Since the discovery of high-$T_c$ superconductivity in iron-based compounds [1, 2], great efforts have been devoted to expanding the family of Fe-based superconductors (FeSCs) [3, 4]. Structurally, all the FeSCs discovered to date contain two-dimensional Fe$_2$X$_2$ ($X =$ As or Se) layers, crystallizing in different crystal-structure types [5]. The relatively simple structures include (i) 11-type FeSe [6], (ii) 111-type LiFeAs [7], (iii) 122-type (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ [8], (iv) 122$^*$-type K$_x$Fe$_2$Se$_2$ [9], and (v) 1111-type LaFeAsO$_{1-x}$F$_x$ [1]. There are also complex structures with perovskite-like blocks serving as the spacer layers [10–13]. In recent years, novel-structure-bearing FeSCs were discovered continually [14–20], which have brought growing vitality in the related research [21, 22].

We proposed a rational route to new FeSCs via a strategy of structural design [5]. Nine structures were suggested to host superconductivity potentially. One of the candidate structures, exemplified as 1144-type ‘KLaFe$_4$As$_4$’, was recently realized in AkAeFe$_4$As$_4$ (Ak = K, Rb, Cs; Ae = Ca, Sr) which show superconductivity at 31–36 K [23]. Additional 1144-type members containing rare-earth element Eu, namely AkEuFe$_2$As$_2$, with Ak = Rb and Cs, were subsequently synthesized [24–26], in which not only superconductivity but also full ferromagnetism (in the Eu sublattice) emerge [25, 26]. Following our structure-design strategy, very recently, we also succeeded in realizing another candidate structure in a series of quinary iron fluoro-arsenides AkCa$_2$Fe$_4$As$_4$F$_2$ (Ak = K, Rb, Cs) [27, 28]. These new 12442-type FeSCs, superconducting at about 30 K, are the first class of iron pnictides that contains separate double Fe$_2$As$_2$ layers.

As a matter of fact, the above two new structures belong to the category of structural intergrowth, similar to the multi-element FeSC Ba$_3$Ti$_2$Fe$_2$As$_2$O discovered earlier [16]. AkAeFe$_4$As$_4$ can be viewed as an intergrowth of AkFe$_2$As$_2$ and AeFe$_2$As$_2$, while AkCa$_2$Fe$_4$As$_4$F$_2$ (Ak = K, Rb, Cs) is an intergrowth of 1111-type CaFeAsF and 122-type AkFe$_2$As$_2$ (Ak = K, Rb, Cs). As expected, lattice match is very crucial.
for obtaining an intergrowth compound [5, 23]. To expand the 12442-type superconducting family, therefore, one should first consider a good lattice match between the constituent crystallographic block layers. Another consideration is to find a higher \( T_c \) as far as possible. Note that there are 1111-type iron oxyarsenides \( RFe_2AsO \) (\( R = \) rare-earth elements) whose lattice parameters \( a \) are close to those of \( AFe_2As_2 \), and additionally, doped \( GdFeAsO \) shows a record high \( T_c \) of 56 K in bulk FeSCs [29], we thus chose \( R = Gd \) and \( Ak = Rb \) (the \( a \) axes of \( GdFeAsO \) and \( RbFe_2As_2 \) are 3.915 Å [29] and 3.863 Å [30], respectively) to explore a 12442-type \( \text{oxyarsenide} \text{FeSC} \). In this Letter, we report synthesis, crystal structure and physical properties of the target compound \( RbGd_2Fe_2As_2O_2 \). The new material is hole doped without extrinsic chemical doping, which exhibits bulk superconductivity at \( T_c = 35 \text{ K} \), the highest \( T_c \) among hole-doped \( \text{oxyarsenide} \text{FeSCs} \).

The target material \( RbGd_2Fe_2As_2O_2 \) was synthesized by a solid-state reaction method, similar to our previous report [27]. The source materials were \( Rb \) ingot (99.75%), \( Gd \) ingot (99.9%), \( Gd_2O_3 \) powder (99.9%), \( Fe \) powders (99.998%) and \( As \) pieces (99.999%). \( Gd_2O_3 \) was heated to 1173 K for \( 10 \) h. After that, mixtures of \( RbFe_2As_2 \), \( GdAs \), \( Gd_2O_3 \), \( FeAs \) and \( As \) pieces were prepared by direct solid-state reactions of their constituent elements at 1023 K for \( 15 \) h. We also prepared an additional intermediate material ‘\( Rb_1.05Fe_2As_2 \)” by reacting \( Rb \) metal and \( FeAs \) at 923 K for \( 10 \) h. After that, mixtures of \( RbFe_2As_2 \), \( GdAs \), \( Gd_2O_3 \), \( FeAs \) and \( Fe_2As \) in the stoichiometric ratio were pressed into pellets, and then loaded in an alumina tube. To avoid the chemical reactions with quartz tubes, a Ta tube was jacketed before putting the sample into an quartz ampoule. This sample-loaded evacuated quartz ampoule was sintered at 1238 K for \( 40 \) h, and then cooled down by switching off the furnace. The product was found to be stable in air.

