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Phys. Rev. B **106**, 094511 — Published 19 September 2022

DOI: [10.1103/PhysRevB.106.094511](https://doi.org/10.1103/PhysRevB.106.094511)

Single crystal growth and superconductivity in RbNi₂Se₂

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We report the synthesis and characterization of RbNi₂Se₂, an analog of the iron chalcogenide superconductor Rb_xFe₂Se₂, via transport, angle resolved photoemission spectroscopy, and density functional theory calculations. A superconducting transition at $T_c = 1.20$ K is identified. In normal state, RbNi₂Se₂ shows paramagnetic and Fermi liquid behaviors. A large Sommerfeld coefficient yields an effective electron mass of $m^* \approx 6m_e$. In the superconducting state, zero-field electronic specific-heat data C_{e_s} can be described by a two-gap BCS model, indicating that RbNi₂Se₂ is a possible multi-gap superconductor. Our density functional theory calculations and angle resolved photoemission spectroscopy measurements demonstrate that RbNi₂Se₂ exhibits relatively weak correlations and multi-band characteristics, consistent with the multi-gap superconductivity.

PACS numbers:

I. INTRODUCTION

Since the discovery of copper oxide superconductors, researchers have extensively searched for superconductivity in materials with transition metals^{1,2}. Significant progress has been made in iron pnictide and chalcogenide compounds, where several structural systems have been identified with the highest T_c of 55 K achieved in LaFeAsO³. Superconductivity was also observed in the compounds containing Cr, Mn, and Eu under pressure, such as CrAs, KCrAs, CrSiTe₃, MnP, and EuTe₂⁴⁻⁸. Among all of them, superconductivity has been found to be in the vicinity of an antiferromagnetic (AF) or ferromagnetic (FM) order. Nickel oxide materials have analogous structures with copper oxide superconductors. Superconductivity with $T_c = 9 - 15$ K has also been observed in films of nickel-based compounds⁹⁻¹¹.

ANi₂Se₂ ($A = \text{K, Cs, and Tl}$) crystalizes in the ThCr₂Si₂ structure and shows metallic behavior and Pauli paramagnetism. At low temperatures, superconductivity emerges with the superconducting (SC) transition temperatures of $T_c \approx 0.8$ K for KNi₂Se₂ polycrystals, 2.7 K for CsNi₂Se₂, and 3.7 K for TlNi₂Se₂ single crystals¹²⁻¹⁴. While K_{0.95}Ni_{1.86}Se₂ single crystals do not show superconductivity down to 0.3 K, suggesting that the superconductivity is sensitive to the stoichiometry of the samples¹⁵. As a comparison, $A_x\text{Fe}_2\text{Se}_2$ system exhibits T_c s ranging from 20 - 30 K. With different amount of iron vacancies, $A_x\text{Fe}_{2-\delta}\text{Se}_2$ exhibits a variety of AF orders and iron vacancy orders¹⁶⁻¹⁹. The replacement of Fe by Co suppresses the superconductivity and induces a FM order in RbCo₂Se₂^{20,21}. The ANi₂Se₂ superconductors with a formal valent state of Ni^{1.5+} have been revealed to exhibit remarkable properties. In particular, they usually exhibit a large Sommerfeld coefficient γ ,

suggesting a large density of states and unconventional pairing at low temperature^{13,14}. One possibility that was proposed was that the large Sommerfeld coefficient might be induced by local charge order¹². However, angle resolved photoemission spectroscopy (ARPES) measurements yield weak electronic correlations in KNi₂Se₂ and TlNi₂Se₂. The origin of the large Sommerfeld coefficient may be driven by the large density states at the Fermi energy and the Van Hove singularity in the vicinity of the Fermi energy^{22,23}.

In this work, we report the successful synthesis and characterization of RbNi₂Se₂ single crystals. The crystal structure, electronic band structure, and transport properties have been investigated. We find that RbNi₂Se₂ is a Pauli paramagnetism and exhibits a SC transition at $T_c = 1.20$ K. Normal-state specific heat measurements suggest an effective electronic mass enhancement with $m^* \approx 6m_e$. In SC state, a two-gap BCS model can match well with the zero-field electronic specific heat, indicating that RbNi₂Se₂ is a possible multi-gap superconductor. Comparison with the density functional theory (DFT) calculations and ARPES measurements reveals that RbNi₂Se₂ is a weakly correlated superconductor with multi bands crossing the Fermi level.

II. EXPERIMENTAL AND CALCULATION DETAILS

Single crystals of RbNi₂Se₂ were grown by the self-flux method^{19,21}. The precursor NiSe was prepared by heating Ni powders and Se pellets at 500°C. Then, the NiSe powders and Rb were put into an alumina crucible according to stoichiometry and sealed in an evacuated silica tube. The mixture was kept at 150°C for 5 h, then

