Charge-density wave, superconductivity and \textit{f}-electron valence instability in EuBiS$_2$F

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Superconductivity (SC) and charge-density wave (CDW) are two contrasting yet relevant collective electronic states which have received sustained interest for decades. Here we report that, in a layered europium bismuth sulfide fluorido, EuBiS$_2$F, a CDW-like transition occurs at 280 K, below which SC emerges at 0.3 K, without any extrinsic doping. The Eu ions were found to exhibit an anomalously temperature-independent mixed valence of about $+2.2$, associated with the formation of CDW. The mixed valence of Eu gives rise to self electron doping into the conduction bands mainly consisting of the in-plane Bi-6\textit{p} states, which in turn brings about the CDW and SC. In particular, the electronic specific-heat coefficient is enhanced by ~50 times, owing to the significant hybridizations between Eu-$4f$ and Bi-6\textit{p} electrons, as verified by band-structure calculations. Thus, EuBiS$_2$F manifests itself as an unprecedented material that simultaneously accommodates SC, CDW and \textit{f}-electron valence instability.

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\section{I. INTRODUCTION}

Charge-density wave (CDW) and superconductivity (SC) are different collective electronic orders, although both are associated with Fermi surface instabilities owing dynamically to electron-phonon interactions (for conventional BCS superconductors). CDW, usually occurring in low-dimensional materials, generally shows periodic modulations of conduction electron density and crystalline lattice in real space. In contrast, SC, appearing in materials not limiting to low dimensionality, exhibits an intriguing electronic ordering in momentum space due to condensation of Cooper pairs, without any static lattice deformation. Basically they are competing orders, nevertheless, coexistence of SC and CDW is frequently observed in low-dimensional systems by various experiments\textsuperscript{1-3}. In recent years, the relationship between CDW and SC has become a hot topic in cuprate high-temperature superconductors\textsuperscript{4-7} as well as 'conventional' superconductors that bear CDW instability\textsuperscript{1,2,8}. Currently, CDW is also considered as an intertwined electronic orders, not simply competing with SC\textsuperscript{9}. Recently, SC was discovered in a quasi-two-dimensional (Q2D) bismuth chalcogenide, LaO$_{1-x}$F$_x$BiS$_2$\textsuperscript{10} (The chemical formulae is preferably written as LaBiS$_2$O$_{1-x}$F$_x$ according to standard nomenclature\textsuperscript{11}). This new class of materials consists of BiS$_2$ bilayers that are believed to be responsible for SC. Band structure calculations\textsuperscript{12,13} reveal that the undoped parent compound LaBiS$_2$O belongs to a band insulator with an energy gap of ~0.8 eV\textsuperscript{13,15}. The conduction bands near Fermi level consist mainly of in-plane Bi-6\textit{p} states. Upon electron doping, these conduction bands are partially filled, which leads to Q2D Fermi surface (FS) sheets. A minimal electronic model including Bi-6\textit{p}$_x$ and 6\textit{p}_y orbitals was thus constructed\textsuperscript{12}. Interestingly, the resultant two bands have a Q1D character with a double minimum dispersion, making FS nesting possible. Possible CDW phases due to Q1D distortions of the Bi and/or S atoms were proposed for $x \sim 0.5$\textsuperscript{12,15}. Nevertheless, except for an inflection point in the temperature dependence of resistivity in La$_{0.5}$M$_{0.1}$BiS$_2$O ($M$=Th, Ti, Zr and Hf), which was speculated to be related to a CDW effect\textsuperscript{16}, no more signatures in physical properties for a CDW transition have been observed so far.

Here we report a series of evidences for a CDW transition at $T_{\text{CDW}} \sim 280$ K in an isostructural compound, EuBiS$_2$F, synthesized for the first time. Unlike other parent compounds such as LaBiS$_2$O\textsuperscript{17} and SrBiS$_2$F\textsuperscript{18} that are undoped insulators, surprisingly, EuBiS$_2$F itself is metallic, and moreover it exhibits SC below 0.3 K. By various experimental approaches, we demonstrate that EuBiS$_2$F is actually self doped due to partial electron transfer from the Eu ions to the BiS$_2$ bilayers. The Eu ions exhibit an anomalously temperature-independent mixed valence of about +2.2. The electronic specific-heat coefficient extracted from the experimental data is as large as 73 mJ K$^{-2}$mol$^{-1}$, ~50 times larger than those of its analogues, suggesting significant hybridizations between Eu-$4f$ and Bi-$6p$ electrons. Therefore,

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to our knowledge, EuBiS$_2$F represents the first material that simultaneously bears SC, CDW and $f$-electron valence instability.