Powder x-ray diffraction (XRD) was carried out on a PANalytical x-ray diffractometer (Empyrean) with a \( CuK_{\alpha 1} \) monochromator (Johansson 1 x Ge111 Cu/Co) at room temperature. The collected XRD data (20° ≤ θ ≤ 150°) were used for a Rietveld refinement. The structural refinement was based on the 12442-type structural model [27], using the software Rietan-FP [31]. The occupation factor of each atom was fixed to 1.0. The refinement easily converges, which yields a weighted reliable factor of \( R_{wp} = 0.12(1) \) and a goodness-of-fit of \( S = 1.12 \), indicating the high quality of the refined crystallographic data.

The physical property measurements were done on a physical property measurement system (Quantum Design, PPMS-9) and a magnetic property measurement system (Quantum Design, MPMS-XL5). We employed a standard four-electrode method and the ac transport option for the electrical resistivity measurement. For the Hall measurement, four electrodes were made on a thin-square sample, forming a cross-shaped configuration. The excitation current was 20 mA, and the magnetic field swept from −80 to 80 kOe. The heat capacity was measured by a thermal relaxation method using a square-shaped sample plate (22.5 mg). The dc magnetic susceptibility was measured using a sample rod whose demagnetization factor is estimated to be 0.12(1).

### Table 1. Crystallographic data of \( RbGd_2Fe_2As_2O_2 \) in comparison with those of \( KCa_2Fe_4As_4F_2 \) [27]. The space group is \( 14nmm \) (No. 139). The atomic coordinates are as follows: \( K/Rb \) 2\( (0, 0, 0) \), \( Ca/Gd \) 4\( (0.5, 0.5, z) \), \( Fe \) 8\( (0.5, 0.5, z) \), \( As1 \) 4\( e(0.5, 0.5, z) \), \( As2 \) 4\( e(0, 0, z) \), \( F/4d(0.5, 0, 0.25) \).

|                  | \( \text{RbGd}_2\text{Fe}_2\text{As}_2\text{O}_2 \) | \( \text{KCa}_2\text{Fe}_4\text{As}_4\text{F}_2 \) |
|------------------|-----------------------------------------------|-----------------------------------------------|
| \( a \) (Å)      | 3.9014(2)                                     | 3.8684(2)                                     |
| \( c \) (Å)      | 31.343(2)                                     | 31.007(1)                                     |
| \( V \) (Å³)     | 477.06(4)                                     | 463.99(3)                                     |
| Coordinates \( z \) | \( 0.2138(1) \)                             | \( 0.2085(2) \)                             |
| \( \text{Fe} \)  | \( 0.1138(2) \)                             | \( 0.1108(1) \)                             |
| \( \text{As}1 \) | \( 0.0697(2) \)                             | \( 0.0655(1) \)                             |
| \( \text{As}2 \) | \( 0.1591(2) \)                             | \( 0.1571(1) \)                             |
| Bond distances   | \( \text{Fe}−\text{As}1(\text{Å}) 2.391(6) \) | \( \text{Fe}−\text{As}1(\text{Å}) 2.390(3) \) |
|                  | \( \text{Fe}−\text{As}2(\text{Å}) 2.413(6) \) | \( \text{Fe}−\text{As}2(\text{Å}) 2.409(3) \) |
| As height from Plane | \( \text{As}1(\text{Å}) 1.382(13) \) | \( \text{As}1(\text{Å}) 1.405(3) \) |
|                  | \( \text{As}2(\text{Å}) 1.420(13) \) | \( \text{As}2(\text{Å}) 1.436(3) \) |
| Bond angles      | \( \text{As}1−\text{As}1(°) 109.4(3) \) | \( \text{As}1−\text{As}1(°) 108.0(2) \) |
|                  | \( \text{As}2−\text{As}2(°) 107.9(3) \) | \( \text{As}2−\text{As}2(°) 106.8(2) \) |