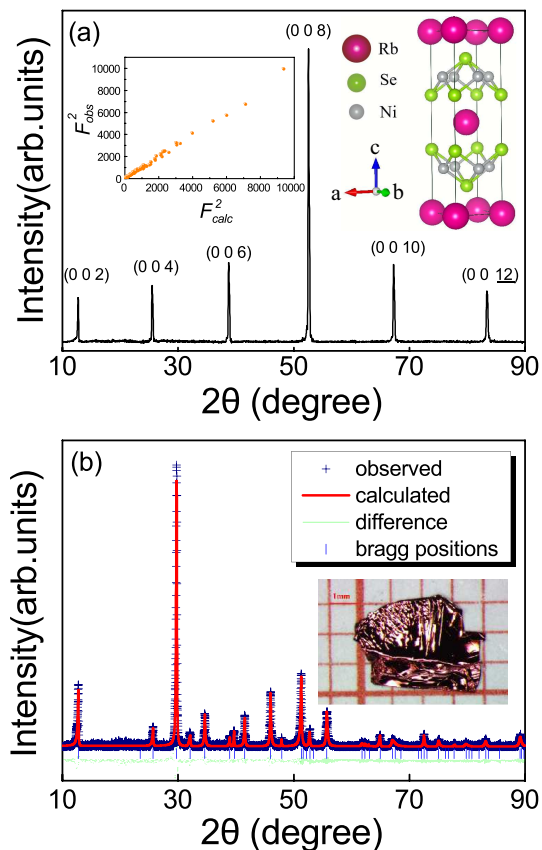


FIG. 1: (a) XRD measurement on the ab plane of RbNi_2Se_2 single crystal. The inset on left is the refinement on single crystal diffraction. The inset on right shows the crystal structure. The pink, green, and gray balls represent Rb, Se, and Ni ions. (b) A pattern of XRD measured on powder samples. The inset is a photo of RbNi_2Se_2 single crystal.

heated to 760°C in 40 h and kept for 5 h, after that heated to 1050°C in 40 h and held for 5 h. The temperature was cooled down to 700°C at a rate of $3.5^\circ\text{C}/\text{h}$ before the furnace was shut down. To prevent the reaction of Rb with water and air, all of the processes were conducted in an argon-filled glove box. Shiny plate-like single crystals with a typical size of $4 \times 5 \times 1 \text{ mm}^3$ were grown as shown in the inset of Fig. 1(b). The samples are air sensitive and were kept in an argon filled glove box. During the measurements, the samples were shortly exposed to air.

Single crystal x-ray diffraction (XRD) were conducted on a SuperNova (Rigaku) x-ray diffractometer. The sample was blown by N_2 during the data collection to avoid exposure to air. The elemental analysis was measured by using an energy-dispersive x-ray spectroscopy (EDS) (EVO, Zeiss). Electrical transport, magnetic and specific heat measurements were performed on a physical property measurement system with a dilution refrigerator (PPMS, Quantum Design). The in-plane resistivity $\rho_{ab}(T)$ was measured using the standard four-probe method on a rectangular sheet crystal to keep current flowing in the ab -plane. The Vienna *Ab initio*

TABLE I: Single-crystal of RbNi_2Se_2 refinement at 150 K.

Formula weight	223.14
Crystal system	Tetragonal
Space group	I4/mmm
Unit-cell parameters	$a = b = 3.9272(3) \text{ \AA}$ $c = 13.8650(5) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Atomic parameters	
Rb	$2b(0,0,1/2)$
Ni	$4d(0,1/2,3/4)$
Se	$4e(1/2,1/2,0.6502(1))$
Density	3.466 g/cm^3
F(000)	198
Radiation	Mo $K\alpha$ ($\lambda = 0.7107\text{\AA}$)
2θ for data collection	10.794° to 60.562°
Index ranges	$-4 \leq h \leq 5, -5 \leq k \leq 5,$ $-11 \leq l \leq 18$
Reflections collected	808
Independent reflections	119
Data/restraints/parameters	119/0/5
Goodness-of-fit on F^2	1.204
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0378, wR_2 = 0.1001$
Largest diff. peak/hole/ $e \text{ \AA}^{-3}$	$3.06/-2.04$

Simulation Package (VASP) was employed for the DFT calculations²⁴. ARPES measurements were performed on a helium-lamp based system with a DA30 electron analyzer. Single crystals were cleaved *in-situ* in ultra-high vacuum with a base pressure better than 5×10^{-11} Torr at 30 K. Energy and angular resolutions were better than 20 meV and 0.1° , respectively.

III. RESULTS AND DISCUSSIONS

All peaks from single crystal XRD can be indexed with the ThCr_2Si_2 -type structure (space group: I4/mmm), which are illustrated in the insets of Fig. 1(a). The determined lattice parameters are $a = b = 3.9272(3)$, and $c = 13.8650(5) \text{ \AA}$ at 150 K with the volume of unit cell between that of KNi_2Se_2 and CsNi_2Se_2 . Details of the atom coordinates and other key information are shown in Table I. To show the quality of the samples, we present a $\theta-2\theta$ scan of a single crystal along the ($H = 0, K = 0, L$) in Fig. 1(a) and an XRD pattern on a powder sample which was grounded from single crystals in Fig. 1(b), where (H, K, L) are Miller indices in reciprocal lattice units. No peaks from impurity could be identified. The EDS results for several single crystals are rather homogenous and the determined average atomic ratios are $\text{Rb:Ni:Se} = 1.16(4):2.04(3):2.00$ when the content of Se is normalized to be 2, close to the stoichiometry of RbNi_2Se_2 .