II. EXPERIMENTAL METHODS

a. Sample’s synthesis The EuBiS$_2$F polycrystalline sample was synthesized by a solid-state reaction in sealed evacuated quartz tubes. All the starting materials were bought from Alfa Aesar. The stoichiometric mixtures of EuS [presynthesized by reacting Eu (99.9%) and S (99.995%) pieces in sealed evacuated quartz tubes at 1073 K for 20 h], EuF$_2$ (99.9%) and Bi$_2$S$_3$ (99.995%) powders, loaded in an evacuated quartz ampule, were heated in a muffle furnace to 1053 K for 20 h. The reacted mixtures were ground for homogenization in an agate mortar, pressed into pellets, and sintered at 1053 K for another 20 h. This process was repeated until nearly single-phase sample was obtained. An argon-filled glove box was employed for the operations above to avoid the contamination of water and oxygen as far as possible.

b. X-ray diffractions and crystal structure Powder x-ray diffraction (XRD) was carried out at room temperature and at low temperatures down to 13 K on a PANalytical x-ray diffractometer (Model EMPYREAN) with a monochromatic CuK$_{\alpha1}$ radiation. The lattice parameters were precisely determined using Si powders as the internal standard reference material. The crystal structure was refined based on the CeBiS$_2$O-type structure model$^{[19]}$ by a Rietveld analysis using the code Rietan-2000$^{[20]}$. With the exact lattice parameters, all the structural refinements were easily convergent. The resultant weighted reliable factor $R_{wp}$ is 7.1–9.0%, and the ‘goodness of fit’ parameter $S$ is 1.1–1.5, indicating good reliability for the refined crystal structure.

c. Physical property measurements The electrical resistivity was measured with a standard four-electrode method on a Quantum Design PPMS-9. The as-prepared sample’s surface with silver paint. The dc magnetization was measured on a Quantum Design PPMS-9. The heat capacity was measured using a relaxation method on a PPMS-9. The heat capacity of EuBiS$_2$F was measured on a Quantum Design PPMS-9. The as-prepared resistivity was measured with a standard four-electrode method on a Quantum Design PPMS-9. The as-prepared resistivity was measured with a standard four-electrode method on a Quantum Design PPMS-9. The as-prepared signals from the sample holder were carefully removed.

d. Mössbauer spectroscopy Mössbauer studies on $^{151}$Eu at various temperature (up to 388 K), were performed by using a conventional constant acceleration drive and $\sim$50 mCi $^{151}$Sm$_2$O$_3$ source. All spectra obtained were analyzed in terms of least square fit procedures to theoretical expected spectra. The experimental spectra were analyzed by two Lorentzian lines from which values for the isomer shift ($S$) and the spectral area of the resonance absorption lines were derived. The analysis considered also the exact shape of the source emission line$^{[22]}$. The velocity calibration was performed with an $\alpha$-iron foil at room temperature and the reported $S$ values are relative to Eu$_2$O$_3$ at room temperature.

e. Electronic structure calculations We carried out electronic structure calculations using the Vienna Ab-initio Simulation Package (VASP)$^{[23]}$. The experimental crystal structure parameters at 15 K were employed for the calculations. The strong Coulomb repulsion of the Eu-4f electrons was included using local spin density approximation plus a $U$ parameter (LSDA+$U$). The plane-wave basis energy cutoff was set at 540 eV.

III. RESULTS AND DISCUSSIONS

A. Crystal structure and bond valence sum of Eu

EuBiS$_2$F crystallizes in the tetragonal CeBiS$_2$O-type structure$^{[19]}$ with space group $P4/nmm$ (No. 129). The crystal structure, as depicted in the top inset of Fig. 1(a), can be viewed as an intergrowth of fluorite-like Eu$_2$F$_2$ block layers and NaCl-like Bi$_2$S$_2$ bilayers along the crystallographic c axis. The XRD patterns for the EuBiS$_2$F sample were well reproduced using the crystal structure model by Rietveld refinement$^{[20]}$. No obvious extra reflections appear, indicating monophasic EuBiS$_2$F within the XRD detecting limit ($\sim$ 2 wt. % in normal conditions).

The refined structural data were tabulated in Table S1 of the Supplemental Material (SM)$^{[24]}$. The room-temperature lattice parameters $a=4.0508(1)$ Å and $c=13.5338(3)$ Å are 0.7% and 2.1% smaller, respectively, than the counterparts of SrBiS$_2$O$^-[3.341(1)]$ is remarkably reduced, compared with those ($\sim 3.39$) of other CeBiS$_2$O-type parent compounds. Since the $c/a$ ratio decreases upon electron doping for the CeBiS$_2$O-related systems$^{[11]}$, one may speculate that EuBiS$_2$F could be self electron doped (see previous examples of self doping in Refs. 30, 31) owing to possible mixed valence of Eu. An alternative approach to verify this speculation is to calculate the bond valence sum$^{[32]}$ of Eu (Eu-BVS) by the formulae $\sum \exp(-\frac{R_{0}-d_{ij}}{s_{ij}})$, where $R_{0}$ is empirical parameters (2.04 Å and 2.53 Å for Eu–F and Eu–S bonds, respectively$^{[32]}$) and $d_{ij}$ denotes the measured bond distances between Eu and the nine coordinating anions. The resultant Eu-BVS values are 2.14(2) – 2.18(2), weakly depending on temperature (in comparison, the Sr-BVS value in SrBiS$_2$F is calculated to be 2.05(4) at based on the crystallographic data in Ref. 18). This means that the Bi$_2$S$_2$ bilayers are indeed self doped, accounting in turn for the anomalously small c/a ratio in EuBiS$_2$F.
FIG. 1. Crystal structure and its temperature dependence for EuBiS$_2$F. (a) Powder x-ray diffractions and their Rietveld refinement profiles at 300 K (top) and 15 K (bottom). Top inset: the crystal structure of EuBiS$_2$F. Bottom inset: an enlarged plot showing the (200) and (220) reflections. (b) Temperature dependence of lattice parameters $a$, $c$, $c/a$, and the bond valence sum of Eu (Eu-BVS). The solid line is a guide to the eye.

