Dominant role of processing temperature in electric field induced superconductivity in layered ZrNBr

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Abstract

Recently, as a novel technique, electronic double-layer transistors (EDLTs) with ionic liquids have shown strong potential for tuning the electronic states of correlated systems. EDLT induced local carrier doping can always lead to dramatic changes in physical properties when compared to parent materials, e.g. insulating-superconducting (SC) transition. Generally, the modification of gate voltage \((V_G)\) in EDLT devices produces a direct change on the doping level. Here, we report that the processing temperature \((T_P)\) also plays a dominant role in the electric field induced superconductivity in layered ZrNBr single crystals. When applying \(V_G\) at \(T_P \geq 250\) K, the induced SC state is irreversible in the material, which is confirmed in the zero resistance and diamagnetism after long-time relaxation at room temperature and/or by applying reverse voltage, whereas the solid/liquid interface induced reversible insulating-SC transition occurs at \(T_G \leq 235\) K. These experimental facts support another electrochemical mechanism that electric field induced partial deintercalation of Br ions could cause permanent electron doping into the system. Our findings in this study will extend the potential of electric fields for tuning bulk electronic states in low-dimension systems.

1. Introduction

As one of the most effective methods of controlling electric fields, electronic double-layer transistor (EDLT) devices with ionic liquid can induce exotic states in strongly correlated parent materials upon modifying local carrier density. The EDLT induced transition between insulating and superconducting (SC) phase [1–6], full phase diagram through the charge density wave (CDW) and superconductivity in 1T-TiSe\(_2\) [7], and enhancement of SC transition temperature [8] have attracted remarkable attentions in material science. In general, applying gate voltages \((V_G)\) causes polarization of the cations and anions in ionic liquid, which can lead to the accumulation of the corresponding carriers on the crystal surface. Thus, the induced SC states mainly form in a rather thin layer with a thickness of \(1\)–\(2\) nm as reported in previous studies [1, 2]. The carrier density equilibrates again in the material after releasing the \(V_G\) at temperatures higher than the melting point of the selected liquid electrolyte, leading to the disappearance of the induced SC phase. Another characteristic of the general EDLT device is that modifying \(V_G\) produces a direct change on local carrier doping levels, whereas controlling the processing temperature \((T_P)\) causes significant influence on the tuning process and the electrochemical window (EW) of the selected ionic liquid. When applying the same \(V_G\) at different temperatures, the solid/liquid interface results in a certain doping level around crystal surface as reaching the equilibrium between \(V_G\) and polarized electrolyte. A relatively higher temperature could improve the mobility of
ions and decrease the response time for the equilibrium [9]. The leakage current between gate and source electrodes increases with increasing temperature.

In recent studies, electric field is capable of tuning the bulk property by controlling ions rather than the local carriers governed in EDLT devices. Electrolyte gating of epitaxial thin film of VO₂ suppresses the metal–insulator transition and stabilizes the metallic phase through the electric field induced creation of oxygen vacancy [10]. The transformation between the three phases SrCoO₃₋ₓ, SrCoO₂.₅, and HSrCoO₂.₅ can be induced through the control of the insertion and extraction of oxygen and hydrogen ions independently in an electric field [11]. Furthermore, the electric field could induce a clear percolation transition from a short-range magnetically ordered insulator to a robust long-range ferromagnetic metal in La₁₋ₓSrₓCoO₃₋δ [12, 13]. On the other hand, the developed control of the electric field makes it possible to access a complete set of competing electronic phases from band insulators and superconductors, to a reentrant insulator on the monolayers of WS₂ [14].

Here, we present a temperature $T_G$ dominated evolution of the electric field induced superconductivity in layered ZrNBr with a hexagonal [Zr₂N₂] layer. The parent ZrNBr is an insulator with an energy gap of ~3 eV, which turns into a superconductor with $T_c = 14$ K upon intercalation [15]. When applying proper $V_{GS}$ at $T_G$ ≥ 250 K, the induced SC state is irreversible in the material as confirmed in zero resistance and diamagnetism after long-time relaxation without $V_G$ at room temperature and/or applying reverse voltage, whereas a reversible insulating-SC transition occurs in the gating process with $T_G < 235$ K. These facts strongly imply that another electrochemical mechanism such as electric field induced partial deintercalation of Br ions is a valid explanation of the irreversible superconductivity. An unknown SC transition at 11 K is found to coexist with the primary transition at 14 K upon systematically modifying of $T_G$ and $V_G$.

