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Low-temperature ac conductivity of semiconducting NbO_2

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We report the first investigation of electrical conduction in single-crystal NbO_2 below 196 K. We employed ac admittance measurements down to $T=4.2$ K at frequencies between 5 and 92 kHz. The conductivities σ along both the a and c axes increased with frequency and generally increased strongly with temperature. In addition σ_c went through a number of peaks as a function of T, each of which was accompanied by an inflected change in the dielectric permittivity, indicating the presence of four different relaxation processes. Only the process around 25 K showed up in σ_a. The multiplicity of σ_c peaks may be due in part to the complicated distorted-rutile crystal structure of NbO_2 below 1080 K. The lowest- and highest-temperature σ_c processes are accounted for using relaxation-time expressions derived from reaction rate theory. Each process seems to involve small electronic polarons making adiabatic transitions between Nb^{+4} ions having displaced sets of vibrational levels. The electron is thought to be thermally activated from an oxygen vacancy onto a pair of Nb ions. Ionic rearrangement via tunneling or over the barrier hopping are involved. Values are determined for various pertinent energies.

I. INTRODUCTION

At room temperature the n-type semiconductor[1] niobium dioxide (NbO_2) has a tetragonal, distorted rutile structure[2,3] with C_{4h}^6 ($I4_1/a$) space-group symmetry. NbO_2 undergoes a crystallographic transition[4] of second order[5] near 1080 K. It has the rutile structure of the D_{4h}^{14} ($P4_2/mnm$) space group in its high-temperature phase. In the high-temperature (HT) phase NbO_2 has two formula units per unit cell with a Nb-Nb separation,[3] a_{HT}, of 4.830 ± 0.004 Å along the a axis of the crystal lattice, whereas the Nb-Nb separation, c_{HT}, along the c axis is 2.982 ± 0.003 Å. In the low-temperature (LT) phase NbO_2 has 32 formula units per unit cell with unit cell axes $a_{\mathrm{LT}}=2\sqrt{2}a_{\mathrm{HT}}$, and $c_{\mathrm{LT}}=2c_{\mathrm{HT}}$. In the LT phase the distortion from rutile is due to displacements of the Nb and O ions.[3] The niobium atom displacements in the basal plane are $\simeq\pm0.03a_{\mathrm{HT}}$ along the x or y low-temperature axes, while z displacements are $\simeq\pm0.05c_{\mathrm{HT}}$. Oxygen atoms are displaced by $\simeq\pm0.015a_{\mathrm{HT}}$ along the x or y low-temperature axes and by $\simeq\pm0.01c_{\mathrm{HT}}$ in the z direction. Some oxygen atoms move by $\simeq0.001c_{\mathrm{HT}}$ in the z direction.

Electrical transport experiments have shown that NbO_2 also undergoes a transition in both its electrical conductivity,[1,6,7] and its magnetic susceptibility[8] in the neighborhood of 1070 K. The conductivity below this temperature is activated due to small polarons[6,9] whose number and mobility both decrease exponentially with decreasing temperature. Above 1070 K, NbO_2 has semiconductorlike conductivity along the a-axis with a smaller activation energy than that in the low-temperature phase, and conductivity which is nearly independent of temperature along the c axis. Measurements of the dc resistivity have shown[10] that an electrical phase transition involving a drop in resistance can be induced at room temperature by applying enough hydrostatic pressure to a sample of polycrystalline NbO_2. Recent measurements[11] of dc resistance of n-type NbO_2 single crystals in the LT phase between 196 and 410 K using hydrostatic pressures from 1 to 6000 atm indicate that the conduction is via adiabatic hops of small polarons.

Electrical resistivity data on NbO_2 single crystals are lacking below 196 K. dc resistivity measurements below 200 K are very difficult because of the high resistivity of NbO_2 at such temperatures. However, ac admittance measurements can be made on high-resistivity samples. Hence, in order to determine the nature of electrical conduction in NbO_2 at low temperatures and to look for effects which might be connected with the displacements of atoms from the simple arrangement found in rutile (TiO_2), we have made the first investigation of electrical conduction in single-crystal NbO_2 below 196 K using ac admittance measurements at frequencies between 5 and 92 kHz.