In order to detect the possible superstructured CDW phase predicted[13, 15], we performed low-temperature XRD measurements down to 13 K. No splitting for the (200) or (220) peak was detectable, as seen in the bottom inset of Fig. 1(a). Also, the structural fittings using the superstructures of $\sqrt{2} \times \sqrt{2} \times 1$[13] (with space group Cmma) or $\sqrt{2} \times 2\sqrt{2} \times 1$[12] (with space group P22_1) could not give a better refinement. Although static long-range CDW order cannot be detected by the conventional XRD technique, considering the strong evidences for a CDW transition at 280 K (see the following sections), we suppose that a dynamic and/or short-range CDW ordering is still likely. Indeed, theoretical calculations[13] indicate shallowness of the double-well potential with respect to the in-plane S(1) displacement, which leads to absence of static CDW order. Further experimental investigations with other techniques such as synchrotron XRD and electron diffractions at low temperatures are expected to be helpful to clarify this issue.

Figure 1(b) show temperature dependence of the crystal structural parameters and the Eu-BVS. The lattice parameters $a$ and $c$ decrease monotonically with decreasing temperature. A subtle anomaly around 280 K can be detected, and it is more evident in $c/a$ ratio. As stated above, the decrease in $c/a$ means more electron doping on the BiS$_2$ bilayers. Thus, the small decrease in $c/a$ below 280 K suggests further electron transfer from the Eu atoms to the BiS$_2$ bilayers with decreasing temperature. Indeed, the Eu-BVS value exhibits a detectable variations. At lower temperatures, both $c/a$ and Eu-BVS saturate, indicating a stable mixed-valence state for Eu.

B. Electrical transport properties

Figure 2 shows the temperature dependence of resistivity, $\rho(T)$, for the EuBiS$_2$F polycrystalline sample. Unlike the parent compound SrBiS$_2$F that shows semiconducting behaviour[18, 29], EuBiS$_2$F is virtually metallic, due to the self doping effect. More surprisingly, the $\rho(T)$ curve exhibits a broad hump below $\sim$ 280 K, resembling the CDW transitions in Q2D systems like Cu$_x$TiSe$_2$[8]. The resistivity anomaly cannot be ascribed to the increase of the Eu valence, because the latter would generate more electron carriers in the conducting BiS$_2$ bilayers, which would lower (rather than raise) the resistivity. Moreover, the hump is not even related to the Eu-4$f$ electrons, because we observed a similar hump, due to the CDW instability, in an Eu-free sample (Sr$_{0.7}$Ca$_{0.3}$)$_{0.75}$La$_{0.25}$BiS$_2$F (see Fig. S1 in the SM[24]). Therefore, this $\rho(T)$ hump is interpreted by a gap (probably a pseudogap) opening at Fermi level ($E_F$) because of the formation of dynamic/short-range CDW below 280 K. Here we note that no obvious nonlinear $I-V$ relations...
associated with the sliding of CDW was observed down to 2 K.

At lower temperatures, a superconducting transition takes place with a zero-resistance temperature of 0.3 K at zero field [see the inset of Fig. 2(a)]. The superconducting transition temperature $T_c$ is reduced by a factor of 10, compared with the BiS$_2$-based superconductors synthesized under ambient pressure [24, 26]. This could be due to the formation of CDW which loses partial FSs, relatively low electron doping, and pair breaking by the Eu magnetic moment. The superconducting transition was also demonstrated by the magnetoresistivity measurement at fixed temperatures, as shown in Fig. 2(b). The upper critical fields ($H_{c2}$) were determined using the criteria of 90% $\rho_n$, where $\rho_n$ stands for the normal-state resistivity. The temperature dependence of $H_{c2}$ shows positive curvature below $T_c$, possibly due to large anisotropy in $H_{c2}$ [27] (note that the sample is polycrystals). The $\mu_0H_{c2}$ value at 0.018 K is 0.16 T, which is obviously smaller than the Pauli limiting field, $\mu_0H_P=1.84$ $T_c \approx 0.4$ T.

