-Slichter peak at T_c , and the gap ratio $2\Delta/k_BT_c \approx 3.6$, both are consistent with the conventional BCS theoretical predictions, and thus the superconductivity may be attributed to a phonon-based mechanism [37]. Further theoretical calculations reveal that, despite the large Coulomb interaction and presence of a narrow band in A₃C₆₀ superconductors, the system is still not considered to be a Mott-Hubbard insulator. The superconductivity can be explained by a strong-coupling scenario with an enhanced Coulomb pseudopotential μ^* due to the strong electron interactions [38].

Recently, aromatic hydrocarbons have attracted a lot of attention because some of them can show superconductivity upon doping of alkaline metal or alkaline earth metal. In 2010, researchers synthesized K_{3.3}picene and found superconductivity with T_c 's of 7 and 18 K [39]. Subsequently superconductivity with 5 K in potassium-doped phenanthrene and superconductivity with 33 K in potassium-doped 1,2:8,9dibenzopentacene were reported [40,41]. Unfortunately, no repeat experiments on superconductivity at 33 K have been reported. Some experiments show that superconductivity may disappear if the aromatic materials are made in a pure state [42,43]. However, it remains unclear whether the compounds showing superconductivity are the same as those materials without superconductivity [42,43]. There is a theoretical prediction that the T_c is directly proportional to the number of benzene rings [41] in the constructing molecule. In recent years, it has been reported that there might be a very high superconducting transition temperature in K₃*p*-terphenyl, whose T_c can be as high as 120 K [44]. However, the diamagnetic volume at low temperatures in K₃*p*-terphenyl is only about 0.04%, thus it is insufficient to conclude that diamagnetic behavior is derived from superconductivity [45]. These experiments suggest that researchers can obtain superconductors with different T_c 's by adjusting the arrangement and number of benzene rings in molecular crystals. The existence of a positive pressure dependence of T_c and its correlation with

enhanced local magnetic moments suggest that the superductivity may be unconventional [40,46]. Since the superconducting shielding volume in all these aromatic superconductors is still low, the actual crystal structure and chemical formula which are responsible for superconductivity remain unclear. Considering that some of the reports of superconductivity in these materials are hard to reproduce, one cannot rule out the possibility that some observations of superconductivity are due to impurity phases.

In this paper, we report the synthesis of a new aromatic material which shows indications of superconductivity upon doping samarium, a magnetic rare-earth metal, into 1,3,5-triphenylbenzene at a molar ratio of 3:1. The T_c of Sm₃ 1,3,5-triphenylbenzene is about 4.3 K and the magnetic shielding fraction is only about 1%. A small shielding fraction seems to be a common feature in aromatic hydrocarbons [47]. Magnetization measurements show that the superconductivity observed in this compound has the characteristics of a type II superconductor.

II. EXPERIMENTAL DETAILS

The samples are synthesized by means of a solid-state reaction. Samarium metal (> 99%; GRINM) is ground into powder and mixed with 1,3,5-triphenylbenzene (> 99%; Alfa Aesar) at a molar ratio of 3:1. Then the mixture is ground and pressed into pellets. All procedures are handled in a glovebox filled with argon gas (O $_2$ and H $_2O$ at less than 0.1 ppm). The pellet is then put into an Al₂O₃ crucible and sealed in a quartz tube under a high vacuum. The quartz tube is placed in a furnace, heated up to 500 K in 600 min, and kept at this temperature for 6 days. Finally, we get samples of a dark color. The samples are not sensitive to air, thus we can make several kinds of measurements. The x-ray diffraction (XRD) measurements are performed on the raw material 1,3,5-triphenylbenzene and the resultant sample at room temperature with a Bruker D8 Advanced diffractometer with $CuK_{\alpha 1}$ radiation. XRD patterns are obtained in the 2θ range from 10° to 90°. The morphology and surface compositions of Sm₃ 1,3,5-triphenylbenzene are investigated by scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS) methods with a Phenom ProX instrument. An accelerating voltage of 15 kV is used for the EDS measurements. Magnetization measurements are carried out on a superconducting quantum interference device with the vibrating sample option (SQUID-VSM; Quantum Design).