2. Experimental details

Pristine ZrNBr single crystals were grown using a well-established chemical transport method [16]. A schematic configuration of the device is described in figures 1(a) and (b). Compared to conventional field effect transistors, no drain voltage was applied when applying $V_{GS}$ between gate and source, and no terminal was connected to ground. Ionic liquid of diethylmethyl (2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl) imide (DEME-TFSI) and 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) were chosen as the gate electrolyte. Proper $V_{GS}$ were applied at several temperatures between 220 and 300 K. All processes of applying $V_G$ were performed in a vacuum to avoid the influence of oxygen and water in the air. The applied $V_G$ was maintained during the cooling down of the system and released after the appearance of ±0.1 nA of leakage current. The temperature dependence of electrical resistance $R(T)$ discussed in the present study was measured in a warming up process. At each temperature selected for applying $V_{GS}$, systematic measurements of $R(T)$ were performed on a new crystal. After the measurement of $R(T)$ with the highest $V_G$ around the EW limit at each process temperature $T_G$, the system was kept at the same temperature without $V_G$ for 1–2 h. The $R(T)$ measured
after the relaxation process is named final 0 V, which was followed by the $R(T)$ with a reverse $V_G$. After completing all resistance measurements, the temperature dependence of the magnetization $M(T)$ on the same single crystal was measured using a SQUID magnetometer (Quantum Design SQUID VSM). The XPS measurements were performed on a Thermo Scientific ESCALAB 250X spectrometer fitted with a monochromatic Al $K_\alpha$ x-ray source. The composition of polycrystalline samples were estimated using Oxford X-Max energy dispersive x-ray spectroscopy (EDX).

3. Results and discussion

3.1. Device and material
As shown in figures 1 (a) and (b), the EDLT device with ionic liquid is designed on a common sample platform for multi-function probe in PPMS. Figure 1(c) shows a layered ZrNbBr crystal used in the present study, and the typical size of single crystal is approximately $300 \times 200 \times 10 \mu$m$^3$. Layered crystals were fixed on a SiO$_2$ surface grown on a Si substrate. A Pt foil with thickness of 50 $\mu$m was used as gate electrode. Four Pt wires were configured on the crystal surface using silver colloids for electrical transport measurements. The ionic liquid was applied between Pt foil and crystal. As applying positive and negative gate voltages, cations and anion can be accumulated onto the crystal surface, respectively. The hexagonal shape corresponds to the crystal structure with space group of $R\overline{3}m$ (No. 166). Figure 1(d) shows examples of the x-ray diffraction (XRD) pattern observed on single crystal (top) and polycrystalline samples (bottom). Lots of single crystals were ground into fine powders, although the preferred orientation of [000] could not be completely avoided in polycrystalline samples. For single crystal, only diffraction peaks of [001] are confirmed, whereas systematic diffraction peaks confirmed in polycrystalline samples are used to calculate the lattice constant $a = b = 3.6408(2)$ Å and $c = 29.2781(3)$ Å. Based on the obtained lattice parameters, the structure along $a$ axis is shown in figure 1(e). The double honeycomb [Zr$_2$N$_2$] layers are sandwiched by Br layers, Br[Zr$_2$N$_2$]Br.