To further understand the anomaly around 280 K in $\rho(T)$, we measured the temperature dependence of Hall coefficient ($R_H$). As shown in Fig. 2(c), at room temperature, $R_H$ is negative, indicating dominant electron transport. If assuming single band scenario, the carrier density is estimated to be $n = 1/|e|R_H = (2.1 \pm 0.3) \times 10^{27}$ m$^{-3}$, equivalent to a Hall number of $V_{cdw}/(2e|R_H|) = 0.24 \pm 0.03$ electrons per formula unit (fu). This electron density corresponds to an Eu valence of +2.24(3), if assuming that all the electron carriers in the conduction band (CB) come from the Eu-4$f$ orbitals [see the schematic energy-band diagrams in Fig. 2(c)]. Below 280 K, $R_H$ increases steeply, and then it changes the sign at lower temperatures. This peculiar $R_H(T)$ behaviour strongly suggests FS reconstructions owing to a CDW transition. In Sr$_{1-x}$La$_x$BiS$_2$F system, as a comparison, the $R_H(T)$ is either positive (for $x \leq 0.45$) or negative (for $x \geq 0.5$) [28, 31, 32]. We speculate that a pseudogap opens below $T_{CDW}$, which could lower the $E_F$ a little, as shown in the left diagram in Fig. 2(c). As a result, more transferred electrons are expected, accounting for the small increase of Eu valence below 280 K.

C. Magnetic properties

The magnetic properties Eu$^{2+}$ and Eu$^{3+}$ ions are very different because of different electron filling on the 4f orbitals ($4f^7$ and $4f^0$, respectively). The ground state

FIG. 2. Electrical transport properties and superconductivity in EuBiS$_2$F. (a) Temperature dependence of resistivity showing a CDW-like anomaly at 280 K and superconductivity at 0.3 K (inset). (b) The magnetoresistivity as a function of magnetic field at low temperatures. The inset plots the upper critical field, $H_{c2}$, by the criteria of 90% $\rho_n$, where $\rho_n$ stands for the normal-state resistivity. (c) Temperature dependence of Hall coefficient in which a turning point at 280 K is seen. Upper inset: field dependence of Hall resistivity at some fixed temperatures. Bottom inset: schematic energy-band diagrams for $T < T_{CDW}$ (left) and $T > T_{CDW}$ (right), respectively. CB (VB) denotes the conduction band (valence band) in the BiS$_2$ bilayers.
of the former is $^8S_{7/2}$ with an effective local-moment of $g\sqrt{S(S+1)}=7.94 (\mu_B)$. In contrast, the ground state of the latter is $^7F_3$, which has zero magnetic moment. Nevertheless, the excited states $^7F_J$ ($J=1, 2, ..., 6$), due to the spin-orbit interaction $\lambda L S$, give rise to a comparable Van Vleck paramagnetic susceptibility ($\chi_{vv}$) [37]. Here the coupling constant $\lambda$ also measures the energy of the first excited state. The $\lambda$ value is 480 K for free Eu$^{3+}$ ions [38], and it has a small change in solids, e.g., $\lambda=471$ K for EuBO$_3$ and $\lambda=490$ K for EuF$_3$ [37]. Consequently, the $\chi_{vv}(T)$ is featured by a temperature-independent plateau in the low-temperature regime (say, $T \leq 100$ K), and Curie-like paramagnetism with an effective magneton number of 3.4 per Eu$^{3+}$ for high-temperature region ($T > 200$ K) [37]. In EuBiS$_2$F system, therefore, we can correctly analyze the temperature dependence of magnetic susceptibility, $\chi(T)$, with an extended Curie-Weiss law,

$$\chi = \chi_0 + C/(T + \theta_N).$$

In the low-temperature limit, the first term $\chi_0$ includes $\chi_{vv}$ in addition to Pauli paramagnetism (and Landau diamagnetism) of conduction electrons and Langevin diamagnetism from the core-shell electrons of all the constituent elements. At the high-temperature side, $\chi_{vv}$ is included to the second term, where $C$ denotes Curie constant and $\theta_N$ is termed as paramagnetic Neel temperature. One may obtain the effective moment by the formula $m_{\text{eff}} = \sqrt{3k_B}/C/N_A$, where $k_B$ and $N_A$ denote Boltzmann and Avogadro constants, respectively.

Figure 3(a) shows the temperature dependence of magnetic susceptibility, $\chi(T)$, for the EuBiS$_2$F sample at $T \leq 100$ K. No magnetic transition is evident down to 2 K. The $\chi(T)$ data can be well fitted by Eq. (1), except for minor deviations below 10 K. The fitted effective paramagnetic moment is 7.2 $\mu_B$ $\cdot$ $\mu^{-1}$, which means that the concentration of Eu$^{2+}$ is 83% (hence the Eu valence is $+2.17$, fully consistent with the Eu-BVS value above).