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the magnetic susceptibility χ for a bulk sample of Sm₃ 1,3,5triphenylbenzene measured in zero-field-cooled (ZFC) and field-cooled (FC) modes under a magnetic field of 10 Oe. The sample has a mass of about 1 mg. Since the total magnetization signal is very small, the data are a bit noisy. When the field is increased, the total magnetization becomes stronger and the noise is weaker. The χ -versus-T plot in the inset shows a drastic decrease below 4.3 K, which is determined as the superconducting transition temperature T_c . We can see that



FIG. 1. Temperature dependence of the magnetic susceptibility χ measured in the ZFC and FC modes at 10 Oe for the sample Sm₃ 1,3,5-triphenylbenzene. Inset: Enlarged view of χ versus *T* near the transition temperature.

the transition is very sharp, with a width of less than 1 K. The diamagnetic signal χ measured in the ZFC mode can be attributed to the magnetic shielding of the Meissner effect in the superconducting state. By subtracting ZFC data from FC data at 2.5 K, we can obtain $\Delta \chi$, which is about 2.5×10^{-4} emu g^{-1} Oe⁻¹. Assuming that the density of the sample is about 3.5 g/cm³, according to the formula $V_S = 4\pi \Delta \chi \rho$ (V_S is the shielding fraction), we get a magnetic shielding fraction of about 1%. It should be emphasized that, for all the polycyclic aromatic hydrocarbon superconductors reported to date, the shielding fractions are very small [47]. Although these shielding fractions can be increased by pressing the powder samples into tablets [39,40], they are still very small compared to those of other superconductors. It has been discussed that these small shielding fractions in powder samples may be attributed to the penetration depth effect. According to London's theory, when the penetration depth is larger than the grain size, the measured diamagnetization can be very small [39]. For organic superconductors, the superfluid density is very low, thus the London penetration depth is very large, yielding a possibility for this explanation. But this scenario remains valid only when the sample is constructed of unconnected grains and the superconducting phase is in the percolative form. Another characteristic of the magnetic susceptibility is that the signal measured in the FC mode is small or unmeasurable. The small FC magnetization and the clear difference between ZFC and FC magnetizations were observed in other type II superconductors with strong vortex pinning [48]. Following this logic, the small FC magnetization in the present samples may be attributed to the vortex pinning, perhaps arising from the pinning by the grain boundaries. In general, the magnetic shielding volume estimated in London's theory in this type of superconductors is small; further investigation is needed to unravel the reason.

In order to rule out other possibilities for the observed superconductivity, we have checked the literature and found that some Sm-based superconductors exist. These include, for example, Sm₁ phenanthrene ($T_c = 6 \text{ K}$) [49], Sm₁ picene



FIG. 2. Temperature dependence of the magnetic susceptibility χ measured in the ZFC and FC modes under different magnetic fields.

 $(T_c = 4 \text{ K})$ [50], and Sm₁ chrysene $(T_c = 5-6 \text{ K})$ [50], which all show small superconducting volumes. For inorganic superconductors, we know that $SmBa_2Cu_3O_7$ and $SmFeAsO_{1-x}F_x$ are superconductors. Upon checking the literature, we have not found any form of superconductors made by the alloy or compounds of Sm and carbon, in either binary or multielement compounds. Besides, we have tried to synthesize Sm with other organic molecules, such as Sm-doped 1,3,5-Tris(bromomethyl)benzene and Sm-doped triphenylene, using the same method, and the samples are not superconductive. Furthermore, if we synthesize the sample at an elevated temperature, such as 600 K, with a mixture of Sm and 1,3,5-triphenylbenzene, no uniform phase is formed and no superconductivity is observed. All these findings point to the fact that the superconductivity observed here may arise from the Sm-doped 1,3,5-triphenylbenzene.

