Microscopic Origin of Structural Disorder in $\delta$ – NbN: Correlation of Superconductivity and Electronic Structure

Shailesh Kalal, 1 Sanjay Nayak, 2 Akhil Tayal, 3 Jens Birch, 2 Rajeev Rawat, 1 and Mukul Gupta 1

1 UGC-DAE Consortium for Scientific Research, University Campus, Indore-452 001, India
2 Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83, Linköping, Sweden
3 Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany

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Rock-salt type niobium nitride ($\delta$ – NbN) is a well-known superconductor having superconducting transition temperature ($T_C$) $\approx$ 18 K and a large superconducting gap $\approx$ 3 meV. The $T_C$ of $\delta$ – NbN thin film exhibits a large scattering irrespective of the growth conditions and lattice parameter. In this work, we investigate the atomic origin of suppression of $T_C$ in $\delta$ – NbN thin film by employing combined methods of experiments and ab-initio simulations. Sputtered $\delta$ – NbN thin films with different disorder were analyzed through electrical resistivity and x-ray absorption spectroscopy. A strong correlation between the superconductivity and the atomic distortion induced electronic reconstruction was observed. The theoretical analysis revealed that under N-rich growth conditions, atomic and molecular N-interstitial defects assisted by cation vacancies form spontaneously and are responsible for the suppression of $T_C$ in $\delta$ – NbN by smearing its electronic densities of states around Fermi level.

One of the crucial issues in the development of superconducting NbN based technology is to achieve the optimum $T_C$. In the literature, it is well documented that the growth techniques and conditions play a vital role in determining $T_C$. Polakovic et al. have reported that $T_C$ as a function of $N_2$ gas pressure shows a dome like behavior with maximum value of $\approx$ 14 K at a specific range of $N_2$ concentration (17-20%). Similar results have been reported by Choudhuri et al. where $T_C$ of NbN thin films maximizes at a certain nitrogen pressure. Through Hall measurements Chockalingam et al. demonstrated that $T_C$ of NbN thin films deposited at different $R_{N_2}$ was governed by carrier density caused by Nb and/or N vacancies concentration. However, this work does not shed light on a drastic reduction of the carrier density with samples grown at higher $N_2$ partial pressure ($R_{N_2}$). Similar results have been widely reported in the literature. Often, the atomic disorder has been attributed to the reduction of the $T_C$ in this superconductor. Thus, to uncover the microscopic origin of the widely speculated structural disorder and consequently its effect on superconductivity, we synthesize $\delta$ – NbN thin films using a dc-magnetron sputtering technique. A detailed report on structural and transport characterization of grown films has been published elsewhere where XRD result confirms that the sample grown at $R_{N_2}$ = 30, 65, 100%.

| $R_{N_2}$ (%) | LP (± 0.006 Å) | $T_C$ (K) |
|---------------|---------------|----------|
| 16            | 4.376         | 12.8     |
| 25            | 4.415         | 6.9      |
| 30            | 4.421         | -        |
| 65            | 4.486         | -        |
| 100           | 4.505         | -        |
| Theoretical (this work) | 4.41 | - |
| Experimental [16] | 4.40 | 17.3 |
| Theoretical [20] | 4.45 | 18.2 |

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The initial rise where a strong I$_2$ arises for the sample deposit at R$_{N2}$, which indicates XANES 400 eV arises for the sample deposit at R$_{N2}$. Here, we note presence of electronic sub-band transition specific x-ray absorption near edge spectroscopy (XANES) measurements are presented in Fig. 1. The values of R$_{N2}$, LP and T$_C$ are given in table I where a strong correlation between structure and superconductivity is noticed. Here with increase in R$_{N2}$, the LP is continuously increasing and consequently a reduction in the T$_C$ is seen.

In order to understand the effect of growth conditions on the electronic structure, we performed element specific x-ray absorption near edge spectroscopy (XANES) measurements both at Nb and N K-edges as shown in Fig. 2(a) and (b), respectively. We note that Nb K-edge splits into two components K1 and K2 (see inset of Fig. 2(a)). The initial rise K1 is due to the transitions from 1s core level to unoccupied admixed 4$d$-5$p$ levels while the second absorption rise K2 arises due to transitions from the 1s core level to the Laporte-allowed states of pure 5$p$ symmetry. The absorption edge of sample deposit at R$_{N2}$ = 16% is shifted to higher energy by 3 eV as compared to elemental Nb (see inset of Fig. 2(a)), which indicates that Nb atom bears positive charge due to the formation of NbN compound. Further, with R$_{N2}$ ≥ 25% d band is delocalizing around the Fermi level ($E_{K1}$).