The Eu$^{3+}$ ions (with a population of 17%) should give considerable contribution to $\chi_0$. Indeed, the fitted $\chi_0$ value is as large as 0.0032(2) emu mol$^{-1}$. By referring to the Van Vleck susceptibility of EuF$_3$ ($\sim 0.006$ emu mol$^{-1}$ below 100 K) in which the Eu valence is totally $3^+ [37]$, the $\chi_{vv}$ value of EuBiS$_2$F is then estimated to be 0.001 emu mol$^{-1}$ below 100 K. Since the Langevin diamagnetic susceptibility is negligibly small (about $-1.5 \times 10^{-4}$ emu mol$^{-1}$) [38] within the fitting errors, then, the Pauli susceptibility can be roughly estimated to be $\sim 0.002$ emu mol$^{-1}$. This unusually large value of Pauli susceptibility suggests substantial hybridizations between Eu-4$f$ and CB (see band structure calculations in Section III). Figure 3(b) shows the high-temperature range of $\chi(T)$, which was also fitted with Eq. (1). The fitting gives smaller $\chi_0$ but larger $C$ values, because $\chi_{vv}$ is now included in the second term of Eq. (1). By subtraction of the fitted curve from the experimental data, the residual susceptibility $\Delta \chi$ shows a hump-like anomaly where the magnetic susceptibility tends to drop [by $(5 \pm 2) \times 10^{-5}$ emu mol$^{-1}$] at around 280 K. At first sight, it seems to be related to the change in Eu valence. However, similar hump in $\chi$ was also observed in an Eu-free analogous sample (Sr$_{0.7}$Ca$_{0.3}$)$_{0.75}$La$_{0.25}$BiS$_2$F (see Fig. S2 in the SM[24]). Thus we speculate that the 'drop' of $\chi$ at 280 K is mainly resulted from the loss of Pauli paramagnetic susceptibility when a (pseudo)gap opens at the CDW transition. Here we note that the decrease of $N(E_F)$ in the CDW phase for LaBiS$_2$O$_{0.3}$F$_{0.7}$ calculated[13] is just equivalent to the loss of Pauli magnetic susceptibility.

The possible variation in Eu valence can be analyzed as follows. If $P_{3+}$ denotes the concentration of Eu$^{3+}$ [so that the fraction of Eu$^{2+}$ is $(1-P_{3+})$], one may calculate $P_{3+}$ by the relation,

$$\chi = \chi_0 + P_3 \cdot \frac{C_{3+}}{T} + (1-P_{3+}) \cdot \frac{C_{2+}}{T + \theta_N}. \quad (2)$$

With $C_{2+}=7.875$ emu mol$^{-1}$ K$^{-1}$ and $C_{3+}=1.45$ emu mol$^{-1}$ K$^{-1}$, the Eu valence was obtained as plotted in Fig. 3(d). One sees that the Eu valence does not change so much around 280 K, but it tends to increase rapidly below 220 K, which is quantitatively consistent with the Eu-BVS values shown in Fig. 3(b).

One may also obtain the information of Eu valence from the field-dependent magnetization at 2 K [Fig. 3(c)] which shows a saturation at high magnetic fields. The saturation magnetization is significantly smaller than the expected value ($gJ=7.0 \mu_B$ $\cdot$ $\mu^{-1}$) for Eu$^{2+}$ ions only. By fitting the $M(H)$ data using a Brillouin function with consideration of Weiss molecular field $B_{\text{m.w.}} = \xi M$, the saturation magnetization is determined to be $5.58 \mu_B$ $\cdot$ $\mu^{-1}$, corresponding to the Eu valence of $+2.20$, consistent with

FIG. 3. Magnetic properties of EuBiS$_2$F. Temperature dependence of the dc magnetic susceptibility [(a): $T \leq 100$ K; (b): $T \geq 220$ K]. The solid lines are the fitted curves. The difference (multiplied by 100) between the experimental data and the fitted ones is shown in the lower part of (b). (c) Field dependence of magnetization at 2 K. The dotted line is a Brillouin fit. (d) The Eu valence estimated by the magnetic susceptibility. See details in the text.
the conclusion from the Curie-Weiss fitting above. The fitted parameter $\xi$ is a negative value ($-0.40$), reflecting dominant antiferromagnetic interactions among the Eu localized moments, also agreeing with the positive value of $\theta_N$ in Eq. (1).

D. Mössbauer spectroscopy

Mössbauer spectroscopy (MS) is a powerful technique to study the Eu valence. The isomer shift $S$ of the nuclei of Eu$^{2+}$ and Eu$^{3+}$ ions falls in two nonoverlapping ranges: $S_{2+} = -7.7 \sim -13.5$ mm s$^{-1}$ and $S_{3+} = -0.01 \sim +2.6$ mm s$^{-1}$ (relative to Eu$_2$O$_3$). Thus, MS easily identifies the valence state of Eu and, in the case of inhomogeneous mixed valence, the concentration of each Eu species can be determined by the relative absorption intensity. For the fast valence fluctuation (VF) scenario, the mean Eu valence can also be quantitatively evaluated by the relative absorption intensity.