Figure 2 shows the temperature dependence of the magnetic susceptibility χ under different magnetic fields with measurements in the ZFC and FC modes for the sample Sm_3 1,3,5-triphenylbenzene. As we can see, the diamagnetic signals get smaller and smaller with increasing magnetic fields. However, even when the magnetic field is increased up to 1000 Oe, we still see a decrease in χ at 4 K. This result suggests that the H_{c2} of the sample may be large, far beyond 1000 Oe. It should be noted that even though the steplike transition still exists, above 200 Oe the diamagnetic signal disappears; instead, a paramagnetic background emerges. This may be understood in that the superconducting portion of the sample is very small; most areas of the sample are nonsuperconducting and contribute a relatively large paramagnetic signal. Due to the paramagnetic background, the magnetic susceptibility of the nonsuperconducting portion becomes more and more prominent when the magnetic field gets higher and higher. Such clear paramagnetic background signals can be clearly seen in the following measurements of magnetization hysteresis loops (MHLs). One can see in Fig. 2 that, when the magnetic field is small, the signal shows some



FIG. 3. (a) Magnetization hysteresis loops (MHLs) of Sm₃ 1,3,5triphenylbenzene from 2.5 to 5 K. Inset: Enlarged view of the MHLs at 4 K. (b) Magnetization hysteresis loops (Δ MHLs) of Sm₃ 1,3,5triphenylbenzene with the MHL measured at 5 K subtracted; the latter is taken as the background.

noise. This is due to the small superconducting signal of the sample compared with the resolution of the instrument.

Figure 3(a) shows the MHLs of Sm₃ 1,3,5triphenylbenzene with a range of magnetic field from -1000 to 1000 Oe at different temperatures. An enlarged view of the MHL at 4 K is shown in the inset in Fig. 3(a). As we can see, Meissner-effect-like behavior is detectable, although a relatively strong paramagnetic background exists. From the Meissner-effect-like behavior, we can roughly determine the H_{c1} of the sample at 2.5 K, which is about 89 Oe. This is smaller than the value of 175 Oe at 2 K for K_3 phenanthrene with a T_c of 5 K [40]. Here H_{c1} means the threshold at which the magnetic field starts to penetrate the sample and is determined by the point of deviation from the linear line on the slope of the initial magnetization curve [51]. The inset in Fig. 6 shows the specific way in which to define H_{c1} . The shielding behaviors of MHLs decay gradually with increasing temperature and disappear at 5 K. It should be emphasized that when the temperature is lower than 4 K, the hysteresis loop exhibits some jumps between 0 and 1000 Oe. This phenomenon appears in repeated measurements, and we think it may be induced by the flux jump effect. Figure 3(b) shows the subtracted magnetization hysteresis loops (Δ MHLs) of Sm₃ 1,3,5-triphenylbenzene with an MHL at 5 K as background, i.e., $\Delta M = M(H, T) - M(H, 5 K)$.



FIG. 4. (a) X-ray diffraction patterns for Sm_3 1,3,5triphenylbenzene powders. Inset: Schematic molecular structure of Sm_3 1,3,5-triphenylbenzene. (b) X-ray diffraction patterns for the raw material 1,3,5-triphenylbenzene. Inset: Schematic molecular structure of 1,3,5-triphenylbenzene.

And the Meissner-effect-like behaviors become more visible after subtracting the background. The superconductivity can be repeatedly observed in samples in different rounds of synthesis. We have tried 10 rounds of synthesis; at least 50% reproducibility is achieved if the same fabrication procedures are followed.

Figure 4(a) shows the XRD patterns of samarium-doped 1.3.5-triphenylbenzene at a molar ratio of 3:1. Figure 4(b) shows the XRD pattern of the raw material of 1,3,5triphenylbenzene, which crystallizes in the space group *Pmmm.* The lattice parameters determined here are a =7.47 Å, b = 19.66 Å, and c = 11.19 Å, which are consistent with previous results [52]. Comparing the XRD results in Figs. 4(a) and 4(b), it is obvious that the XRD pattern changes greatly after doping 1,3,5-triphenylbenzene with samarium. By fitting to the XRD pattern, we find that the Sm-doped sample may crystallize in the space group P2/m. And the lattice parameters determined are a = 6.7384 Å, b = 4.4798 Å, c =5.6726 Å, and $\beta = 90.746^{\circ}$ for Sm₃ 1,3,5-triphenylbenzene. The space group and lattice constants are determined by the FULLPROF program with a self-consistent fitting to the peak positions [53]. The insets in Figs. 4(a) and 4(b) present the schematic molecular structure of Sm-doped and pure 1,3,5triphenylbenzene, respectively. For 1,3,5-triphenylbenzene, which consists of four benzene rings, three benzene rings are connected with the middle benzene ring by C-C bonds at the interval position. We stress that, for Sm₃ 1,3,5triphenylbenzene, the drawing in the inset in Fig. 4(a) is just a schematic. From the XRD data we can only obtain the space group and approximate lattice structure. Here the difficulty is that we do not know the occupation sites of the Sm atoms and the 1,3,5-triphenylbenzene molecules or the orientations of the latter within a unit cell. For a precise determination of the structure we need to do further refined diffraction measurement experiments with a synchrotron and quantum theory calculations. These efforts are left for the