Temperature dependence of the resistivity for

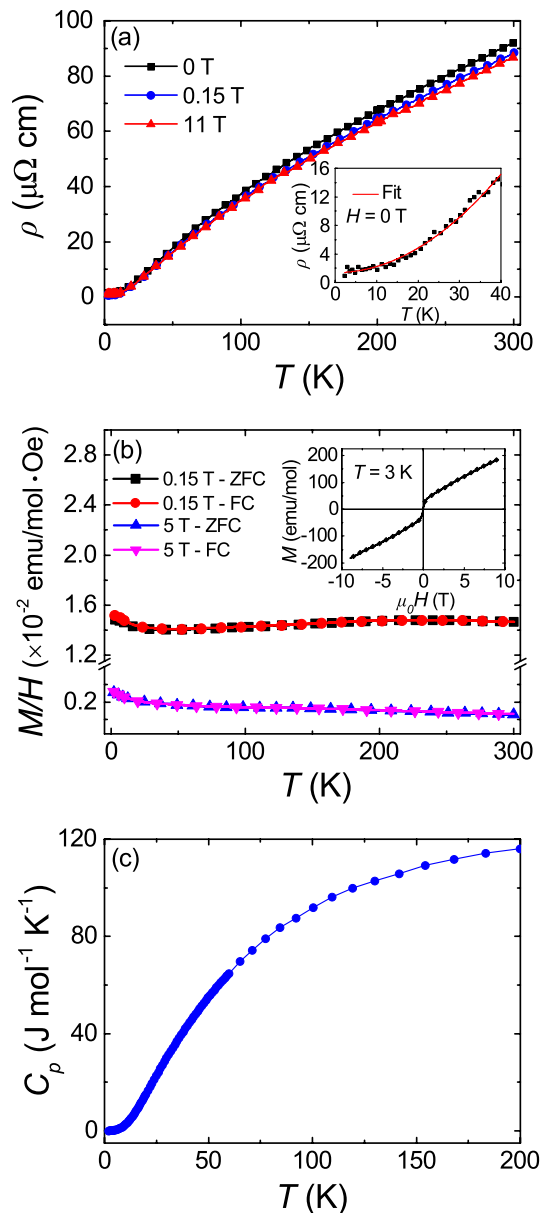


FIG. 2: (a) Temperature dependence of in-plane resistivity $\rho_{ab}(T)$ with magnetic fields $H = 0, 0.15,$ and 11 T along the c axis. The inset shows the fitted result using $\rho_{ab}(T) = \rho_0 + AT^2$ from 1.8 to 40 K. The red line is a fitting curve. (b) Temperature dependence of ZFC and FC magnetic susceptibility with applying various external magnetic fields along the c axis. The inset shows a magnetization hysteresis loop at 3 K. (c) Temperature dependence of $C_p(T)$ from 2 to 300 K.

RbNi₂Se₂ is shown in Fig. 2(a). The electric current is applied in the ab -plane. The value of ρ_{ab} is about $92.1 \mu\Omega\text{-cm}$ at 300 K and only about $1.5 \mu\Omega\text{-cm}$ at 1.8 K. The residual resistivity ratio (RRR) of 61.4 [$\rho_{ab}(300 \text{ K})/\rho_{ab}(1.8 \text{ K})$] suggests remarkable metallicity and high quality of the single crystals^{15,25,26}. The resistivity measured at $0, 0.15,$ and 11 T shows a metallic behavior without any anomaly or obvious magnetic field

dependence. The resistivity ρ_{ab} below 40 K can be well described by the equation $\rho_{ab}(T) = \rho_0 + AT^2$ as shown in the inset of Fig. 2(a), where $\rho_0 = 1.211 \mu\Omega\text{-cm}$ and $A = 0.012 \mu\Omega\text{-cm/K}^2$, consistent with a paramagnetic Fermi liquid behavior²⁷. The magnetic susceptibility is nearly independent of temperature, yielding a Pauli paramagnetic behaviour as shown in Fig. 2(b). A weak FM sign is revealed from the hysteresis loop shown in the inset of Fig. 2(b), which could be ascribed to a small amount of Ni impurity²⁸. The contribution of Ni on the magnetization is estimated to be lower than 1% . The specific heat from 2 to 200 K shown in Fig. 2(c) also suggests that no phase transition occurs in this temperature range.

To explore the possible superconductivity, we show measurements down to 50 mK in Fig. 3. The magnetic susceptibility at low temperatures is shown in Fig. 3(a). A clear diamagnetic response appears below 1.20 K under zero field, indicating a SC transition. The transition shifts to lower temperatures with an increase of the dc bias field, consistent with the Meissner effect of superconductivity. With knowing $T_c \approx 0.8$ K for KNi₂Se₂¹² and $T_c \approx 2.7$ K for CsNi₂Se₂¹³, the diamagnetic response at 1.20 K should correspond to the SC transition of RbNi₂Se₂. We plot the onset SC transition temperatures at various magnetic fields and fit the upper critical field $\mu_0 H_{c2}(0)$ using the Ginzburg-Landau theory with the formula $\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0) \times (1 - t^2)/(1 + t^2)$, where t is the reduced temperature $t = T/T_c$. As shown in Fig. 3(b), the resultant $\mu_0 H_{c2}(0) = 1.38$ T is within the Pauli limit, $\mu_0 H_{c2}^p(0) = 2.37$ T, indicating a weak coupling behavior²⁹.

Figure 3(c) displays the specific heat measured at low temperatures. In normal state, a fit to the specific heat C_p from 1.5 to 3.8 K using $C_p/T = \gamma_N + \beta T^2$ results in the Sommerfeld coefficient $\gamma_N = 30.30 \text{ mJ}\cdot\text{mol}^{-1}\text{K}^{-2}$ and $\beta = 3.67 \text{ mJ}\cdot\text{mol}^{-1}\text{K}^{-4}$, as shown in the inset. The Debye temperature Θ_D is estimated to be of 167 K from the equation $\Theta_D = (12\pi^4 NR/5\beta)^{1/3}$, where $N = 5$ is the number of atoms in each formula unit and R is the ideal gas constant. The γ_N for RbNi₂Se₂ is comparable with that of KNi₂Se₂ ($\sim 44 \text{ mJ}\cdot\text{mol}^{-1}\text{K}^{-2}$)¹², CsNi₂Se₂ ($\sim 77 \text{ mJ}\cdot\text{mol}^{-1}\text{K}^{-2}$)¹³, and TlNi₂Se₂ ($\sim 40 \text{ mJ}\cdot\text{mol}^{-1}\text{K}^{-2}$)¹⁴. The effective mass of electrons m^* can be estimated through Eq. 1³⁰:

$$m^* = \hbar^2 k_F^2 \gamma_N / \pi^2 n k_B^2 \quad (1)$$

where k_B is the Boltzmann constant and the carrier density n is calculated by the number of electrons (Z) per cell volume (V). Using a spherical Fermi surface approximation, the Fermi wave vector can be estimated by $k_F = (3\pi^2 n)^{1/3}$. Assuming that Ni contributes 1.5 electrons ($Z = 6$), we obtain $k_F = 9.4 \times 10^9 \text{ m}^{-1}$. The estimated effective mass of electrons $m^*/m_e = 6$ for RbNi₂Se₂ is significantly enhanced compared with the bare electron mass m_e . Combining the parameters from fitting the electronic specific heat and the quadratic temperature dependent regime of resistivity, the Kawasaki-Woods ratio, A/γ_N^2 ,