Figure 4(a) shows the $^{151}$Eu Mössbauer spectra at some typical temperatures of 90, 200, 297 and 388 K. At low temperatures (90 and 200 K), two absorption lines (or peaks) appear at $-13.5$ and $-0.5$ mm s$^{-1}$, which are obviously identified to the Mössbauer resonance absorptions of Eu$^{2+}$ and Eu$^{3+}$ nuclei, respectively. Since there is only one equivalent site in the crystal structure even at low temperatures, the two separate lines indicate slow Eu VFs (or even static charge ordering of Eu$^{2+}$ and Eu$^{3+}$) with the time scale of $\tau_{vf} > 10^{-9}$ s (note that the probing time of MS is about $10^{-8}$ s). The intensity of the minor line is about $1/3$ of the major one, therefore, the mean Eu valence is $\sim +2.25$, basically consistent with the above conclusion drawn from the crystal structure and magnetic interactions.

At 388 K, the Eu$^{3+}$ line almost vanishes because the VFs are much faster. The isomer shift is then formulated by $S_{3+} = (1 - P_{3+})S_{2+} + P_{3+}S_{3+}$. With $S_{2+} = -11.6$ mm s$^{-1}$, $S_{3+} = -13.5$ mm s$^{-1}$ and $S_{3+} = 0$ mm s$^{-1}$, the Eu valence at 388 K can be estimated to be $+2.14(2)$.

By the data fitting using the exact shape of the emission spectrum of $^{151}$Sm$_2$O$_3$ and considering quadrupole interactions, we were able to obtain the refined $S$, the full linewidth at half maximum ($\Gamma$) and the peak intensities ($I$), which are plotted respectively in Fig. 4(b). All these MS parameters point to a transition at 280 K. The most prominent feature is the $\Gamma$ value is peaked at 280 K. The sharp decrease in $\Gamma$ below 280 K suggests that the Eu VFs slow down, probably in connection with the dynamic CDW. The isomer shifts and the relative intensity of the minor line respectively reflect fast VFs with $\tau_{vf} < 10^{-9}$ s and slow VFs with $\tau_{vf} > 10^{-9}$ s. At 273 K, for example, one may roughly estimated that 51(1)% of the Eu ions are in Eu$^{3+}$ state with fast VFs, and 14(2)% of the Eu ions are in Eu$^{2+}$ state with slow VFs. So, the overall Eu valence is $+2.19(3)$ at 273 K.

E. Specific heat

Heat capacity of a solid may supply important information not only for phase transition but also for electronic and magnetic states. Fig. 5(a) shows the temperature dependence of specific heat, $C(T)$, of EuBiS$_2$F$_2$. The $C(T)$ data tend to saturate to 120 J K$^{-1}$ mol$^{-1}$ at room temperature, consistent with the high-$T$ limit for lattice specific heat (i.e., the Dulong-Petit value $3NR=15R=124.7$ J K$^{-1}$ mol$^{-1}$, where $N$ counts the number of elements per fu, $R$ is the gas constant). One sees an anomaly around 280 K, a signal of second-order transition, further supporting a CDW-like transition.

In EuBiS$_2$F$_2$, the specific heat is contributed due to several different origins including crystalline lattice ($C_{lat}$), conduction electron ($C_{el}$) and Eu magnetism ($C_m$). One may correctly separate them out by considering different contribution weights in different temperature regions. Since no magnetic ordering takes place above 2 K, and the magnetic susceptibility well follows Curie-Weiss law above 10 K, $C_m$ is then expected to be very small above 10 K at zero magnetic field. Therefore, we make use of a conventional approach, in which the low-$T$ lattice contribution is taken as $\beta T^3$, to extract $C_{el}$. The plot of $C/T$ vs $T^2$ in the inset of Fig. 5(a) gives $\gamma=73.3$ mJ K$^{-2}$ mol$^{-1}$ and $\beta=1.19$ mJ K$^{-4}$ mol$^{-1}$. The resultant Debye temperature, $\theta_D = [(12/5)NR\pi^2/\beta]^{1/3}=201$ K,
is reasonably in between with those of LaBiS$_2$O$_{0.5}$F$_{0.5}$ (221 K) and YbBiS$_2$O$_{0.5}$F$_{0.5}$ (186 K) [10], which vice versa guarantee the reliability of the Sommerfeld parameter. Notably, the fitted $\gamma$ value is over 50 times of that of Sr$_{0.5}$La$_{0.5}$BiS$_2$F (1.42 mJ K$^{-2}$ mol$^{-1}$) [24]. Its corresponding $N(E_F)$ $\approx$ $3\gamma/(\pi\hbar^2)$ is as large as 30 eV$^{-1}$ fu$^{-1}$, which is about 25 times of the bare density of states of LaBiS$_2$O$_{0.5}$F$_{0.5}$ (1.22 eV$^{-1}$ fu$^{-1}$) [12]. The greatly enhanced $\gamma$ is related to the unusually large Pauli magnetic susceptibility above, mainly originating from the hybridization between conduction electrons and the Eu 4f electrons (see band structure calculations in Section 4.4).