FIG. 5. Scanning electron microscope image and compositional analysis of the Sm_3 1,3,5-triphenylbenzene sample. EDS spectrum in which samarium, carbon, and oxygen are detectable. Inset: SEM image of one area of the sample. The yellow rectangle shows the area of the EDS measurement. The brightness of the frame reflects the composition of Sm.

future. However, since the superconducting shielding fraction seems to be small, it remains unclear whether or not the structure determined here reflects a superconducting phase. One possible explanation for the small magnetic shielding volume is that the penetration depth is much larger than the superconducting grain size, thus the total magnetization of the granular samples can be very small.

Figure 5 shows the SEM image and composition analysis. The inset displays an SEM photograph of the sample surface and the yellow rectangle shows the distribution of Sm. The brightness of the yellow color indicates the intensity of the EDS signal of samarium. One can see clearly that samarium is uniformly distributed in the body of the sample. The figure represents the compositional analysis (EDS) spectrum with the indices of different elements. The position and intensity of the peaks in the EDS spectrum correspond well to the expected elements. The oxygen element peaks can also be seen due to exposure to air.

Figure 6 shows the *H*-versus-*T* phase diagram of the Sm₃ 1,3,5-triphenylbenzene sample. On the basis of data shown in the inset, we obtain H_{c1} versus *T*, which is represented by black squares. The method of defining H_{c1} has been reported in the discussion about Fig. 3. We try to fit $H_{c1}(T)$ with the empirical formula $H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^2]$. We get the value $H_{c1} \approx 126$ Oe at 0 K. The green line is the fitting line. Based on the data shown in Fig. 2, the H_{c2} -versus-*T* phase line is obtained and represented by red circles. Here T_c is determined by the crossing point of the two linear lines corresponding to the normal-state flat background and the steep superconducting transition line, as shown in the inset in Fig. 1. It is difficult to determine the value of H_{c2} at



^[2] For a recent review, see, for example, A. Ardavan, S. Brown, S. Kagoshima, K. Kanoda, K. Huroki, H. Mori, M. Ogata, S. Uji, and J. Wosnitza, J. Phys. Soc. Jpn. 81, 011004 (2012).



FIG. 6. *H*-versus-*T* phase diagram. Black squares represent H_{c1} and red circles represent H_{c2} . Inset: Method of defining H_{c1} .

0 K. However, based on the trend of $H_{c2}(T)$ near T_c , we can conclude that $H_{c2}(0)$ should be very high.

IV. CONCLUSIONS

In conclusion, by using a solid-state reaction method, we successfully synthesize Sm₃ 1,3,5-triphenylbenzene samples. The magnetic susceptibility of the samples shows a diamagnetic transition at about 4.3 K. The diamagnetic transition is proved to be a superconducting transition by further measuring the temperature dependence of the magnetization under different magnetic fields and MHLs. The MHLs indicate a type II superconductivity for this compound. Fitting to the index peaks of the XRD patterns of the sample Sm₃ 1,3,5-triphenylbenzene reveals that it crystallizes in the space group P2/m with a = 6.7384 Å, b = 4.4798 Å, c = 5.6726 Å, and $\beta = 90.746^{\circ}$. The SEM image shows that the samarium element is uniformly distributed in the sample. Since the superconducting volume determined here is still quite small, it remains to resolve whether the superconductivity can be attributed to the determined structure. Thus further efforts to resolve the superconducting phase are worthwhile. However, we must note that Sm doping is necessary for the emergence of superconductivity.

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- [3] D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. Lett. 41, 95 (1980).
- [4] S. S. P. Parkin, M. Ribault, D. Jérome, and K. Bechgaard, J. Phys. C 14, 5305 (1981).