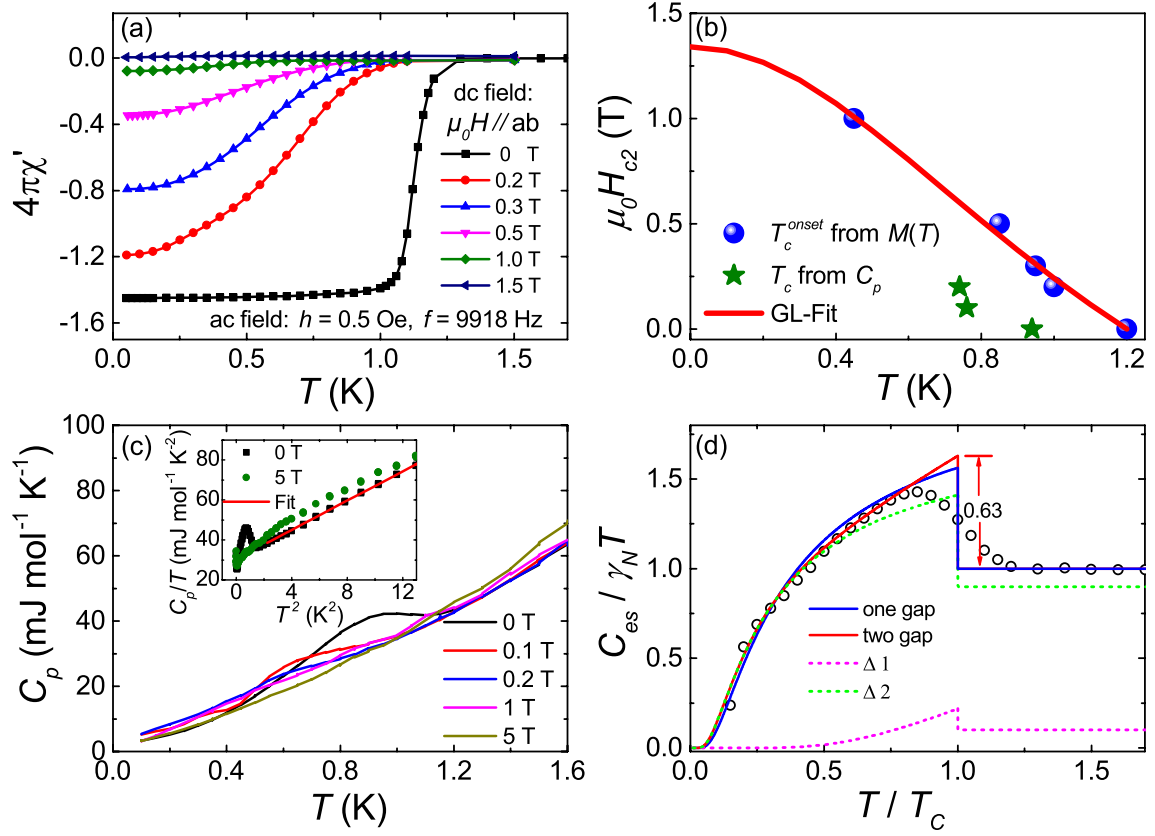


FIG. 3: (a) Diamagnetization of superconductivity under various magnetic fields. (b) Upper critical field H_{c2} , as a function of temperature. The blue circles and green stars are derived from the onset of magnetization and the specific heat based on an entropy-conserving construction. The red solid line shows a fit with the Ginzburg-Landau expression as discussed in the text. (c) The low-temperature specific heat of RbNi₂Se₂, measured at various fields near superconducting transition. The inset shows the Schottky anomaly at zero field and 5 T and a fitting of C_p in normal state. (d) Reduced temperature T/T_c dependence of electronic specific heat divided by temperature and γ_N , $C_{es}/\gamma_N T$, in the SC state at zero field, where $C_{es} = C_p - C_{lattice} - C_N$. The two solid lines show the fitting curves of the one-gap BCS model and the two-gap model to $C_{es}/\gamma_N T$, respectively. The dashed lines show the contributions from two different gaps, Δ_1 and Δ_2 , respectively.

is calculated to be $0.94 \times 10^{-5} \mu\Omega \cdot \text{cm} (\text{mol} \cdot \text{K}^2 \text{mJ})^2$, close to $\sim 10^{-5} \mu\Omega \cdot \text{cm} (\text{mol} \cdot \text{K}^2 \text{mJ})^2$ of heavy fermion systems³¹. This scaling relation indicates RbNi₂Se₂ exhibiting the heavy-fermion behavior.

In SC state, the specific heat data reveals an anomaly under zero field with a maximum at 0.85 K [Fig. 3(c)], suggesting bulk superconductivity. Applying an external magnetic field, the SC transition moves quickly to lower temperatures. As shown in the inset of Fig. 3(c), an upturn appears on C_p/T below $T^2 < 0.1$ K². The small upturn could be described by the Schottky anomaly for paramagnetic impurity spins¹², which can be well fitted by $C_N = D(H)T^{-2}$ with $D(H=0) = 0.07$ mJ·K·mol⁻¹.