3.2. $V_G$ dependence of $R(T)$ at different $T_G$
Figures 2(a)–(d) show the temperature dependence of the resistance $R(T)$ in different $V_G$s applied at 220, 235, 250, and 300 K, respectively. For all temperatures in the range of 220–300 K, the absolute resistance at normal-state decreases monotonically with increasing $V_G$ (supporting information is available online at stacks.iop.org/NJP/21/023002/mmedia, section 1), implying that the carrier doping level is effectively controlled by $V_G$. For $T_G = 220$ K, $R$ shows a transition around 14 K with magnitude of $10^5$ $\Omega$ at 3 V. As $V_G$ increases up to 5.5 V, low-temperature $R(T)$ decreases to a level of $10^2$ $\Omega$ with the same transition temperature. This implies that the carrier density increases monotonically with increasing $V_G$. The coexistence of a SC state and bulk insulating/semiconducting characteristics indicates a relatively low carrier doping level and tiny amounts of induced SC components in the transport channel. $R(T)$ with different $V_G$s applied at 235 K shows a similar overall tendency (figure 2(b)). A metallic feature, resistance decreasing with decreasing temperature, is present in low-temperature $R(T)$ (<150 K) when applying $V_G$ up to 5 and 5.5 V, and the absolute $R(T)$ is of order $10^{-1}$ $\Omega$ below $T_c$, although this value is still not considered as zero resistance. With increasing temperature $T_G$ up to 250 and 300 K, the zero resistance ($10^{-3}$–$10^{-6}$ $\Omega$) is present at $V_G \geq 2.5$ V as shown in figures 2(c) and (d), respectively. However, the metallic $R(T)$ appears when applying $V_G \geq 3.3$
V leads to a slight enhancement in resistance with a clear SC transition, implying that the electric irreversible changes between insulating and SC states strongly depend on the processing temperature. Superconductivity is irreversible in the system. All these experimental facts suggest that the reversible and releasing the two quarters provides direct evidence that the induced high-conductance state disappears immediately upon using R.

To further understand the effect of applying a V applied at different temperatures results in different electronic states.

3.3. Reversible and irreversible SC transitions

To further understand the effect of applying V at different temperatures, we measured the isothermal resistance when scanning V. V was swept with 5 mV s \(^{-1}\) at several selected temperatures. A full V \(_G\) scanning loop consists of four quarters (0 V \(\rightarrow\) +5 V \(\rightarrow\) 0 V \(\rightarrow\) −5 V \(\rightarrow\) 0 V). When increasing V from 0 to 5 V at 220 K, R decreases monotonically as shown in figure 3(a). After the former two quarters, R is almost recovered to the initial value at 0 V. Applying negative V \(_G\) causes a weak hysteresis of R. The perfect recovery of R in the former two quarters provides direct evidence that the induced high-conductance state disappears immediately upon releasing the V \(_G\), which is consistent with the general EDLT effect. When increasing the temperature T \(_G\) to 230 K (figure 3(b)), R shows a decrease of near 44% and 21% after the former two quarters and a full loop, respectively. Furthermore, a dramatic decrease (76%) has been confirmed when scanning V \(_G\) at 240 K (figure 3(c)). It appears that the completely irreversible change in resistance occurs at temperatures above \(\approx 235\) K, which suggests the important role of T \(_G\) in the tuning process.

Correspondingly, the reversible and irreversible changes between insulating and SC states were investigated using R(T) in several critical V \(_G\)s applied at this temperature region as shown in figures 3(d)–(f). The process of applying these V \(_G\)s is described in Experimental details. As T \(_G\) = 220 K, R(T) with final 0 V shows the insulating behavior, which is very close to the initial state. Such a perfect recovery from SC to insulating state is significantly in agreement with the isothermal V \(_G\) dependence of resistance (figure 3(a)). Compared to +5.5 V applied at 235 K (figure 3(e)), final 0 V could only restore R(T) back to 10\(^7\) Ω with a steep transition at 14 K. Further application of −4.5 V could restore the R(T) back to an insulator-like state. A rather weak and clear drop can still be confirmed around 14 K, implying that partial induced SC states remain in the material. As temperature T \(_G\) increases to 250 K (figure 3(f)), final 0 V causes no obvious change compared to +5.5 V. The application of −4.5 V leads to a slight enhancement in resistance with a clear SC transition, implying that the electric field induced superconductivity is irreversible in the system. All these experimental facts suggest that the reversible and irreversible changes between insulating and SC states strongly depend on the processing temperature T \(_G\), supporting again that the irreversible superconductivity is not induced by the general EDLT effect but some

![Figure 3. Reversible and irreversible changes between insulating and superconducting states.](image-url)
other mechanism such as electric field induced partial deintercalation of Br. Similar electric field induced vacancy formation was observed in MNCI (M: Hf and Zr) [17] and VO₂ [10, 18]. Furthermore, it was reported that the VO₂ films were seriously damaged by the application of a rather low V̄G (2 V) at room temperature for several hours [19], implying that the processing time may be another important factor as well as Tc and V̄G.