Figure 5(b) zooms in the $C(T)$ data below 20 K. At zero magnetic field, a peak appears at 1.6 K with a high maximum up to 10.41 J K$^{-1}$ mol$^{-1}$. Under a magnetic field of 5 T, the peak is suppressed, forming a broad hump centered at about 3.5 K. Since the ground state of Eu$^{2+}$ has zero orbital angular momentum, Schottky-like contribution is not expected. Hence the peak should be of magnetic origin. It is noted that, on the right side of the peak, there is no specific jump (or a divergence), as opposed to an ordinary long-range magnetic ordering. This lets us consider that the specific anomaly comes from freezing of non-ordered Eu$^{2+}$ spins, i.e., a spin glass transition. Similar observation was reported in (Eu,Sr)S$_{17}$ and EuCu$_2$Si$_3$ [11]. To extract $C_m$ below 10 K more accurately, the $C(T)$ data from 10 K to 20 K was fitted by a polynomial with odd-power terms, $C \approx C_{el} + C_{lat} = A_1 T + A_3 T^3 + A_5 T^5 + A_7 T^7$ (the resultant $A_1$ and $A_3$ agree well with the above $\gamma$ and $\beta$ values). Then the magnetic contribution $C_m$ below 10 K was obtained by removing the contributions of $C_{lat}$ and $C_{el}$. Consequently, the magnetic entropy can be calculated by $S_m = \int_0^T (C_m/T) dT$, as shown in Fig. 5(c), which is 12.4 J K$^{-1}$ mol$^{-1}$ at 20 K under zero field. Furthermore, nearly the same $S_m$ value can be achieved under 5 T for integrating up to 60 K. The released magnetic entropy equals to 72% of $R\ln(2S+1)$ ($S=7/2$ for Eu$^{2+}$). Considered omission of magnetic entropy above 20 K, the resultant $S_m$ value actually gives an upper limit of the Eu valence of +2.28 below 20 K.

F. Band structure calculations

To interpret above experimental results, we performed a first-principles calculation using local spin density approximation with consideration of on-site Coulomb interaction (LSDA+$U$), particularly paying attention to the Eu-4f electronic states (the issue of CDW instability was well documented by Yildirim [14]). We first investigated the influence of the parameter $U$. Fig. 6(a) shows the variations of Eu-4f bands of EuBiS$_2$F with $U=0, 1, ..., 6$ eV. In all the cases, there is a large gap between occupied and unoccupied levels, as shown in the inset. Another prominent feature is that the highest occupied band (HOB) locates around $E_F$, regardless of the different $U$ values. This fact suggests that the Eu-4f frontier occupied level in the HOB is pinned by the chemical potential of the conduction bands. The filled states in HOB actually represents Eu$^{2+}$, whilst the empty states in HOB, i.e., the 4f holes, correspond to Eu$^{3+}$.

Figure 6(b) shows the calculated band structure of EuBiS$_2$F with a realistic value of $U=3$ eV. There are seven flat bands near $E_F$, all coming from the Eu-4f orbitals. The HOB crosses $E_F$, and hybridizes with the Bi-6p bands (see the zoom-in plot at the bottom). Furthermore, this HOB donates electrons to the Bi-6p bands, and leaves hole pockets around the M point [see also the FS in Fig. 6(d)]. Consequently, although undoped, the CB of EuBiS$_2$F is filled with the transferred electrons. Due to the 2D structure, cylindric-like FSs are presented [Fig. 6(d)]. Except for the 4f-hole pockets, two electron-type FS sheets appear around the X point, similar to the case of LaBiS$_2$O$_{1-x}$F$_x$ with $x=0.25$ [12]. This 2D-like FS sheets have considerable nesting areas for developing CDW instability.

Figure 6(c) shows the calculated electronic DOS of EuBiS$_2$F. Obviously, the sharp peaks come from the Eu-4f orbitals. They are basically divided into two
FIG. 6. Band calculations for EuBiS$_2$F using LSDA+$U$ method. (a) Variations of Eu-4$f$ bands with different $U$ values. DOS denotes to density of states. (b) Calculated band structure of EuBiS$_2$F with $U=3$ eV. The contributions of the relevant orbital states are distinguished by different colors. The lower panels zoom in the band dispersions crossing the Fermi level ($E_F=0$). (c) Total and projected DOS with $U=3$ eV. Inset: an enlarged plot near $E_F$. (d) Fermi surfaces of EuBiS$_2$F derived from the band structure in (b).

groups, which are about 7 eV apart (corresponding to an effective Hubbard $U \sim 7$ eV). The frontier HOB nearby $E_F$ is mainly contributed from the $f_{x^2-y^2}$ wave function. The DOS at $E_F$, $N(E_F)$, mainly comprises of Bi-6$p$ ($0.75 \times 2$ eV$^{-1}$ f.u$^{-1}$) and Eu-4$f$ (21.6 eV$^{-1}$ f.u$^{-1}$). The total $N(E_F)$ is about 20 times of that of LaBiS$_2$O$_{0.5}$F$_{0.5}$[13], well accounting for the enhancement of electronic specific-heat coefficient as well as Pauli susceptibility.