In order to get information about the SC gap, we extract the electronic specific heat C_{es} by subtracting the phonon contribution $C_{lattice}$ that is extrapolated from the fitting in the normal state with zero field and Schottky anomaly C_N from the total C_p , $C_{es} = C_p - C_{lattice} - C_N$. The electronic specific heat data $C_{es}(\gamma_N T)^{-1}$ against T/T_c are shown in Fig. 3(d), where γ_N has been revealed in the normal state. The T_c is de-

termined to be 0.94 K using an equal-area entropy construction. The heat jump at transition is 0.63, smaller than that of the theoretical value of 1.43 in the BCS weak-coupling scenario³². We employ both one-gap and two-gap BCS models $C_{es} = \sum C_i \exp(-\Delta_i/k_B T)$ to fit the electronic specific heat, where Δ_i is the size of the i^{th} SC gap at 0 K. The one-gap model reveals $\Delta_0/k_B T_c = 0.30$ that is smaller than the value of 1.76 in the BCS theory³³. In the two-gap model, the total specific heat can be considered as the sum of electronic contributions from two bands. Our fitting yields the sizes of two gaps of $\Delta_1/k_B T_c = 2.51$ and $\Delta_2/k_B T_c = 0.25$, respectively. The ratio of the contributions from the two gaps is $\sim 1.5 : 1$ as presented by the dashed lines in Fig. 3(d). The better fitting using the two-gap model indicates that RbNi₂Se₂ may be a multi-gap superconductor.

The electron-phonon coupling strength is also calculated by employing the inverted McMillan formula³⁴:

$$\lambda_{ep} = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_c)}{(1 - 0.62\mu^*) \ln(\Theta_D/1.45T_c) - 1.04} \quad (2)$$

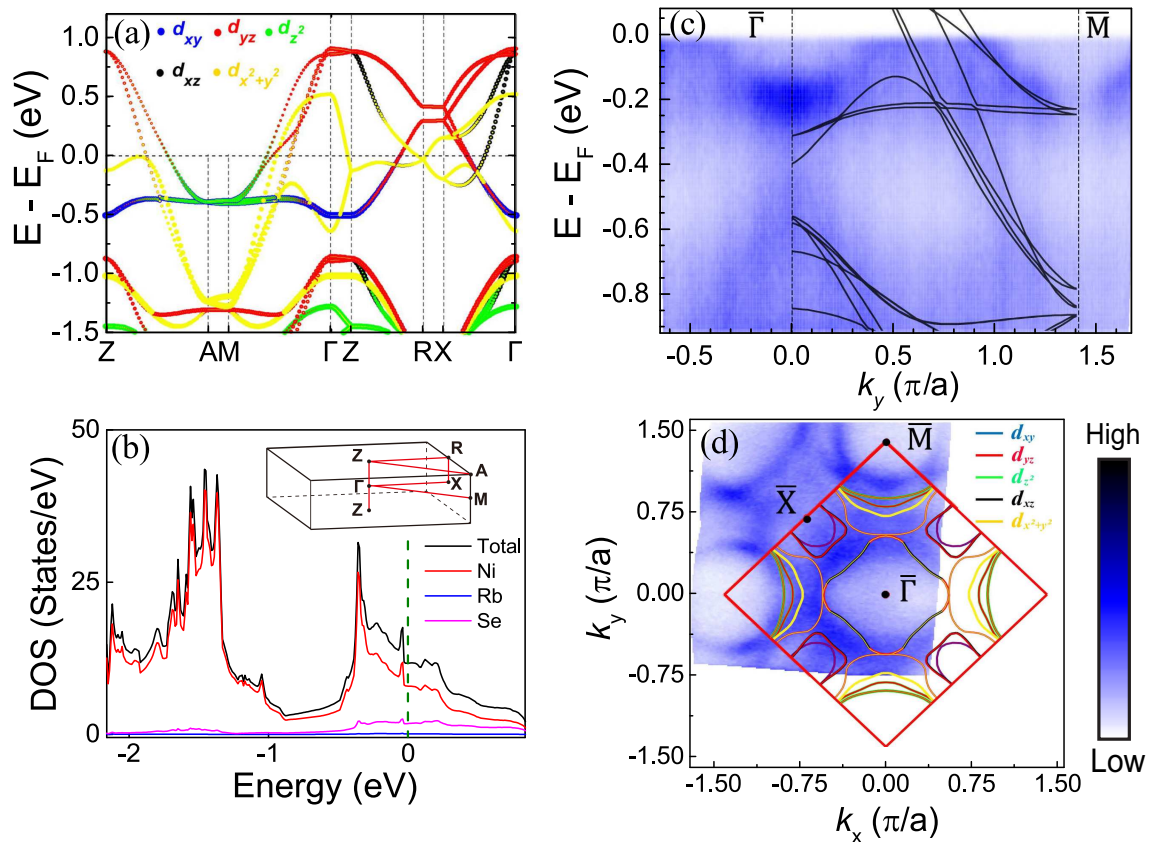


FIG. 4: (a) Projected band structure of Ni 3d in RbNi₂Se₂. Colors of the circle represent the different nickel orbitals, and the weight of each orbital is displayed by the size of the circles. The dashed lines are guide to eyes. (b) Density of states (DOS) near the Fermi level of RbNi₂Se₂. The red, blue and purple curves represent contributions from Ni, Rb and Se, respectively. Inset: The coordinates of the high symmetry \mathbf{k} -path in reciprocal space of the tetragonal unit cell. (c) Measured spectral images along the high symmetry direction $\Gamma \sim M$. The black lines are band structure calculated by the DFT. (d) The Fermi surface mapping at 35 K with the Brillouin zone (BZ) marked by a red square.

where μ^* represents the Coulomb repulsion pseudopotential, which we adopt $\mu^* = 0.13$ for this system³⁵. Generally, the λ_{ep} for strongly coupled superconductors are close to 1, and $\lambda_{ep} \rightarrow 0.5$ is viewed as weak coupled superconductors³⁴. The λ_{ep} for RbNi₂Se₂ is 0.49, suggesting that RbNi₂Se₂ is a weakly coupled superconductor, consistent with the specific heat analysis.