Figure 1 shows the XRD pattern of the as-prepared \( \text{RbGd}_2\text{Fe}_2\text{As}_2\text{O}_2 \) sample. Most of the reflections can be well indexed with a 12442-type lattice [\( I4/nmm \), \( a \approx 3.89 \text{ Å} \), \( c \approx 31.3 \text{ Å} \)]. The remaining unindexed weak reflections come from unreacted \( Gd_2O_3 \). We thus make a two-phase Rietveld analysis. The result shows that the mass fraction of the main phase \( \text{RbGd}_2\text{Fe}_2\text{As}_2\text{O}_2 \) is 94% after a microabsorption correction [31]. Let us first examine changes of the crystal structure owing to the intergrowth between \( \text{RbFe}_2\text{As}_2 \) and \( \text{GdFeAsO} \). The \( a \) axis (see table 1) is nearly the same as the average (3.889 Å) of those of \( \text{GdFeAsO} [29] \) and \( \text{RbFe}_2\text{As}_2 [30] \). Meanwhile, the \( c \) axis is close to the expected value \( 2c_{\text{GdFeAsO}} + c_{\text{RbFeAsO}} = 31.317 \text{ Å} \) of the structural intergrowth. Nonetheless, there are atomic adjustments in each building blocks. While the ‘\( \text{GdFeAsO} \)’ block...
become slender (a: 3.915 Å → 3.901 Å; c: 8.435 Å → 8.538 Å), the ‘RbFe2As2’ block goes the opposite (a: 3.863 Å → 3.901 Å; c: 7.224 Å → 7.134 Å). The structural reconstructions reflect charge redistribution between the two building blocks. As a result, the apparent Fe valence in RbGd2Fe4As4O2 becomes 2.25+, which is a mean value of 2+ in GdFeAsO and 2.5+ in RbFe2As2, leading to a self doping level of 0.25 holes/Fe.

Table 1 compares crystal structures of the two 12442-type materials. The lattice parameters a and c of the oxyarsenide are 0.84% and 1.1% larger, respectively, due to the incorporations of larger ions of Rb⁺ and O²⁻. KCa2Fe4As4F2 is structurally featured by the obviously unequal Fe−As bond distances [27]. Similar case is seen in RbGd2Fe4As4O2. Nonetheless, the As height from the Fe plane and the band angles of As1−Fe−As1 and As2−Fe−As2, which are considered to be the relevant structural parameters that control Tc [32–34], show that the value of RbGd2Fe4As4O2 is closer to the ideal one that generates the highest Tc. This could serve an explanation for a higher Tc in RbGd2Fe4As4O2 (see below).

Figure 2 shows temperature dependence of resistivity [ρ(T)] of RbGd2Fe4As4O2. Although the ρ(T) data were obtained from polycrystalline samples, empirically they may represent the in-plane resistivity behavior for FeSCs. The ρ(T) curve indicates a metallic conduction with a broad humpback at ~150 K. Such a humpback is frequently observed in hole-doped FeSCs [8, 27, 35]. Similar phenomena in heavy hole-doped AKFe2As2 (AK = K, Rb and Cs) is explained as an incoherent-to-coherent crossover in relation with an emergent Kondo lattice effect [36]. The ρ(T) data show a linear behaviour from ~75 K to 35 K below which a sharp superconducting transition shows up. The transition width (defined by the temperature interval of the resistivity drop from 90% to 10%) is only 0.6 K, albeit of polycrystalline samples. The midpoint and zero-resistance temperatures (Tc^{mid} and Tc^{zero}) are 34.6 and 33.8 K, respectively, as shown in the inset of figure 2.

The superconducting resistive transitions under external magnetic fields are shown in figure 3. With increasing magnetic field, Tc^{onset} decreases slowly, but Tc^{zero} decreases rapidly. We employed conventional criteria to extract the upper critical fields [Hc2(T)] and the irreversible field [Hirr(T)]. Namely, Tc(Hc2) and Tc(Hirr) are defined as the temperatures at which the resistivity drops to 90% and 1% of the extrapolated normal-state value. The derived superconducting phase diagram is depicted in the inset of figure 3. Hc2(T) is almost linear with a slope of $\mu_0 H_{c2} \rho(T)$. In the superconducting state, a magnetic shielding is almost 100% at 2 K because of the insulating spacer layers in the 12442-type structure. Indeed, one sees a large gap between Hc2(T) and Hm(T) curves, consistent with the enhanced anisotropy due to weak interlayer coupling. The exceptionally high value of the initial Hc2(T) slope, which suggests very short superconducting coherence lengths, deserves further investigations.