II. EXPERIMENTAL DETAILS

All our experiments were performed at Purdue University. However, boules of NbO_2 grown by the Czochralski-Kyropoulos technique in a tri-arc furnace were provided by S. H. Shin, F. Pollak, and P. M. Raccah when they were at Yeshiva University. We oriented the boules of NbO_2 by the Laue back reflection x-ray method. Thin, disc-shaped monocrystalline samples were cut from the boules using a Sheffield-Cavitron ultrasonic machine cutter and a Buehler Isomet low-speed diamond saw. One of the samples had its a axis perpendicular to the two flat parallel surfaces; the other one had its c axis perpendicular to the flat surfaces. The diameter of the a-direction samples was 6.70 ± 0.05 mm with a thickness equal to 0.690 ± 0.005 mm. The diameter of the c-direction sample was equal to 8.20 ± 0.05 mm with a thickness of 0.760 ± 0.005 mm. Polishing the samples involved a five-step process requiring various powder-liquid mixtures, and went as follows: (1) no. 600 grit silicon carbide power, (2) 14.5-μm aluminum oxide powder, (3) 3200 mesh grinding compounds extra fine, (4) 0.05-μm gamma micropolish, and (5) syton suspension. For the first three steps the grinding was done on top of a flat piece of glass; for the fourth step a marble stone and a special nylon cloth (Buehler 40-7058) positioned on the marble stone were used, and for the last, a special polishing microcloth (Buehler 40-7218) also positioned on the aforementioned flat marble stone was used. Once this process was completed, the samples' flat surfaces were uniform to within ±0.0005 inch. The samples were then etched with a 10% bromine—90% methanol solution for one minute and finally rinsed, first with pure methanol and then with distilled water. The above process was necessary in order to prevent stray capacitance often associated with surface damage. A Commonwealth Scientific "Millatron" machine was used to sputter pure aluminum to form thin-film electrodes on each sample's flat surfaces. These electrodes showed satisfactory endurance throughout our experiments. During the sputtering process the samples were etched for 5 min by exposing them to a 500-eV argon-ion beam, and then the aluminum electrodes were sputtered on for 60 min until a layer 4200 Å thick was formed. Care was taken to avoid getting any metal contamination on the sample edges by masking them with Crystal Bond 509, Aremco Products, Ossining, NY, during the sputtering process.

Controlling the temperature within $\pm0.4\,^{\circ}\mathrm{C}$ through the entire temperature range of our measurements was necessary in order to obtain reliable results since balancing our six-figure resolution 1615-A General Radio Co. capacitance bridge would not have been possible if changes in conductivity larger than few parts per million had occurred due to thermal fluctuations. The cryostat we employed consisted of two Pyrex Dewars—one inside the other—sealed together near the top of the outer Dewar. The outer Dewar was for liquid nitrogen, whereas the inner Dewar was for liquid helium or liquid nitrogen. The cryostat was able to keep liquid helium for 7 h. The sample was enclosed in a cylindrical copper cell located inside the cryostat's liquid helium chamber at 10 in. above the bottom of the latter. A $\frac{1}{16}$-in.-diam brass rod attached to the bottom of the copper cell extended 9 in. below it. This brass rod was immersed in liquid helium. It allowed us to equilibrate the sample's temperature at any selected value between 4.2 and 64 K when combined with the effect of an electronically controlled heater. In this temperature range the temperature was measured by means of a Ge resistance thermometer. For the temperature range between 64 and 77 K our cold finger-heater arrangement did not succeed in keeping the thermal fluctuations within ±0.1 K; thus we had to use another method in order to make measurements in that range. This time the cryostat's inner chamber was filled with liquid nitrogen. Various temperatures in the range between 64 and 77 K were reached and stabilized by pumping on the liquid-nitrogen bath either through a Cartesian manostat, or through a needle valve. The vapor pressure of the bath was read with a mercury or an oil manometer and the temperature was deduced from vapor pressure tables. From 77 up to 200 K selected temperatures were reached by properly adjusting the electronically controlled heater. The cryostat inner chamber had low-pressure helium gas acting as a heat exchange medium, whereas the outer chamber was filled with liquid nitrogen.

Our electronic setup was the well-known, three-terminal, capacitance bridge arrangement[12] with the addition of a lock-in amplifier which helped us to filter the signal from the background noise and also served as a null detector. In order to test if a Schottky barrier was present at the junction between the sputtered aluminum thin film electrodes and the sample surfaces we applied up to 230 V of dc bias voltage in parallel with the capacitance bridge detector output. The effect of dc bias, if any, was less than 10^{-17} F in the capacitance measurements, and less than 10^{-6} in the dissipation factor measurements at all the frequencies used.