- [5] H. Taniguchi, M. Miyashita, K. Uchiyama, K. Satoh, N. Moeri, H. Okamoto, K. Miyagawa, K. Kanoda, M. Hedo, and Y. Uwatoko, J. Phys. IV France 114, 273 (2004).
- [6] D. Jérome, Science 252, 1509 (1991).
- [7] K. Kanoda, Hyperfine Interact. 104, 235 (1997).
- [8] R. McKenzie, Science **278**, 820 (1997).
- [9] P. Garoche, R. Brusetti, D. Jérome, and K. Bechgaard, J. Phys. Lett. 43, 147 (1982).
- [10] N. Joo, P. Auban-Senzier, C. R. Pasquier, P. Monod, D. Jérome, and K. Bechgaard, EPJ B 40, 43 (2004).
- [11] M. Takigawa, H. Yasuoka, and G. Saito, J. Phys. Soc. Jpn. 56, 873 (1987).
- [12] S. Belin and K. Behnia, Phys. Rev. Lett. 79, 2125 (1997).
- [13] I. J. Lee, S. E. Brown, W. G. Clark, M. J. Strouse, M. J. Naughton, W. Kang, and P. M. Chaikin, Phys. Rev. Lett. 88, 017004 (2001).
- [14] P. M. Chaikin, M.-Y. Choi, and R. L. Greene, J. Magn. Magn. Mater. 31, 1268 (1983).
- [15] S. Yonezawa, Y. Maeno, K. Bechgaard, and D. Jérome, Phys. Rev. B 85, 140502(R) (2012).
- [16] F. L. Pratt, T. Lancaster, S. J. Blundell, and C. Baines, Phys. Rev. Lett. **110**, 107005 (2013).
- [17] H. Mayaffre, P. Wzietek, D. Jérome, C. Lenoir, and P. Batail, Phys. Rev. Lett. 75, 4122 (1995).
- [18] K. Kanoda, K. Miyagawa, A. Kawamoto, and Y. Nakazawa, Phys. Rev. B 54, 76 (1996).
- [19] S. M. De Soto, C. P. Slichter, A. M. Kini, H. H. Wang, U. Geiser, and J. M. Williams, Phys. Rev. B 52, 10364 (1995).
- [20] G. Koutroulakis, H. Kuhne, H. H. Wang, J. A. Schlueter, J. Wosnitza, and S. E. Brown, arXiv:1601.06107.
- [21] K. Izawa, H. Yamaguchi, T. Sasaki, and Y. Matsuda, Phys. Rev. Lett. 88, 027002 (2001).
- [22] K. Ichimura and K. Nomura, Phys. Soc. Jpn. 75, 051012 (2006).
- [23] T. Arai, K. Ichimura, K. Nomura, S. Takasaki, J. Yamada, S. Nakatsuji, and H. Anzai, Phys. Rev. B 63, 104518 (2001).
- [24] K. Ichimura, M. Takami, and K. Nomura, J. Phys. Soc. Jpn. 77, 114707 (2008).
- [25] Y. Oka, H. Nobukane, N. Matsunaga, and K. Nomura, J. Phys. Soc. Jpn. 84, 064713 (2015).
- [26] D. Guterding, S. Diehl, M. Altmeyer, T. Methfessel, U. Tutsch, H. Schubert, M. Lang, J. Muller, M. Huth, H. O. Jeschke, R. Valentí, M. Jourdan, and H.-J. Elmers, Phys. Rev. Lett. 116, 237001 (2016).
- [27] D. Guterding, M. Altmeyer, H. O. Jeschke, and R. Valenti, Phys. Rev. B 94, 024515 (2016).
- [28] H. Elsinger, J. Wosnitza, S. Wanka, J. Hagel, D. Schweitzer, and W. Strunz, Phys. Rev. Lett. 84, 6098 (2000).
- [29] J. Wosnitza, X. Liu, D. Schweitzer, and H. J. Keller, Phys. Rev. B 50, 12747 (1994).
- [30] S. Wanka, J. Hagel, D. Beckmann, J. Wosnitza, J. A. Schlueter, J. M. Williams, P. G. Nixon, R. W. Winter, and G. L. Gard, Phys. Rev. B 57, 3084 (1998).