To check the multi-band character, we conducted DFT calculations and ARPES measurements on the electronic band structure. Figures 4(a) and 4(b) show the calculated electronic bands of Ni ions and the integrated density of states of Ni, Rb, and Se. The electronic states near the Fermi surface are governed by the 3d orbitals of Ni ions. In Fig. 4(c), the measured electronic structure of RbNi₂Se₂ is compared with the band structure obtained from the DFT calculations. The calculated curves (black lines) are scaled and overlaid onto the photoemission intensity along the $\Gamma - M$ direction. The theoretical and experimental data match qualitatively with a renormalization factor of about 1.8. This factor is relatively small compared to other iron-based superconductors³⁶, indicating that the electronic correlations are moder-

ate. The moderate correlations suggest that the superconductivity is most likely originated from the electron-phonon coupling, similar to the two-gap superconductor MgB₂^{37,38}. Figure 4(d) shows the photoemission intensity map of the Fermi surface, overlaid with the DFT calculated Fermi surfaces. The multiple Fermi pockets observed are consistent with the multi-band behavior of this compound, reinforcing the condition for the two-gap feature in the SC state. The band structure is reminiscent of the closely-related compound RbCo₂Se₂²¹. However, the 3d_{x²+y²} flat band that induces itinerant ferromagnetism in RbCo₂Se₂ is observed here to be well below the Fermi level, due to the electron doping resulted from the replacement of Co by Ni. A progressive substitution of Ni by Co is expected to uplift the peak in DOS at ~ 0.4 eV to the Fermi level.

As ANi₂Se₂ ($A = \text{K, Cs, and Tl}$) superconductors, RbNi₂Se₂ also exhibits an enhanced effective electron mass with a large Sommerfeld coefficient from specific heat. However, ARPES data reveal that the electronic correlation is not strong. To understand the reason of the large Sommerfeld coefficient, γ is estimated with λ_{ep}

and $N(0)$ at the Fermi level through the relationship³⁹:

$$\gamma = \frac{\pi^2 k_B^2 N(E_F)(1 + \lambda_{ep})}{3} \quad (3)$$

From the DOS in Fig. 4(b), $N(E_F)$ is estimated to be 11.68 states/eV per formula, resulting in $\gamma = 40.98$ mJ·mol⁻¹K⁻² that is close to the experimental value of 30.30 mJ·mol⁻¹K⁻². Therefore, the result suggests that the large γ_N is related to the large DOS at the Fermi level as proposed in KNi₂Se₂²², instead of the heavy fermion state. We note the electron-paramagnon interactions will also play a role in this system. While an estimation of the effect on the Sommerfeld coefficient is beyond the scope of this work⁴⁰. For ANi₂Se₂ ($A = \text{K, Rb, and Cs}$), the increase of the atomic radiuses of alkali metals works as applying a pressure to the Ni-Se layers. The DOS of Ni $3d$ orbitals at the Fermi surface, the Sommerfeld coefficient γ_N , and the electronic correlations are all enhanced. In the framework of the BCS theory, the SC transition temperature T_c increases accordingly, as the experimental observations in KNi₂Se₂, RbNi₂Se₂, and CsNi₂Se₂¹²⁻¹⁴.

IV. SUMMARY

In summary, we have successfully synthesized single crystals of RbNi₂Se₂ and characterized the physical properties. RbNi₂Se₂ is found to be a weakly coupled superconductor with $T_c = 1.2$ K. In normal state, RbNi₂Se₂ exhibits Fermi liquid behavior and Pauli paramagnetism. In the SC state, the zero-field electronic specific heat can be well described with a two-gap BCS model, indicating

that RbNi₂Se₂ possesses multi-gap feature. DFT calculations and ARPES measurements demonstrate that multi electronic bands of the $3d$ orbitals of Ni ions cross the Fermi level. Our analyses reveal that the large Sommerfeld coefficient of RbNi₂Se₂ is originated from the large DOS at the Fermi surface.

V. ACKNOWLEDGMENTS

We thank Shiliang Li for fruitful discussions. Work at Sun Yat-Sen University was supported by the National Natural Science Foundation of China (Grants No. 12174454, No. 11904414, No. 11904416, No. 11974432, No. U2130101), the Guangdong Basic and Applied Basic Research Foundation (No. 2021B1515120015), Guangzhou Basic and Applied Basic Research Foundation (No. 202201011123), National Key Research and Development Program of China (No. 2019YFA0705702, No. 2018YFA0306001, No. 2017YFA0206203), and GBABRF-2019A1515011337. Work at SLAB was supported by NSF of China with Grant No. 12004270, and GBABR-2019A1515110517. ARPES work at Rice is supported by the Robert A. Welch Foundation Grant No. C-2024 (M. Y.). P. D. is also supported by US Department of Energy, BES under Grant No. DE-SC0012311. Work at Berkeley was funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 (Quantum Materials program KC2202).