In order to confirm the irreversible characteristic, the magnetic responses of the same single crystal were measured after completing the electrical transport measurements. After applying V̄G at 220 and 235 K, no SC transition was observed in the temperature dependence of magnetization M(T). As shown in figure 3(e), a weak drop is confirmed at approximately 14 K with huge resistance. This suggests that only a small amount of the induced SC components remain in the system after applying −4.5 V. It is reasonable that such a weak SC signal can scarcely be detected in M(T). As Tc increases up to higher than 250 K, the primary SC transition at 14 K is confirmed in M(T) (figure 3(g)). Furthermore, one can see that the diamagnetism is clearly weakened by a three day annealing at 120 °C, although Tc shows no apparent shift (open circles in figure 3(g)). The apparent annealing effect suggests that the induced SC phase is sensitive to high-temperature treatment. Figure 3(h) shows the M(T) measured on a polycrystalline sample using a different gate electrolyte EMIM-BF₄. When applying V̄G = 2 V at room temperature, a clear transition is also confirmed at 14 K, strongly implying that the electric field induced irreversible SC state is independent of the gate electrolyte.

3.4. V̄G and Tc dependence of Tc

On the other hand, we also explored the V̄G dependence of the induced SC transition temperature. The R(T) measured after applying different V̄G at 250 K is selected as a typical example. When applying V̄G from 2.0 to 2.7 V (figure 4(a)), a primary SC transition together with another weak drop was observed around 14 and 11 K, which are named Tc1 and Tc2, respectively. As mentioned previously, zero resistance was realized by increasing V̄G to higher than 2.7 V. Thus, we reasonably consider that the induced SC states with V̄G ≤ 2.5 V have rather poor homogeneity. By increasing V̄G from 2.7 to 5.5 V (figure 4(b)), the primary transition at Tc1 is slightly weakened, and the transition around Tc2 becomes gradually obvious. Increasing V̄G results in the decreasing of SC components with Tc1 as well as increasing the contribution from SC states with Tc2. Furthermore, long-time relaxation without voltage at 250 K appears to cause a weak reverse effect (figure 4(c)). Surprisingly, the transition at Tc2 disappears immediately when applying negative voltage (−4.5 V). A two-day relaxation at room temperature causes no apparent change on the electric field induced SC transition at Tc1 or the bulk metallic characteristic, except for a slightly increased resistance.

To quantitatively characterize the V̄G dependence of the two induced SC transitions, we determine Tc1 and Tc2 as the temperatures corresponding to the peaks observed in the normalized dR/dT (figure 4(d)). The two transitions can be clearly seen in dR/dT, which displays an alternating change between Tc1 and Tc2 as discussed previously. The SC states with Tc1 and Tc2 dominate at the low and high V̄G, respectively. As shown in figure 4(e), the Tc1 and Tc2 values obtained at different V̄G are compared with Tc3 determined using conventional extrapolation methods (supporting information, section 2). Both Tc1 and Tc2 show a weak V̄G dependence; Tc decreases with increasing V̄G. The V̄G dependence of Tc2 is consistent with the Tc dependence of doping levels observed in bulk intercalated superconductors such as Li₂M₄₋ₓ HINCNI [20] and AEₓM₄₋ₓ HINCNI [21]. The V̄G dependence of Tc2 (open circles in figure 4(e)) suggests that the anomaly at Tc2 is not a random SC transition caused by non-homogeneity but an unknown SC phase. Such results have high reproducibility as confirmed in

Figure 4. V̄G dependence of superconducting transition temperatures observed when applying V̄G at 250 K. R(T) in an expanded scale for V̄G = 2.0–3.0 V (a), 3.3–5.5 V (b), and several critical V̄G (c). Normalized dR/dT is used to determine Tc1 and Tc2 (d). V̄G dependence of Tc1 and Tc2 is compared with Tc3 determined in a different method (e). The filled and open circles represent Tc values obtained in two verification experiments on a single crystal #1 and #2.
another single crystal (supporting information, section 2). However, the absence of $T_{c2}$ in $M(T)$ and $R(T)$ after applying negative $V_G$ indicates the metastable characteristic of the SC states with $T_{c2}$.