Similarly, we observed clear changes in the line shape of N K-edge spectra with increase in R$_{N2}$ (see Fig. 2(b)). A sharp transition at threshold of around 400 eV arises for the sample deposit at R$_{N2}$ = 16%. Here, we note presence of electronic sub-band transition levels labeled as a, b, c, d. DOS analysis reveals (see Fig. S2 of SM) these features are results of transition from N-1$s$ core level to unoccupied N-2$p$ orbitals. It is well-known that the TMNs in octahedral bonding coordination (e.g. δ − NbN) metal d orbitals splits into two electronic sub-bands (e$_{g}$ and t$_{2g}$) owing to its hybridized characteristics of N-2$p$ orbitals. Feature a (centred at 402.8 eV) in N K-edge XANES spectra is a consequence of hybridized N-2$p$ and t$_{2g}$ level of Nb-4$d$ orbitals, feature b (centered at 406.8 eV) is a consequence of hybridized N-2$p$ and e$_{g}$ level of Nb-4$d$ orbitals. The feature c and d arises due to higher order hybridization between N-2$p$ and Nb-5$s$-5$p$ orbitals. Further at R$_{N2}$ = 25%, feature b become broad and at R$_{N2}$ = 30%, sharp a* feature (404.9 eV) arises in between a and b, whose intensity is gradually increases with increase in R$_{N2}$.

To identify the atomic origin of above mentioned features, we simulate N K-edge XANES spectra for multiple defect configurations using multi scattering theory (see Fig. S1 of SM [19]). We obtained the relaxed atomic structure of various point defects: (i) isolated N-vacancy (V$_N$), (ii) multiple N-vacancy (2V$_N$), (iii) Nb vacancy (V$_{Nb}$), (iv) N interstitial (N$_i$), (v) N antisite (N$_{Nb}$), (vi) Schottky type defect (V$_N$ − Nb$_i$), and (vii) interstitial N$_2$ molecules (N$_{2i}$) from SIESTA codes and used them to construct atomic cluster for simulation of ab-initio XANES spectra (computational details of simulations are given in section II of SM [19]). First, to establish the credibility of numerical parameters used in simulations, we obtained N K-edge spectra for pristine δ − NbN. Clearly, features a, b, c, and d are reproduced in simulations. The experimental spectrum obtained for the sample grown at R$_{N2}$ = 16% is in well agreement with the theoretically calculated spectra of δ − NbN having V$_{Nb}$ (see Fig. 2(b) and (c)). A thorough comparison between experimental (Fig. 2(b)) and simulated (Fig. 2(c)) XANES spectra of N K-edge, revealed that appearance of a* peak centred around 404.9 eV for the sample grown at higher R$_{N2}$ is probably a signature of either N$_i$ or N$_{2i}$ defects in δ − NbN.