IV. CONCLUDING REMARKS

We have demonstrated a series of signatures for a CDW transition in EuBiS$_2$F, albeit no static long-range superlattice order was detected by XRD. They include a clear kink in the $c/a$ ratio, a resistivity hump, a kink in Hall coefficient, a subtle magnetic susceptibility drop, and a specific-heat hump, all at $T_{CDW} \sim 280$ K. The slowing down of Eu VFs below $T_{CDW}$ suggests a dynamic CDW ordering. Such a dynamic CDW is supported by the theoretical calculations which indicate dynamic in-plane displacements of S(1) owing to the shallowness of the double-well potential[13]. Very recently, 'checkerboard stripe' electronic state was observed on the cleaved surface of NdO$_{0.7}$F$_{0.3}$BiS$_2$ single crystals[42]. Although the nanoscale electronic inhomogeneity was considered to be due to the atomic defects on the cleaved surface, it could be in some relations to the CDW instability.

As is known, CDW mostly originates from the FS nesting[1, 2]. Since the shape and the size of the FS sheets are predominantly decided by the electron filling in the CB of BiS$_2$-based materials[12], the electron doping level should be crucial for the occurrence of CDW. Our finding in EuBiS$_2$F implies that the CDW instability is optimized at around $x \sim 0.2$. To verify this point, we synthesized samples of (Sr,Ca)$_{0.75}$La$_{0.25}$BiS$_2$F, in which the electron doping was fixed to $x=0.25$. We indeed observed a similar CDW anomaly in this designed system (see Figs. S1 and S2 in SM[24]).

It is the mixed valence of Eu that considerable amount of electron carriers are transferred into the CB, which induces SC as well as CDW. Table I summarizes the Eu valence in EuBiS$_2$F determined via various methods at different temperature ranges. Basically, the Eu valence is about +2.2, nearly independent of temperature down to 2 K. This result is very unusual, since the Eu valence mostly increases remarkably with decreasing temperature, e.g., in the systems of Eu$M_2$Si$_2$ ($M=$Cu[39], Pd[43], Ir[44, 45]) and EuNi$_2$P$_2$[45, 46] where Eu VFs were present. As for the crystal structure of EuBiS$_2$F, there is only one crystallographic site for the Eu ions. Therefore, the mixed valence of Eu means existence of VFs. Indeed, according to the Mössbauer results above,
VF frequencies decrease rapidly. At temperature far below $T_{\text{CDW}}$, the VFs of Eu$^{2+}$ and Eu$^{3+}$ are slower than $10^8$ Hz. These observations suggest that Eu should have unequivalent Eu sites in short time scale, which could be realized in the proposed CDW phase with distortions of BiS layers. Thus, the Eu valence is ‘pinned’ by the formation of CDW, resulting in the unique temperature-independent mixed-valence. In turn, the Eu VFs (no matter how slow they are) should be in favor of an unusual dynamic CDW state.

The emergence of SC under the CDW transition suggests that EuBiS$_2$F is also a CDW superconductor, like the well known NbSe$_2$. The formation of CDW generally loses a portion of FSs, which leads to a decrease of $T_c$. In this sense, CDW competes with SC, as usual. However, an anharmonic model calculation shows that the CDW instability is also essential for the SC, suggesting more profound relationship between SC and CDW.

Finally we would like to emphasize that the occurrence of SC at the (self) electron doping level corresponding to $x \approx 0.2$ is also surprising. Previous reports indicate that, in an analogous system of Sr$_{1-x}$La$_x$BiS$_2$F, SC appears for $x > 0.3$, below which the samples show insulating behaviour, and the optimal doping is at $x \approx 0.5$. According to the band structure calculations, the FSs undergo a Lifshitz transition, characterized by a change in FS topology, with electron doping. The two doping levels, $x \sim 0.2$ and $x \sim 0.5$, have very different FS topologies. Therefore, the superconducting state in EuBiS$_2$F might be different from those of other BiS$_2$-based materials. It was predicted that the Lifshitz filling level (like the case of EuBiS$_2$F), the superconducting state is weak topological due to strong spin-orbit coupling. Further investigations are called for to verify this prediction.

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**TABLE I. Summary of the Eu valence in EuBiS$_2$F determined via various methods in different temperature ($T$) ranges. Eu-BVS refers to bond valence sum of the Eu ions. The number in parentheses represents the measurement uncertainty for the last digit.**

| Methods       | Eu-BVS        | Magnetization | Mössbauer     | Heat capacity | Fermi surface |
|---------------|---------------|---------------|---------------|---------------|---------------|
| Eu valence    | 2.14(2)–2.18(2) | 2.17(2)–2.20(1) | 2.24(2); 2.19(3); 2.14(2) | $< 2.28$       | 2.25(5)       |
| $T$ (K)       | 310–13        | 300–2         | $\leq 200$; 273; 388 | 0.5–20        | N.A.          |

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