Although the SC phase with $T_{c2}$ is very similar to a conventional EDLT induced high doping level, we consider that the SC state with $T_{c2}$ could be a kind of metastable state with energy higher than the bulk stable state. When applying positive $V_G$, local carriers present at both the stable and the metastable state, inducing SC state with $T_{c1}$ and $T_{c2}$, respectively. It appears that a higher $V_G$ could result in a dominant contribution from the metastable state to the transport channel. When applying a reverse $V_G$, the local carriers at the metastable energy state could be transferred to the stable state, which results in the stable state corresponding to the primary SC phase with $T_{c1}$. One can see some similarity between the electric field induced metastable SC state discussed here and the gate-induced incommensurate/nearly commensurate charge density wave phase transition observed in 1T-TaS$_2$ [22]. However, the origin of such a metastable state is yet unclear.

The same $V_G$ applied at different temperatures appears to induce different electronic states in the present system. Thus, the $V_G$ dependence of $T_{c1}$ and $T_{c2}$ are also sensitive to the temperature $T_G$. Here, we select 220, 235, 250 (figure 4), 280, and 300 K to discuss the role of temperature $T_G$ in the induced SC transition. For $T_G = 220$ K, the primary SC transition is broad and crosses over the temperature region between 14 and 11 K as shown in figure 5(a). It is hard to discuss the $V_G$ dependence of such a broad SC transition, which could be related to the normal-state resistance within the level of kΩ. When increasing the temperature $T_G$ to 235 K (figure 5(b)), the primary SC transition at $T_{c1}$ becomes steep and the weak transition already appears around 11 K. As shown in figures 5(c) and (d), the primary SC transition changes from $T_{c1}$ to $T_{c2}$ upon a slight increase of 0.3 V around 3.0 and 2.7 V for $T_G = 280$ and 300 K, respectively, whereas the similar change takes place in a wide $V_G$ region (3–5 V) at 250 K (figure 4(b)), suggesting that a higher temperature $T_G$ accelerates the evolution of the induced SC phase between $T_{c1}$ and $T_{c2}$. More importantly, it appears that the SC transition at $T_{c1}$ completely disappears when applying $V_G \geq 3.3$ V at 300 K. Upon modifying the temperature $T_G$ and voltage $V_G$, the systematic behaviors of the induced SC transitions imply the connection and different characteristics between $T_{c1}$ and $T_{c2}$ as the following: (1) similar weak $V_G$ dependence, (2) dominant contribution at different $V_G$s, and (3) opposite response to reverse $V_G$.

### 3.5. Anisotropic upper critical field

We investigated the magnetic field dependence of $T_{c1}$ and $T_{c2}$ with configurations of $H||c$ and $ab$ as shown in figure 6. Here, we select the resistance under fields $R(T, H)$ after applying $V_G$s at 250 K as a typical example. $T_{c1}$ and $T_{c2}$ values under magnetic fields are determined using the same method (figure 4(d) and supporting information section 3). As increasing $H$ ($||c$) from 0 to 2.5 T, the SC transition shifts to low temperatures monotonically, and $R(T)$ is almost constant under magnetic fields higher than 3 T as shown in figure 6(a). In contrast, the transitions at $T_{c1}$ and $T_{c2}$ decrease slightly when increasing $H$ ($||ab$) from 0 to 7 T (figure 6(b)). On the other hand, isothermal field dependence of resistance $R(H)$ was also measured to estimate the upper critical field $H_{c2}$ in $c$ and $ab$ as shown in figures 6(c) and (d), respectively. The method used to determine $H_{c2}$ at certain temperatures is described in supporting information section 3. All $T_c$ and $H_{c2}$ values for $T_G = 250$ K are summarized in the $H_{c2}$–$T$ phase diagram as shown in figure 6(e). A huge anisotropy of $H_{c2}$ occurs between $H||c$ and $ab$ plane, which seems related to the 2D-like SC nature. Such an ion-gated 2D SC nature has been experimentally confirmed in the isostructural ZrNCl$_2$ [23]. The SC states mainly induced on the surfaces of the layered ZrNBr crystal could be responsible for the strongly enhanced anisotropy of $H_{c2}$ when applying $H$. 

