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Local structure around the flux pinning centers in superconducting niobium silicon oxynitride $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$

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ABSTRACT

The superconducting transition temperature of niobium silicon oxynitride $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ exhibits a gradual reduction from 16.8 K to around 11 K under an increasing applied magnetic field of up to 14 T. This relatively small T_c reduction under an applied magnetic field suggests a robustness of its superconducting behavior in comparison to that in the parent niobium oxynitride. It was similar to the flux pinning effect observed in the large magnetic hysteresis of the niobium-silicon oxynitrides in our previous study. Both Si *K*-edge XANES and ^{29}Si MAS-NMR indicated that the local structure of pinning centers around the silicon atoms close to cationic vacancies was similar to that of Si in amorphous SiO_2 in the rock-salt structure of niobium oxynitride.

1. Introduction

Oxynitrides are mixed anion compounds containing both oxygen and nitrogen. Most oxynitrides have crystal structures similar to those of the corresponding nitrides because the oxide and nitride anions are similar in size. The anions differ in both charge and covalency having their respectively unique local structure in the whole crystal structures as an average. The local structure determines the characteristic properties of an oxynitride. The large dielectric constants of $M\mathrm{TaO_2N}$ (M=Sr, Ba) perovskites could be related to the local polarity in their *cis*-TaO_4N_2 octahedral configuration [1–4]. Photoluminescence in oxynitrides can be tuned to a favorable frequency because the coordination around their emission centers depends on the amount of nitrogen present during their preparation [5–7].

The quaternary niobium oxynitrides $(Nb_{0.95}Mg_{0.05})(N_{0.92}O_{0.08})$, $(Nb_{0.89}Al_{0.11})(N_{0.84}O_{0.16})$, and $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ were recently found to crystallize in a rock-salt structure [8–11]. These materials showed superconducting behavior below ~17 K, with shielding volume fractions ranging between 90% and 100%. The critical current density (J_C) estimated from the isothermal magnetic hysteresis for a Si-doped sample was $\sim 2.5\times10^4$ A/cm^2 at 5 K, four times higher than the corresponding values for Mg- or Al-doped samples [11]. It is likely that cationic vacancies induced by silicon doping act as additional pinning centers in the rock-salt structure. Heat capacity measurements on these three samples revealed some interesting features. The parameter γ in the equation $C=\gamma T+\beta T^3$ is the coefficient for the electronic contribution to the heat capacity, and indicates the amount of electron correlation in a system. For a Si-doped sample, γ had a high value of ~25 mJ/mol K^2, indicating strong correlations. In contrast, γ was 0.1798 mJ/mol K^2 for the Mg-doped sample, and 3 mJ/mol K^2 for the Al-doped sample. The latter two samples behaved as nearly 'free electron' systems [11]. The zero field values of the energy-gap related parameter $2\Delta/k_BT_c$ indicated that all three samples are close to the values for conventional (low-T_c) superconductors.

Magnesium oxide MgO crystallizes in a rock-salt structure, similar to superconducting γ-NbN. It is interesting that niobium nitride can be partially substituted by either aluminum oxide or silicon oxide, Al_2O_3 or SiO_2. Cationic vacancies are introduced in the rock-salt-type lattice of niobium oxynitride Nb(N, O) by the partial substitution of niobium with either Al^{3+} or Si^{4+}. X-ray absorption spectroscopy indicated that the niobium *K*-edge shapes of doped and undoped niobium oxynitrides were very similar [10]. The peak profile was slightly broader for the first and the second nearest neighbors of $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ than for the other three oxynitrides, possibly because the silicon doping causes a relatively large displacement at the octahedral 4*a* sites in the

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crystal structure. Our X-ray absorption studies have not yet clarified the coordination around Si atoms near cationic vacancies.

In the present study, the temperature dependence of the electrical resistivity was measured by changing the applied magnetic field to investigate the superconductivity of $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ in comparison to the parent $Nb(N_{0.87}O_{0.13})$ abbreviated as NbNO after this. The local atomic arrangement was also studied, especially around silicon atoms near cationic vacancies in the rock-salt-type whole structure by applying both ^{29}Si MAS NMR and Si-XANES in relation to the hardness of the superconductivity under magnetic field.

2. Experimental

The sample preparation details were described in our previous manuscript [10]. $NbCl_5$ (Sigma-Aldrich, 99.9%) was dissolved with and without $Si(OC_2H_5)_4$ (Aldrich, 98.0%) at a molar ratio of 9:1 in anhydrous ethanol, along with an equimolar amount of citric acid (Wako Pure Chemicals) for the preparation of $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ and NbNO, respectively. The viscous material was fired at 350 °C for 1 h in air, and the resultant oxide powders were ground. The amorphous oxide precursors were nitrided in an alumina boat with ammonia (Sumitomo Seika Chemicals, 99.9%). The as-nitrided products were thermally annealed at 1200 or 1500 °C for 3 h under 0.5 MPa N_2 in a graphite furnace (High Multi 500, Fuji Dempa Kogyo). Resistivity measurements were carried out using a 14 T PPMS system from M/S Quantum Design, USA at CSR Indore.

Si *K*-edge XANES spectra were measured under vacuum ($<10^{-6}$ Pa) at room temperature using a double-crystal InSb (1 1 1) monochromator at the beam line 1A (BL-1A) station at UVSOR, Institute for Molecular Science, Okazaki, Japan. The energy resolution of the X-rays was 0.5 eV at 2 keV. The data were recorded in total electron yield (TEY) mode. Commercial powders of α-Si_3N_4 (SN-E10, UBE) and SiO_2 (quartz & amorphous, Kojundo Chemical Laboratory Co.) were also measured for reference. All samples were well ground and mounted on adhesive carbon tape in order to avoid surface charging effects.