III. EXPERIMENTAL RESULTS

At 200 K or somewhat above, the ac conductivities along the a axis, σ_a, and along the c axis, were independent of frequency and agreed with the dc values[11] indicating the validity of our ac conductance measurements. Below 200 K the ac conductivities along both the a and c axes generally decreased much less strongly with decreasing temperature then they did at higher temperatures, and both increased with frequency. The latter indicates the occurrence of polarization conduction. In addition, as can be seen in Fig. 1, σ_c at 22.6, 46, and 92 kHz went through four peaks as a function of temperature. Each peak was

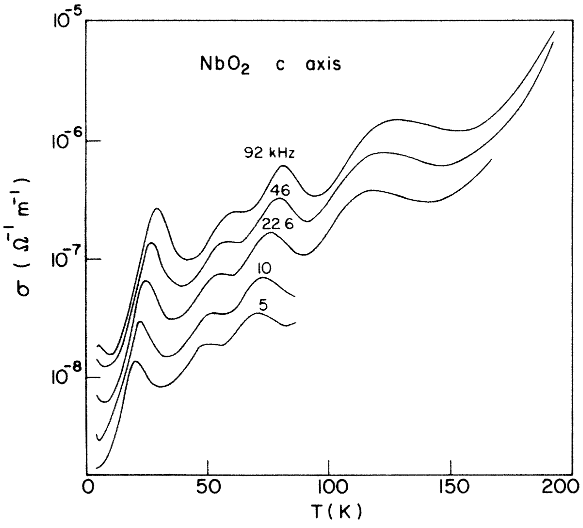

FIG. 1. ac conductivity along the c axis of $\mathrm{NbO_2}$ as a function of temperature at various measuring frequencies. Each curve is the locus of many data points obtained every degree or fraction of a degree at low temperatures and usually every few degrees at high temperatures.

accompanied by a small inflected change in the dielectric permittivity. These results indicate that there are four different relaxation processes involving electrical charge with a component of motion along the c axis. This multiplicity of processes may be due at least partly to the variety of interionic spacings in the distorted rutile structure of NbO_2. On the other hand, σ_a had only one set of peaks centered around 25 K so we show σ_a data only between 15 and 60 K in Fig. 2. The σ_a peaks occur in the same range where the lowest-temperature set of σ_c peaks occur. Further implications of our experimental results will be discussed after we summarize theory used in making a quantitative analysis of two sets of our σ_c peaks.

IV. THEORY APPLICABLE TO OUR RESULTS

Polarization conduction can occur via a charge carrier hopping between the two centers in each of many two-center pairs.[13] Since, as we shall see, our data (or at least some of it) can be interpreted in terms of small polarons hopping between lattice cations, we shall summarize the pertinent theory for such a process. We consider the case in which the two centers in a pair have ground-state energy levels differing by an energy Q. (This energy difference may be caused by an impurity or vacancy being nearer to one center of a pair than it is to the other center.) Under certain conditions[13] the activation energy E_c' for polaron hopping between two centers is[14]

$$E_c' = \frac{(E_r+Q)^2}{4E_r} , \tag{1}$$

where E_r is the ionic "reorganization energy." The activation energy E_c' will be lowered by an amount J, where $2J$ is the one-dimensional, electronic transfer integral of the tight-binding approximation. In the adiabatic approximation the time taken by the polaron to hop between sites is much shorter than the time taken by the surrounding ions to recover from the deformation induced by the electron. Thus J is large (comparable to the polaron binding energy), and the new activation energy E_c becomes[13,15]

$$E_c = E_c' - J . \tag{2}$$

In interpreting our results we shall assume that the centers are separated by a distance R, and that the transfer of the polaron will occur between electronic energy levels differing by W_D. (W_D can be interpreted as the energy required to activate the polaron into the conducting state.) The relative population of the upper level is proportional to $\exp(-W_D/kT)$, where k is Boltzmann's constant and T is the absolute temperature, so that when averaged over all directions the difference between the static and high-frequency dielectric constant is given by[13]

$$\kappa-\kappa_\infty = \frac{4\pi}{3}\frac{Ne^2R^2}{kT}\exp\left[-\frac{W_D}{kT}\right] , \tag{3}$$

where N is the number of pairs per unit volume, and the ac conductivity given by the Debye equations[16] is