Gall et al. studied the energetic of defect formation in TMNs and suggested a cation vacancy (V$_{Nb}$) is the most stable defect in δ − NbN, consistent with our estimation of formation energy (FE). FE plot for various defect configurations is shown in Fig. 3. Estimated FE of V$_{Nb}$ under N-rich growth condition is -0.74 eV. Work of Gall et al. predicted that FE of N$_i$ is very high, which is again consistent with our estimation of high FE = 1.55 eV at N-rich conditions. Further we find even under N-rich conditions, FE of molecular nitrogen (N$_2$) in δ − NbN is very high (4.51 eV). High FE of N$_i$ and N$_{2i}$ in δ − NbN clearly suggests that they will not form spontaneously and their concentration in δ − NbN should be negligible. Interestingly, we find that when V$_{Nb}$ and N$_i$ are in a complex form (V$_{Nb}$-N$_i$) their FE reduces and under N-rich condition, we estimate it to be -0.43 eV (see Fig. 3). Also the estimated binding energy (BE) of V$_{Nb}$-N$_i$ is too high (1.26 eV). The positive BE indicates the preferential stability of the defect complex and higher the magnitude means better the stability (details of method to estimate BE is discussed in section II to SM [19]). Similarly when N$_2$ incorporated near V$_{Nb}$ site, it forms V$_{Nb}$-N$_2i$ defect complex and its FE is 2.21 eV (see Fig. 3). The estimated BE of the V$_{Nb}$-N$_2i$ is 1.56 eV. The FE of N$_2$ further reduces to 0.02 eV when it get coupled with two nearest neighbour V$_{Nb}$ sites (see Fig 3).
Figure 2. (a) Nb K-edge XANES spectra with inset showing first derivative. (b) N K-edge XANES spectra and (c) simulated N K-edge XANES spectra for various defect configurations. Ball-and-stick models of different δ-NbN configurations used in DFT and multiple scattering theory calculations are presented: (d) pristine δ-NbN, (e) with Nb vacancy (V_{Nb}), (f) with interstitial nitrogen (N_{i}) and (g) with molecular nitrogen (N_{2i}).

a very high BE of 5.96 eV. These observations clearly establish that the interstitial atomic (N) and molecular nitrogen (N_{2i}) can be stabilized in δ-NbN through cation (Nb) vacancies.

Further, we analyze the effect of these defects to the atomic structure of δ-NbN. The obtained relaxed LP of δ-NbN is noted to be 4.41 Å. We find that 3.125% of V_{Nb} in δ-NbN reduces the unit cell volume by 0.06%. While V_{Nb}-N_{i} increases the unit cell volume by 0.025% and defect complex V_{Nb}-N_{2i} causes shrinking of unit cell volume by 0.020%. A comparison between experimentally obtained LP (and hence volume, see table I) and theoretically computed volumes suggests that V_{Nb}-N_{i} is predominant in the samples grown with R_{N_{2}}>16% and their concentration increases with increase in R_{N_{2}}. The smaller LP (see table I) of δ-NbN thin film grown at R_{N_{2}}=16% suggest a presence of higher concentration of V_{Nb} in it. Also the estimated lattice relaxation energy, ΔE_{c} [= E_{tot} (without ionic relaxation) - E_{tot} (with ionic relaxation)] of δ-NbN with point defects V_{Nb}, V_{Nb}, N_{i}, V_{Nb}-N_{i}, N_{2i}, V_{Nb}-N_{2i}, and 2V_{Nb}-N_{2i} is 15, 10, 102, 107, 163, 160, and 172 meV/atom, respectively.

Higher values of ΔE_{c} for interstitial defects suggest a substantial lattice distortion of δ-NbN, in agreement with the increment of disorder in the δ-NbN films with increase in R_{N_{2}}.

Next, we shall discuss the role of these point defects (if any) on the superconducting properties of δ-NbN thin films. Using the value of electron-phonon coupling constant ($\lambda$), $T_c$ for the strong coupling superconductors can be obtained via McMillan-Allen-Dynes formalism \[\text{[9, 13, 26, 27]}\], given by:

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)}\right]$$

where $\omega_{\log}$ is a logarithmic average of phonon frequency, $\mu^*$ is the averaged screened electron-electron interaction. The $\lambda$ further calculated as $\lambda = [N(\epsilon_F)/(\omega^2)] \sum_i (I_i)^2 / M_i$, where $M_i$ is the atomic mass of $i^{th}$ atom and $(I_i)^2$ is the square of the electron-phonon coupling matrix element averaged over the Fermi surface \[\text{[26, 27]}\]. $N(\epsilon_F)$ is the electronic density of states at the Fermi level. The $\omega^2$ can be further approximated as $0.5\Theta_D^2$, where $\Theta_D$ is the Debye temperature \[\text{[28]}\]. From eq. 1, it is quite evident that
Figure 3. Formation energy as a function of chemical potential of N₂ for Nb vacancy (V Nb), nitrogen vacancy (V N), interstitial nitrogen (N i), molecular nitrogen (N₂), combination of niobium vacancy with interstitial nitrogen (V Nb-Ni), combination of niobium vacancy with molecular nitrogen (V Nb-N₂), and combination of multiple niobium vacancy with interstitial nitrogen (2V Nb-Ni) configurations.