Figure 5. $V_G$ dependence of transition temperatures when applying $V_G$s at 220 K (a), 235 K (b), 280 K (c), and 300 K (d). The dashed lines are guide lines for induced superconducting transitions at $T_{c1}$ and $T_{c2}$. 

![](image.png)
superconductivity in layered ZrNBr. A small parallelly along the SC layer. Note that Thus, we attempt to interpret the initial positions. This is consistent with the induced SC transition and the insulating state recovered at different temperatures suggest that the temperature consequently results in a permanent electron doping to the system. The negative to escape from the crystal surface. The possible formation of Br vacancies can provide extra electrons, which the other hand, applying the disappearance at reverse characteristics. Meanwhile, the correlation between shows no apparent difference when compared to 250 K. Thus, we can reasonably conclude that the electric process. Thus, the same correction determined in the comparison of Br BE is applied on those of N and Zr. One can see that the spectra for all three elements become slightly broad after applying 3 V at 300 K, in which the superconductivity are not due to the decomposition of ionic liquid caused by parallelly. Figure 6. Magnetic field dependence of $T_c$ and $T_{c2}$. The temperature dependence of resistance $R(T)$ with $H//c$ (a) and $ab$ (b) when applying $\pm$ 3.5 V at 250 K. For both configurations, magnetic fields are always perpendicular to current flowing in $ab$ plane. For $H//c$, $H$ was increased up to 9 T (0.05, 0.1, 0.2, 0.3, 0.5, 1, 1.5, 2, 2.5, 3, 5, 7, and 9 T). For $H//ab$, $H$ was increased up to 7 T (0.05, 0.1, 0.2, 0.3, 0.5, 1, 1.5, 2, 3, 4, 5, 6, and 7 T). The two dashed lines in (b) guide the shift of $T_{c1}$ and $T_{c2}$ under fields. Isothermal field dependence of resistance $R(H)$ with $H//c$ (c) and $ab$ (d) as applying $\pm$ 5.5 and $\pm$ 4.5 V, respectively. For $V_G$ = 5.5 V, $R(H)$ with $H//c$ was measured between 2 and 20 K with an interval of 1 K. $R(H)$ with $H//ab$ was measured at 2, 4, 6, 8, 10, 11.5, 11.75, 12, 12.5, 13, and 14 K. Data of (a) and (b) were measured on the same single crystal #1 as used in figure 4, whereas (c) and (d) were measured on the same single crystal #2. (e) The $H/T$ phase diagram including $T_{c1}$ and $T_{c2}$ values obtained in $R(T)$ and $R(H)$ compared with those of $T_{c1}$ = 235 and 300 K. parallelly along the SC layer. Note that $T_{c1}$ and $T_{c2}$ show comparable field dependence in the configurations of $H//c$ as well as $H//ab$, together with the identical $V_G$ dependence (figure 4(e)), suggesting the similar SC characteristics. Meanwhile, the correlation between $H_{c2}$ and $T_c$ obtained at temperatures $T_{c1}$ = 235 and 300 K shows no apparent difference when compared to 250 K. Thus, we can reasonably conclude that the electric field induced superconductivity shows the same characteristic, although the appearance of SC transition at $T_{c2}$ and its disappearance at reverse $V_G$ and/or high-temperature relaxation can hardly be understood yet. In the present study, we focus on the electric field induced irreversible superconductivity and the unknown SC transition at $T_{c2}$, whereas the quantum phase transition recently revealed in 2D ZrNCl and MoS$_2$ is not discussed here [6, 24].