$$\sigma(\omega) = (\kappa-\kappa_\infty)\frac{\omega^2\tau}{1+\omega^2\tau^2} , \tag{4}$$

with $\kappa-\kappa_\infty$ given by Eq. (3), and $1/\tau$ being the probability per unit time for a jump downwards. Explicit analytical expressions for the polaron hopping rate $1/\tau$ have been derived using a small polaron continuum polarization model and a perturbation approach in one-dimensional molecular crystals in which the polarons hop between lattice ions having equal energies and thus a symmetric potential barrier ($Q=0$).[17] For a nonsymmetric potential barrier a two-site reaction rate approach has been used to derive expressions for the polaron hopping rate for the low- and high-temperature limits and the intermediate temperature range as well.[18] According to the general formulation of reaction rate theory, at very low temperatures ($T \ll T_k/2$, where $kT_k = \hbar\omega_0/\pi$; T_k is the "characteristic temperature" of the reaction rate theory, and ω_0 is the angular frequency of the particular lattice vibration which corresponds to the passage of the small polaron from one ion to a particular neighbor[19]), the lattice rearrangement occurs almost entirely by tunneling, and $1/\tau$, in the adiabatic case, can be expressed as[18]

$$\frac{1}{\tau} = \frac{\pi e^{-n_1\hbar\omega_0/kT}}{2^{n_1}n_1!}[\xi_0 H_{n_1}(\xi_c) - 2n_1H_{n_1-1}(\xi_c)]^2 \times \frac{\omega_0}{2\pi}e^{-n_1\hbar\omega_0/E_r - E_r/\hbar\omega_0} , \tag{5}$$

where n_1 is the vibrational quantum number of the initial state, ξ_0 is the dimensionless configuration coordinate such that $E_r = \frac{1}{2}\hbar\omega_0\xi_0^2$, H_{n_i} are the Hermitian polynomials of order n_i, and $\xi_c = \xi_0/2 + (n_1-n_2)/\xi_0$ with n_2 being the vibrational quantum number of the final state. If the lowest-temperature set of σ_c peaks is due to transitions from a state with $n_1 = 1$ and a state with $n_2 = 0$, then

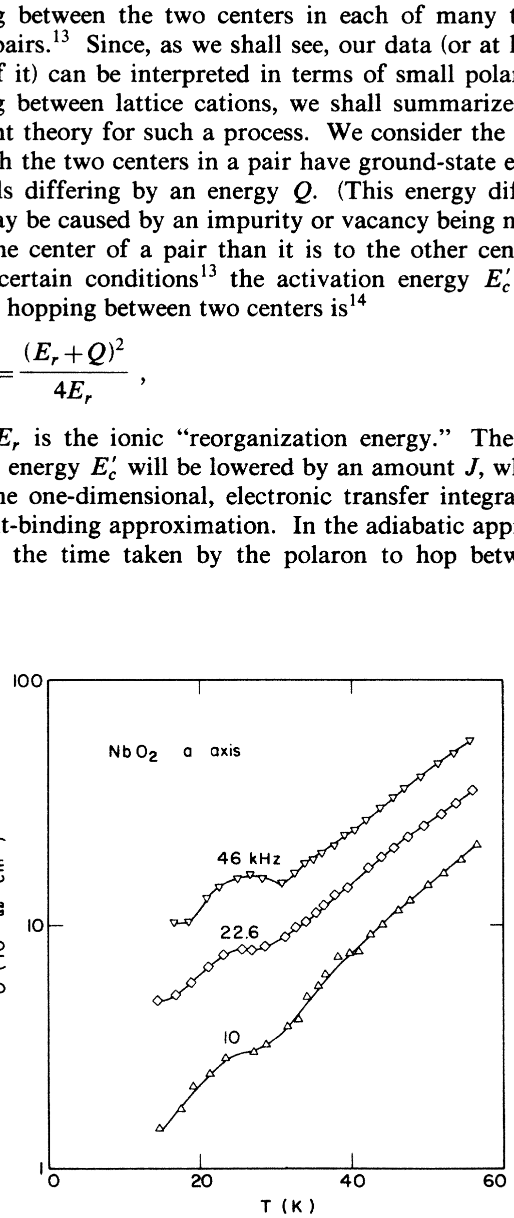

FIG. 2. ac conductivity along the a axis of NbO_2 as a function of temperature at three measuring frequencies.