Figure 4. Calculated total density of state (DOS) for stoichiometric δ-NbN along with Nb vacancy (V Nb), combination of Nb vacancy (V Nb) with interstitial nitrogen (N i), and combination of multiple Nb vacancy with molecular nitrogen (2V Nb-N₂) configurations. Inset shows expanded view of Fermi level. Here, Fermi level is set to 0 eV.

T_C is sensitive to the N(ε)F. Thus, we computed the electronic DOS of NbN with previously determined dominant defects and presented in Fig. 4. A strong smearing in the electronic structure is visible due to the formation of V Nb-Ni or 2V Nb-N₂ defects complex in δ – NbN (see Fig. 4). DOS calculations shows that N(ε)F of pristine δ – NbN (2 × 2 × 2 supercell) is 16.26 states.eV⁻¹. For 3.125% of V Nb, N(ε)F reduces to 14.75 states.eV⁻¹. The computed N(ε)F for V Nb-Ni and 2V Nb-N₂ are 10.50 and 11.15 states.eV⁻¹, respectively. We estimate T_C by substituting the values of ω_ν (269 K), Θ_D (637 K), μ∗ (0.10) computed for δ – NbN in Ref. 3 and the normalized electronic DOS from our simulations in eq. 4. For pristine δ – NbN Gou et al. computed T_C = 18.26 K, a little higher than experimentally obtained ones 4. Using the SIESTA, computed N(ε)F of δ – NbN with 3.125% VNii in eq. 4 estimate of T_C to be 15.78 K. The experimental T_C of δ – NbN sample grown at RN₁=16% is 12.8 K, hinting concentration of VNii is higher than 3.125% in it. Further using the N(ε)F of VNii-Ni and 2V Nb-N₂ configurations in eq. 4 results into T_C of 7.18 K and 8.44 K, respectively. These values are in excellent agreement with the experimentally obtained T_C = 6.9 K of sample grown at RN₁=25%. The absence of superconducting transition (down to 3 K) in the samples grown at RN₁ ≥30% is possibly due to the presence of a large disorder in the films, which occurs in δ – NbN films due to the presence of a large concentration of N-interstitial related defects. We estimate a 50% reduction in N(ε)F as compared to the pristine δ – NbN can push the T_C to below 3 K.

Thus, here we unveil the atomic structure of disordered δ – NbN responsible for suppression of superconducting transition temperature. Under N-rich growth conditions, spontaneously formed cation vacancies are responsible for the stabilization of N-interstitial defects in δ – NbN thin films which are otherwise unfavourable with high formation energies. The positive binding energy of the cation vacancies and anion interstitial defect complex further cements their bonding in the crystal. Formation of the N-interstitial defect complex in δ – NbN causes strong smearing of electronic structure by creating atomic disorder in the films and thus a significant reduction in the N(ε)F which strongly influencing the electron-phonon coupling strength and consequently reduces the T_C. Increase in the T_C of vacuum annealed δ – NbN and degradation of superconducting properties at N₂ atmosphere further support our proposed mechanism. Based on above analysis we suggest that to obtain δ – NbN with high T_C, films should be grown at Nb-rich conditions to avoid N-interstitial defects and annealing of samples in a vacuum is recommended to eliminate residual N atoms.

In summary, we have uncovered the microscopic origin of growth parameter dependence on the T_C of δ – NbN. By probing the electronic structure of disordered δ – NbN samples, we identify point defect complexes consisting of cation vacancies with atomic anion interstitial [VNii-Ni] and cation vacancies with interstitial molecular nitrogen [nVNii-N₂] are responsible for suppression of the T_C in NbN films grown at higher nitrogen partial pressure (RN₁). The suppression of the T_C is caused by smearing of electronic structure and reduction of electronic DOS around Fermi energy due to the formation of point defect complex. We also show that stabilization of atomic and molecular nitrogen in δ – NbN is assisted by cation vacancies. Es-
timated $T_C$ of $\delta$ – NbN with dominant defects identified from first-principles simulations are in good agreement with the experimentally obtained values.

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