Figure 4 shows the temperature dependence of dc magnetic susceptibility (scaled by 4πχ(T)) under a magnetic field of H = 10 Oe. A strong diamagnetic transition occurs at Tc^{onset} = 35.0 K for both field-cooling (FC) and zero-field-cooling (ZFC) data. The volume fraction of magnetic shielding is almost 100% at 2 K after a demagnetization correction. Although the volume fraction of magnetic repulsion is greatly reduced because of magnetic-flux pinning effect, it is still appreciably high (~10%), indicating that the title compound is responsible for the superconductivity. Shown in the inset of figure 4 is the isothermal magnetization curves at 2 and 50 K. Above Tc, it shows a paramagnetic behavior, which is mainly due to the Curie–Weiss paramagnetism of Gd³⁺ spins (S = 7/2). In the superconducting state, a magnetic hysteresis loop is evidently superposed, from which a lower
critical field of about 500 Oe is obtained. Since the corresponding \(H_c^2\) value is much higher, RbGd\(_2\)Fe\(_4\)As\(_4\)O\(_2\) is thus an extremely type-II superconductor.

Bulk superconductivity in RbGd\(_2\)Fe\(_4\)As\(_4\)O\(_2\) is further confirmed by heat capacity measurement. As shown in figure 5, there is a specific-heat jump at \(T_c = 35.5\) K. Under an 8-T magnetic field, the specific-heat anomaly tends to be smeared out and, \(T_c\) decreases slightly by \(\sim 0.5\) K, consistent with the above magnetoresistance measurement. The thermodynamic transition temperature is 34.55 K, based on an entropy-conserving construction (see the lower-right inset). The \(\Delta C/T_c\) value is 170 ± 10 mJ K\(^{-2}\) mol\(^{-1}\), slightly higher than that (150 mJ K\(^{-2}\) mol\(^{-1}\)) of KCa\(_2\)Fe\(_4\)As\(_4\)F\(_2\) [27] but, a little lower than that (186 mJ K\(^{-2}\) mol\(^{-1}\)) of CsEuFe\(_4\)As\(_4\) [26] with almost identical \(T_c\). Note that the Sommerfeld coefficient \(\gamma\) in the normal state cannot be estimated reliably from the \(C(T)\) data, primarily because of the high \(T_c\) value and the Gd magnetism incorporated. The dimensionless parameter \(\Delta C/(\gamma T_c)\) cannot be obtained accordingly. If assuming a weak-coupling scenario that satisfies the Bardeen–Cooper–Schrieffer (BCS) relation \(\Delta C/(\gamma T_c) = 1.43\), conversely, one may estimate that the \(\gamma\) value is about 120 mJ K\(^{-2}\) mol\(^{-1}\). If this is the case, the electronic specific heat achieves \(\sim 36\) J K\(^{-1}\) mol\(^{-1}\) at 300 K, which accounts for the large room-temperature specific heat beyond the Dulong–Petit limit. The low-temperature upturn in \(C(T)\) comes from the Gd\(^{3+}\) moments that could be ordered at lower temperatures. Besides, the upward shift of \(C(T)\) under magnetic field, shown in the upper-left inset of figure 5, is due to field-induced reorientation of the Gd\(^{3+}\) spins.

With formal valence state of Rb\(^{+}\), Gd\(^{3+}\), Fe\(^{2+}\), As\(^{3-}\), O\(^{2-}\), there remains one less positive charge which reflects a self hole doping in the present system. To verify this, we measured Hall coefficient \(R_H\) for the RbGd\(_2\)Fe\(_4\)As\(_4\)O\(_2\) sample. As is seen in figure 6, the \(R_H\) values are positive below 200 K, indicating dominant hole conduction in the temperature region (estimation of the hole concentration is difficult because of multiple energy bands). In between 200 and 250 K, however, there is a sign change, in contrast with positive \(R_H\) below 300 K for KCa\(_2\)Fe\(_4\)As\(_4\)F\(_2\) [27]. The sign change in \(R_H\) resembles the case of the first hole-doped FeSC (La\(_{1-x}\)Sr\(_x\))OFeAs [35], which is probably due to a multi-band effect.

As is known, the \(T_c\) record of hole-doped FeSCs is 38 K [8] and to the best of our knowledge, in hole-doped oxyarsenide FeSCs, the highest \(T_c\) of 25 K remains unchanged for years [35], which was obtained in the 1111-type (La\(_{1-x}\)Sr\(_x\))OFeAs containing separate single Fe\(_2\)As\(_2\) layer. Here, the \(T_c\) value of 35 K in RbGd\(_2\)Fe\(_4\)As\(_4\)O\(_2\) represents a new record for hole-doped oxyarsenide FeSCs, which seems to be relevant to the double Fe\(_2\)As\(_2\) layers. Thus it is of great interest to see whether the \(T_c\) value in 12442-type materials can achieve or even surpass the record of 38 K for the future.
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