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- ¹ J. G. Bednorz, M. Takashige, and K. A. Müller, *Europhys. Lett.* **3**, 379 (1987), URL <http://link.springer.com/10.1007/BF01303701>.
 - ² K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, *Nature* **422**, 53 (2003), ISSN 0028-0836, URL <http://www.nature.com/articles/nature01450>.
 - ³ Z.-A. Ren, G.-C. Che, X.-L. Dong, J. Yang, W. Lu, W. Yi, X.-L. Shen, Z.-C. Li, L.-L. Sun, F. Zhou, et al., *EPL (Europhysics Lett.)* **83**, 17002 (2008), ISSN 0295-5075, URL <https://iopscience.iop.org/article/10.1209/0295-5075/83/17002>.
 - ⁴ W. Wu, J. Cheng, K. Matsubayashi, P. Kong, F. Lin, C. Jin, N. Wang, Y. Uwatoko, and J. Luo, *Nat. Commun.* **5**, 5508 (2014), ISSN 2041-1723, URL <http://dx.doi.org/10.1038/ncomms6508><http://www.nature.com/articles/ncomms6508>.
 - ⁵ Q.-G. Mu, B.-B. Ruan, B.-J. Pan, T. Liu, J. Yu, K. Zhao, G.-F. Chen, and Z.-A. Ren, *Phys. Rev. B* **96**, 140504 (2017), ISSN 2469-9950, URL <https://link.aps.org/doi/10.1103/PhysRevB.96.140504>.
 - ⁶ J.-G. Cheng, K. Matsubayashi, W. Wu, J. P. Sun, F. K. Lin, J. L. Luo, and Y. Uwatoko, *Phys. Rev. Lett.* **114**, 117001 (2015), ISSN 0031-9007, URL <https://link.aps.org/doi/10.1103/PhysRevLett.114.117001>.
 - ⁷ W. Cai, H. Sun, W. Xia, C. Wu, Y. Liu, H. Liu, Y. Gong, D.-X. Yao, Y. Guo, and M. Wang, *Phys. Rev. B* **102**, 144525 (2020), URL <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.102.144525>.
 - ⁸ H. Sun, L. Qiu, Y. Han, Y. Zhang, W. Wang, C. Huang, N. Liu, M. Huo, L. Li, H. Liu, et al., arXiv 2206.06621 (2022), URL <http://arxiv.org/abs/2206.06621>.
 - ⁹ D. Li, K. Lee, B. Y. Wang, M. Osada, S. Crossley, H. R. Lee, Y. Cui, Y. Hikita, and H. Y. Hwang, *Nature* **572**, 624 (2019), ISSN 0028-0836, URL <http://dx.doi.org/10.1038/s41586-019-1496-5><http://www.nature.com/articles/s41586-019-1496-5>.
 - ¹⁰ Q. Gu and H.-H. Wen, *Innov.* **3**, 100202 (2022), ISSN 26666758.
 - ¹¹ X. Ding, S. Shen, H. Leng, M. Xu, Y. Zhao, J. Zhao, X. Sui, X. Wu, H. Xiao, X. Zu, et al., *Science China: Physics, Mechanics and Astronomy* **65**, 267411 (2022), URL <https://link.springer.com/article/10.1007/s11433-021-1871-x>.
 - ¹² J. R. Neilson, A. Llobet, A. V. Stier, L. Wu, J. Wen, J. Tao, Y. Zhu, Z. B. Tesanovic, N. P. Armitage, and T. M. McQueen,