3.6. Scenario for reversible and irreversible SC transitions

The reversible insulating-SC evolution and irreversible superconductivity observed when applying $V_G$ at different temperatures suggest that the temperature $T_{c2}$ plays a dominant role in electric field induced superconductivity in layered ZrNBr. A small $V_G$ (3 V) applied at different $T_{c2}$ also induces different electronic states (supporting information, section 4), implying that the observations including the irreversible superconductivity are not due to the decomposition of ionic liquid caused by $V_G$ that are outside of the EW [25, 26]. Furthermore, no obvious change of XRD has been confirmed as compared to the pristine ZrNBr, which could exclude the possibility of the intercalation of big-size molecule between two adjacent ZrNBr blocks as observed in 2H-TaS$_2$ [27]. These phenomena can hardly be understood with respect to the general EDLT effect. Thus, we attempt to interpret the findings in another scenario. Upon applying $V_G$ at 220 K, short-range motion of partial Br$^{1-}$ ions could be induced by the positive $V_G$, leading to local electron doping in the system. The application of reverse $V_G$ and/or long-time relaxation without $V_G$ could almost push back the Br ions to their initial positions. This is consistent with the induced SC transition and the insulating state recovered at final 0 V (figure 3(d)). Alternatively, we could just use the normal EDLT effect to explain the observations at low $T_{c2}$. On the other hand, applying $V_G$ at temperatures higher than 250 K could make partial Br$^{1-}$ ions gain enough energy to escape from the crystal surface. The possible formation of Br vacancies can provide extra electrons, which consequently results in a permanent electron doping to the system. The negative $V_G$ can only contribute to the improvement of the homogeneity rather than pushing back the Br ions to the material (figure 3(f)).

The scenario about the Br vacancy formation is supported by the XPS and EDX results on polycrystalline samples. The $3d$ spectra of Br, N, and Zr are shown in figures 7(a)–(c), respectively. Here, our concern is mainly with the difference of binding energy (BE) between before and after the gating process rather than fitting the spectra peaks. To reduce the analysis error, we consider that no shift of the BE of Br occurs after the gating process. Thus, the same correction determined in the comparison of Br BE is applied on those of N and Zr. One can see that the spectra for all three elements become slightly broad after applying 3 V at 300 K, in which the
irreversible superconductivity has been confirmed. Note that there is a clear shift of near 0.7 eV in the BE of Zr, whereas no shift for the BE of N is observed. More importantly, the BE of Zr shifts to the lower energy region, corresponding to a slight change from oxidation to a sub-oxidation state of Zr after the gating process. Such experimental facts support the permanent electron doping.

Meanwhile, the chemical composition of polycrystalline samples was characterized using EDX. The scanning electron microscope image and EDX results of one pristine and three gated samples are shown in figures 8(a)–(d), respectively. Four different positions were analyzed for each selected samples. Without considering the instrumental error, the average atomic ratio of Zr:Br for the pristine sample is $1:0.99 \pm 0.02$ (a), which shifts to $1:0.89 \pm 0.01$ (b), $1:0.94 \pm 0.02$ (c), and $1:0.84 \pm 0.04$ (d) after the gating process. Although this kind of average estimation always has a non-negligible error, the Br content obviously decreases in the gating process. A similar vacancy forming process was reported in VO$_2$ film, in which suppression of metal–insulator transition was caused by electric field induced oxygen vacancy formation \cite{10, 28, 29}. As recently reported on YBa$_2$Cu$_3$O$_{7-x}$ \cite{30}, the EDLT induced deoxygenation of the CuO chains causes the modification of Cu coordination, leading to a superconductor-to-insulator transition. Based on the observations in the present

**Figure 7.** XPS spectra of (a) Br3d, (b) N1s, and (c) Zr3d observed in a pristine and gated ($V_G = 3$ V at $T_G = 300$ K) polycrystalline sample of ZrNBr.

**Figure 8.** The scanning electron microscope image and EDX results of pristine (a) and gated (b)–(d) polycrystalline samples of ZrNBr.
study, we reasonably consider that the temperature of 235 K is close to a critical temperature, above which the deintercalation of Br ions could occur when applying proper $V_G$s. Thus, the irreversible superconductivity could be caused by the partial deintercalation of Br in the gating process.

4. Conclusion

In conclusion, we find that the processing temperature $T_G$ as well as the gate voltage $V_G$ plays a dominant role in electric field induced superconductivity in layered ZrNBr. $T_G = 235$ K appears to be a critical temperature between the conventional EDLT effect and electric field induced electrochemical reaction using DEME–TFSI. We consider that such a temperature effect is not limited to a certain type of ionic liquid. The irreversible superconductivity is caused by the partial Br vacancy, which is supported by the shift of BE of Zr and the decrease of Br content on the gated crystal surfaces. Although the mechanism is not clear yet, a metastable SC phase with $T_c = 11$ K has been revealed to coexist with the primary SC transition at 14 K. More exotic phenomena could be expected upon modifying the temperature $T_G$ and voltage $V_G$ using an EDLT device with liquid electrolyte.

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