TABLE I. Parameters in reaction rate analysis of c-axis ac conductivity peaks in NbO$_2$. The energies in the third through ninth columns are in meV.

Peak T's	n_1	W_D	Q	$\hbar\omega_0$	E_r	E_c'	E_c	E_n
21–39 K	1	2.6	18.2	18.2	2.8	39.6	Tunneling	27.3
116–130 K	4	4.6	193	48.2	44.3	318	211	217

$$\frac{1}{\tau}=\frac{1}{\tau^*}e^{-\hbar\omega_0/kT}\ , \tag{6}$$

where

$$\frac{1}{\tau^*}=\omega_0\left[\frac{E_r}{\hbar\omega_0}\right]^2 e^{-\hbar\omega_0/E_r-E_r/\hbar\omega_0}\ . \tag{7}$$

Using σ_c given by Eq. (4) and $1/\tau$ given by Eq. (6) we derived an expression for $d\sigma_c/dT$ and set it equal to zero to find the condition for maximum σ_c. We found that

$$\omega\tau=\left[\frac{\hbar\omega_0-W_D+kT_{\max}}{\hbar\omega_0+W_D-kT_{\max}}\right]^{1/2}\ . \tag{8}$$

Applying an iterative method we used Eqs. (4), (6), and (8) to deduce values for $\hbar\omega_0$, E_r, and W_D from our lowest-temperature σ_c peaks.

From the value of $\hbar\omega_0$ we could deduce a value of Q since $Q=(n_1-n_2)\hbar\omega_0$ and, for the lowest $T\sigma_c$ peaks, $n_1=1$ and $n_2=0$. Table I contains the values which we obtained for these and other relevant energies. A value for the concentration of conducting pairs N can be deduced from the heights of our σ_c peaks, provided that we assume a value for the jump distance R. This will be discussed in Sec. V.

In the temperature range of moderate lattice tunneling, i.e., $2T_k > T > T_k/2$, the reaction rate theory in the adiabatic limit indicates that[18]

$$\frac{1}{\tau}=\kappa_t\frac{\omega_0}{2\pi}e^{-E_c/kT} \tag{9}$$

where κ_t is a tunneling factor whose explicit dependence on temperature is

$$\kappa_t=\frac{(\pi/2)(T_k/T)}{\sin[(\pi/2)(T_k/T)]}\ . \tag{10}$$

Using $d\sigma_c/dT=0$ and the approximation $\omega\tau=1$ at the tops of the σ_c peaks we were able to deduce values of E_c and T_k from the set of σ_c peaks centered around 115 to 130 K. The value of $\hbar\omega_0$ in that temperature range was deduced from $\pi kT_k=\hbar\omega_0$, and the value of Q was deduced from $Q=(n_1-n_2)\hbar\omega_0$ assuming that $n_1=4$, $n_2=0$. The energies we have obtained from our highest temperature set of σ_c peaks are listed in Table I along with those obtained from our lowest T set of peaks. Values of R and N involved in these peaks will be considered in Sec. V.

V. DISCUSSION

Table I shows the characteristic energies we have determined for the relaxation processes involved in the lowest and highest temperature sets of σ_c peaks shown in Fig. 1. All the quantities listed in Table I except E_n have been defined in Sec. IV; $E_n=(n+\frac{1}{2})\hbar\omega_0$ gives the unperturbed vibrational energies of the centers between which polarons hop. The vibrational quantum number of one center is n_1 and that of the other is $n_2=0$.

For the relaxation process occurring at low temperatures E_n is smaller than the activation energy E_c; hence, the small polaron hops must involve lattice ion reorganization via tunneling. This provides support for the $1/\tau$ expression we chose to apply to our low-temperature σ_c peaks. For the process at high temperatures $E_n \gtrsim E_c$; thus the relaxation involves ionic reorganization via over-the-barrier hops as we have assumed in our analysis.

Our values of $\hbar\omega_0$ are close to LO phonon energies found for NbO$_2$ from infrared reflectivity measurements[20] at room temperature. This provides assurance that our analysis is valid.