^{29}Si MAS NMR spectra were recorded after $\pi/2$ pulse irradiation in a magnetic field of 9.41 T on a Bruker MSL400 NMR spectrometer at a Larmor frequency of 79.486 MHz. The measurements were performed using φ7 mm zirconia rotors at a spin rate of 2 kHz with a 5 μs pulse width and a recycle delay of 20 s. The chemical shifts were calibrated with Q8M8 (12.4 ppm) against tetramethylsilane TMS (0 ppm) as an external standard. The above commercial powders were also measured as references for this measurement.

3. Results and discussion

3.1. Superconducting transition under magnetic field

The niobium oxynitride $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ was found to be a conventional superconductor (T_c=16.8 K) with a relatively large magnetic hysteresis [11]. Its critical current density J_c was four times higher than the corresponding values for its analogous oxynitrides. Resistivity measurements were performed on $(Nb_{0.87}Si_{0.09}\square_{0.04})$ $(N_{0.87}O_{0.13})$ and the undoped parent NbNO in the temperature range 2–20 K and in the presence of magnetic fields of 0–14 T, as shown in Figs. 1 and 2 along with their $d\rho/dT$ curves in the insets. Their transition temperatures are as follows: T_{on} is the 'onset' of superconductivity, defined by a 10% drop from the normal state resistance (90% ρ_n), and was 16.62 K and 17.72 K. The mean field transition temperature T_{MF}, defined as the peak in $d\rho/dT$, was 16.35 K and 17.2 K. T_{c0}, as defined by a 90% drop from the normal state value (10% ρ_n), was 15.28 K and 16.76 K, respectively. The temperature at which the resistance fell to zero was 14 K and 16.5 K in zero field. Since the transition is narrow in ~1 K in zero field and broaden in higher fields. $d\rho/dT$ exhibits these features against the applied magnetic field as shown in the insets in Figs. 1 and 2. However, for a more precise discussion, the T_{MF} value derived from $d\rho/dT$ will be used in the remainder of the discussion, unless otherwise stated. There is a marked decrease of T_{c0}~1.5 K on doping the Si, by more than a degree in the onset and T_{MF}. The application of a 14 T magnetic field results in a downward shift to 8.25 K from 16.35 K and 4.86 K from 17.2 K, respectively. This downward shift amounts to ~8 K and ~12.3 K at 14 T, respectively, for $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ and NbNO. $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ shows more robust or hard nature as compared to its undoped counterpart.

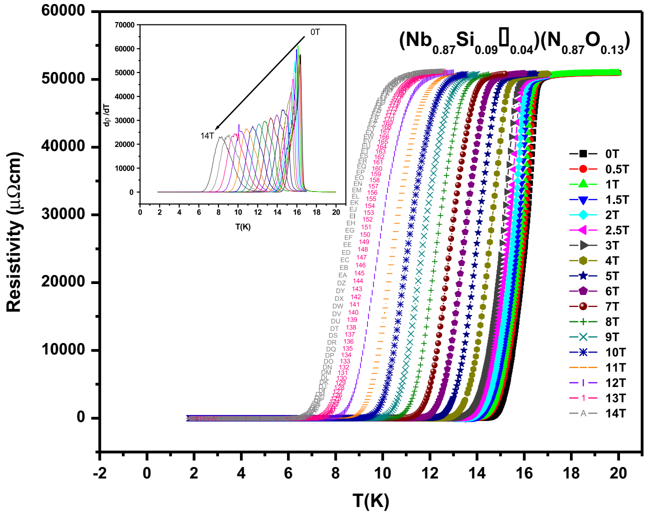

Fig. 1. Superconducting transition behavior of the niobium oxynitride $(Nb_{0.87}Si_{0.09}\square_{0.04})(N_{0.87}O_{0.13})$ under various applied magnetic fields. Inset shows $d\rho/dT$ curves for all fields to get various T_c parameters defined in the text, especially the mean field transition temperature, T_{MF}.

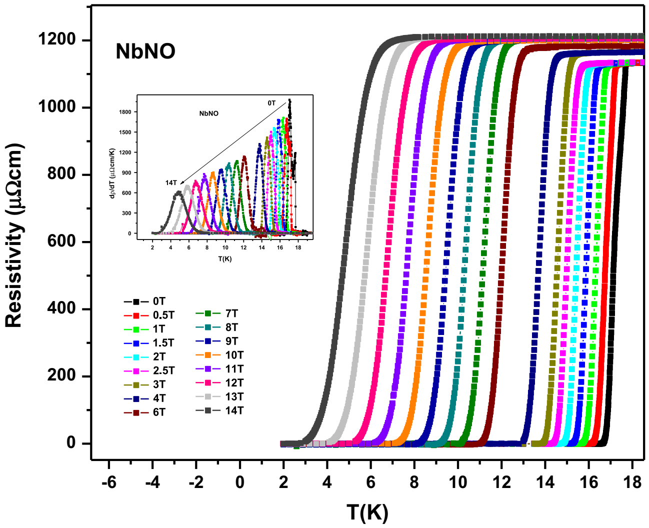

Fig. 2. Superconducting transition behavior of the undoped niobium oxynitride (NbNO) under various applied magnetic fields. Inset shows $d\rho/dT$ curves for all fields to get various T_c parameters and especially for mean field transition temperature, T_{MF}.

The temperature of 90% ρ_n, T_{MF} (from $d\rho/dT$, which is ~50% ρ_n), and 10% ρ_n as defined above, were estimated and are plotted