- Phys. Rev. B **86**, 054512 (2012), ISSN 1098-0121, URL <https://link.aps.org/doi/10.1103/PhysRevB.86.054512>.
- ¹³ Chen, Huimin and Yang, Jinhua and Cao, Chao and Li, Lin and Su, Qiping and Chen, Bin and Wang, Hangdong and Mao, Qianhui and Xu, Binjie and Du, Jianhua and Fang, Minghu, Supercond. Sci. Technol. **29**, 045008 (2016), URL <https://iopscience.iop.org/article/10.1088/0953-2048/29/4/045008>.
- ¹⁴ H. Wang, C. Dong, Q. Mao, R. Khan, X. Zhou, C. Li, B. Chen, J. Yang, Q. Su, and M. Fang, Phys. Rev. Lett. **111**, 207001 (2013), ISSN 0031-9007, URL <https://link.aps.org/doi/10.1103/PhysRevLett.111.207001>.
- ¹⁵ H. Lei, M. Abeykoon, K. Wang, E. S. Bozin, H. Ryu, D. Graf, J. B. Warren, and C. Petrovic, J. Phys. Condens. Matter **26**, 015701 (2014), ISSN 0953-8984, URL <https://iopscience.iop.org/article/10.1088/0953-8984/26/1/015701>.
- ¹⁶ J. Guo, S. Jin, G. Wang, S. Wang, K. Zhu, T. Zhou, M. He, and X. Chen, Phys. Rev. B **82**, 180520 (2010), ISSN 1098-0121, URL <https://link.aps.org/doi/10.1103/PhysRevB.82.180520>.
- ¹⁷ M. Fang, H. Wang, C. Dong, and Q. Huang, J. Phys. Conf. Ser. **449**, 012015 (2013), ISSN 1742-6596, URL <https://iopscience.iop.org/article/10.1088/1742-6596/449/1/012015>.
- ¹⁸ P. Dai, Rev. Mod. Phys. **87**, 855 (2015), ISSN 0034-6861, 1503.02340, URL <https://link.aps.org/doi/10.1103/RevModPhys.87.855>.
- ¹⁹ M. Wang, M. Yi, W. Tian, E. Bourret-Courchesne, and R. J. Birgeneau, Phys. Rev. B **93**, 075155 (2016), ISSN 2469-9950, 1508.04482, URL <https://link.aps.org/doi/10.1103/PhysRevB.93.075155>.
- ²⁰ J. Yang, B. Chen, H. Wang, Q. Mao, M. Imai, K. Yoshimura, and M. Fang, Phys. Rev. B **88**, 064406 (2013), ISSN 1098-0121, URL <https://link.aps.org/doi/10.1103/PhysRevB.88.064406>.
- ²¹ J. Huang, Z. Wang, H. Pang, H. Wu, H. Cao, S.-K. Mo, A. Rustagi, A. F. Kemper, M. Wang, M. Yi, et al., Phys. Rev. B **103**, 165105 (2021), ISSN 2469-9950, URL <https://link.aps.org/doi/10.1103/PhysRevB.103.165105>.
- ²² Q. Fan, X. P. Shen, M. Y. Li, D. W. Shen, W. Li, X. M. Xie, Q. Q. Ge, Z. R. Ye, S. Y. Tan, X. H. Niu, et al., Phys. Rev. B **91**, 125113 (2015), URL <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.91.125113>.
- ²³ N. Xu, C. E. Matt, P. Richard, A. van Roekeghem, S. Biermann, X. Shi, S.-F. Wu, H. W. Liu, D. Chen, T. Qian, et al., Phys. Rev. B **92**, 081116 (2015), ISSN 1098-0121, URL <https://link.aps.org/doi/10.1103/PhysRevB.92.081116>.
- ²⁴ G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993), ISSN 0163-1829, URL <https://link.aps.org/doi/10.1103/PhysRevB.47.558>.
- ²⁵ A. Ehrlich and D. Rivier, J. Phys. Chem. Solids **29**, 1293 (1968), ISSN 00223697, URL <https://linkinghub.elsevier.com/retrieve/pii/0022369768901819>.
- ²⁶ A. E. Böhrer, V. Taufour, W. E. Straszheim, T. Wolf, and P. C. Canfield, Phys. Rev. B **94**, 024526 (2016), ISSN 2469-9950, 1606.00500, URL <https://link.aps.org/doi/10.1103/PhysRevB.94.024526>.
- ²⁷ J. G. Analytis, H.-h. Kuo, R. D. McDonald, M. Wartenbe, P. M. C. Rourke, N. E. Hussey, and I. R. Fisher, Nat. Phys. **10**, 194 (2014), ISSN 1745-2473, URL <http://dx.doi.org/10.1038/nphys2869><http://www.nature.com/articles/nphys2869>.
- ²⁸ Q. Li, C. He, J. Si, X. Zhu, Y. Zhang, and H.-H. Wen, Communications Materials **1**, 16 (2020), ISSN 2662-4443, 1911.02420.
- ²⁹ J.-K. Bao, J.-Y. Liu, C.-W. Ma, Z.-H. Meng, Z.-T. Tang, Y.-L. Sun, H.-F. Zhai, H. Jiang, H. Bai, C.-M. Feng, et al., Phys. Rev. X **5**, 011013 (2015), ISSN 2160-3308, 1412.0067, URL <https://link.aps.org/doi/10.1103/PhysRevX.5.011013>.
- ³⁰ L. E. DeLong, R. P. Guertin, S. Hasanain, and T. Fariss, Phys. Rev. B **31**, 7059 (1985), ISSN 0163-1829, URL <https://link.aps.org/doi/10.1103/PhysRevB.31.7059>.
- ³¹ K. Kadowaki and S. Woods, Solid State Commun. **58**, 507 (1986), ISSN 00381098, URL <https://linkinghub.elsevier.com/retrieve/pii/0038109886907854>.
- ³² J. M. Daams and J. P. Carbotte, J. Low Temp. Phys. **43**, 263 (1981), ISSN 0022-2291, URL <http://link.springer.com/10.1007/BF00116155>.
- ³³ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957), ISSN 0031-899X, URL <https://www.taylorfrancis.com/books/9780429964251><https://link.aps.org/doi/10.1103/PhysRev.108.1175>.
- ³⁴ W. L. McMillan, Phys. Rev. **167**, 331 (1968), ISSN 0031-899X, URL <https://link.aps.org/doi/10.1103/PhysRev.167.331>.
- ³⁵ A. Amon, E. Svanidze, R. Cardoso-Gil, M. N. Wilson, H. Rosner, M. Bobnar, W. Schnelle, J. W. Lynn, R. Gumeniuk, C. Hennig, et al., Phys. Rev. B **97**, 014501 (2018), ISSN 2469-9950, URL <https://link.aps.org/doi/10.1103/PhysRevB.97.014501>.
- ³⁶ M. Yi, Y. Zhang, Z. Shen, and D. Lu, npj Quantum Materials **2**, 57 (2017).
- ³⁷ F. Bouquet, Y. Wang, R. A. Fisher, D. G. Hinks, J. D. Jorgensen, A. Junod, and N. E. Phillips, Europhys. Lett. **56**, 856 (2001), ISSN 0295-5075, 0107196, URL <https://iopscience.iop.org/article/10.1209/epl/i2001-00598-7>.
- ³⁸ F. Bouquet, R. A. Fisher, N. E. Phillips, D. G. Hinks, and J. D. Jorgensen, Phys. Rev. Lett. **87**, 047001 (2001), ISSN 0031-9007, URL <https://link.aps.org/doi/10.1103/PhysRevLett.87.047001>.
- ³⁹ G. Xiao, Q. Zhu, Y. Cui, W. Yang, B. Li, S. Wu, G.-H. Cao, and Z. Ren, Sci. China Physics, Mech. Astron. **64**, 107411 (2021), ISSN 1674-7348, URL <https://link.springer.com/10.1007/s11433-021-1731-3>.
- ⁴⁰ P. K. G. Bedi, Physica C: Superconductivity and its Applications **596**, 1354049 (2022), ISSN 09214534, URL <https://doi.org/10.1016/j.physc.2022.1354049>.