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- [31] J. Muller, M. Lang, R. Helfrich, F. Steglich, and T. Sasaki, Phys. Rev. B 65, 140509(R) (2002).
- [32] R. Beyer and J. Wosnitza, Low Temp. Phys. 39, 225 (2013).
- [33] N. B. Hannay, T. H. Geballe, B. T. Matthias, K. Andres, P. Schmidt, and D. Macnair, Phys. Rev. Lett. 14, 225 (1965).
- [34] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature 350, 600 (1991).
- [35] K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, and S. Kuroshima, Nature 352, 222 (1991).
- [36] T. T. M. Palstra, O. Zhou, Y. Iwasa, P. E. Sulewski, R. M. Fleming, and B. R. Zegarski, Solid State Commun. 93, 327 (1995).
- [37] R. F. Kiefl, W. A. Macfarlane, K. H. Chow, S. Dunsiger, T. L. Duty, T. M. F. Johnston, J. W. Schneider, J. Sonier, L. Brard, R. M. Strongin, J. E. Fischer, and A. B. Smith, Phys. Rev. Lett. 70, 3987 (1993).
- [38] O. Gunnarsson, Rev. Mod. Phys. 69, 575 (1996).
- [39] R. Mitsuhashi, Y. Suzuki, Y. Yamanari, H. Mitamura, T. Kambe, N. Ikeda, H. Okamoto, A. Fujiwara, M. Yamaji, N. Kawasaki, Y. Maniwa, and Y. Kubozono, Nature 464, 76 (2010).
- [40] X. F. Wang, R. H. Liu, Z. Gui, Y. L. Xie, Y. J. Yan, J. J. Ying, X. G. Luo, and X. H. Chen, Nat. Commun. 2, 507 (2011).
- [41] M. Xue, T. Cao, D. Wang, Y. Wu, H. Yang, X. Dong, J. He, F. Li, and G. F. Chen, Sci. Rep. 2, 389 (2012).
- [42] S. Heguri, M. Kobayashi, and K. Tanigakí, Phys. Rev. B 92, 014502 (2015).
- [43] F. D. Romero, M. J. Pitcher, C. I. Hiley, G. F. S. Whitehead, S. Kar, A. Y. Ganin, D. Antypov, C. Collins, M. S. Dyer, G. Klupp, R. H. Colman, K. Prassides, and M. J. Rosseinsky, Nat. Chem. 9, 644 (2017).
- [44] R. S. Wang, Y. Gao, Z. B. Huang, and X. J. Chen, arXiv:1703.06641.
- [45] W. H. Liu, H. Lin, R. Z. Kang, X. Y. Zhu, Y. Zhang, S. Zheng, and H.-H. Wen, Phys. Rev. B 96, 224501 (2017).
- [46] X. F. Wang, Y. J. Yan, Z. Gui, R. H. Liu, J. J. Ying, X. G. Luo, and X. H. Chen, Phys. Rev. B 84, 214523 (2011).
- [47] Y. Kubozono, R. Eguchi, H. Goto, S. Hamao, T. Kambe, T. Terao, S. Nishiyama, L. Zheng, X. Miao, and H. Okamoto, J. Phys. Condens. Matter 28, 334001 (2016).
- [48] H. Yang, B. Shen, Z. Wang, L. Shan, C. Ren, and H.-H. Wen, Phys. Rev. B 85, 014524 (2012).
- [49] X. F. Wang, X. G. Luo, J. J. Ying, Z. J. Xiang, S. L. Zhang, R. R. Zhang, Y. H. Zhang, Y. G. Yan, A. F. Wang, P. Chen, G. J. Ye, and X. H. Chen, J. Phys. Condens. Matter 24, 345701 (2012).
- [50] G. A. Artioli, F. Hammerath, M. C. Mozzati, P. Carretta, F. Corana, B. Mannucci, S. Margadonna, and L. Malavasi, Chem. Commun. 51, 1092 (2015).
- [51] H. Lei, X. Zhu, and C. Petrovic, Europhys. Lett. 95, 17011 (2011).
- [52] Y. C. Lin and D. E. Williams, Acta Cryst. B 31, 318 (1975).
- [53] J. Rodríguez-Carvajal, Physica B 192, 55 (1993).