Since σ_a had a set of peaks corresponding to the lowest-temperature set of σ_c peaks, we infer that in this temperature range there is polaronic hopping with components along both the a and c axes. If this hopping is between a Nb site at the corner and at the center of the smallest rutile-type subcell both a axis and c axis LO phonons may be involved. Using the lowest infrared LO phonon energies in the crude expression $\hbar(\omega_{0_c}\omega_{0_a}^2)^{1/3}$ we obtain a value of 24 meV which is not far from the 18.2 meV value in Table I. For such diagonal hopping between Nb sites we estimate the shortest such hop distance to be given by

$$[2(0.97a_{\mathrm{HT}}/2)^2+(0.95c_{\mathrm{HT}}/2)^2]^{1/2}=3.61\ \text{Å}$$

and the concentration of electrically active pairs to be $8.1\times10^{16}\ \mathrm{cm}^{-3}$.

Since no σ_a peaks were found to accompany the set of σ_c peaks at highest temperatures, we infer that polaronic hopping is only along the c axis in that case. Infrared measurements have revealed a c axis LO phonon with an energy of 45.4 meV. This is very close to the 48.2 meV value of $\hbar\omega_0$ which we deduced from our high $T\sigma_c$ peaks (see Table I). For hops between the closest Nb sites along the c axis we have $R\simeq2.85$ Å. Using this value and our high $T\sigma_c$ peak values in Eqs. (3) and (4) we find the concentration of conducting pairs to be $N=1.66\times10^{18}\ \mathrm{cm}^{-3}$.

Before completing the discussion of the foregoing analysis of our results we shall consider an alternative, more phenomenological method of analyzing our data. Such a method has been used to interpret low-temperature conductivity maxima[12] in nonstoichiometric TiO$_2$. It involves the Debye equations (as did our method). However

TABLE II. Comparison of values of parameters obtained by analyzing the lowest- and highest-temperature ac conductivity peaks in NbO_2 using a distribution of phenomenological relaxation times with those obtained using a single relaxation time from reaction rate theory.

Method	Q (meV) Low T	Q (meV) High T	τ^* (s^{-1}) Low T	τ^* (s^{-1}) High T	W_D (meV) Low T	W_D (meV) High T
Distribution of τ	15.1–20.4	184–216	1.28×10^{-9}	3.5×10^{-14}	2.2	3.5
Reaction rate τ	18.2	193	1.26×10^{-9}	2.9×10^{-14}	2.6	4.6

it assumes that the two-center pairs have a range of ground-state energy differences, $Q\pm\frac{1}{2}\Delta Q$, and consequently a range of relaxation times. It is assumed that each relaxation time occurs with equal probability in the range $\tau_1\leq\tau\leq\tau_2$, where

$$\tau_1=\tau^*\exp[(Q-\tfrac{1}{2}\Delta Q)/kT]$$

and

$$\tau_2=\tau^*\exp[(Q+\tfrac{1}{2}\Delta Q)/kT] .$$

This approach was used previously[21] to analyze our results even though it has been criticized[22–24] as lacking in physical meaning due to the difficulty in justifying the above distribution of relaxation times. Applying this alternative method to our data we obtained the values for Q, τ^*, and W_D which are listed in Table II. For comparison we also list in Table II the values obtained from our analysis which used reaction rate expressions for $1/\tau$. From Table II it can be seen that there is a very reasonable, or even sometimes close, correspondence between parameter values obtained from our method of analysis involving τ from reaction rate theory and those from the alternative method considered just above. This correspondence is a useful check on the accuracy of our more complicated reaction rate analysis.

Since the room-temperature resistivity of our samples indicated that they may be slightly nonstoichiometric, we believe that most likely the origin of the charge carrier on a conducting pair is an electron trapped at an oxygen vacancy being thermally activated on to a pair of cations. A nonstoichiometric origin of charge carriers is quite reasonable in terms of the concentrations of conducting pairs deduced above (8.1×10^{16} cm^{-3} from the lowest-temperature σ peaks and 1.66×10^{18} cm^{-3} from the highest-T set of σ_c peaks) since they would require quite small deviations from stoichiometry because there are 2.8×10^{22} Nb ions/cm^3.

The greatly different concentrations of conducting pairs which we deduced from the sets of σ_c peaks at lowest and at highest temperatures might be due to pairs of Nb^{+4} ions being involved in the lowest-T σ_c peaks while pairs containing Nb^{+4} and an impurity ion are involved in the highest-T σ_c peaks. Impurity involvement in the latter would be consistent with the fact that some of our samples contained 2.4×10^{18} Sb atoms/cm^3 according to a proton-induced x-ray emission (PIXE) analysis made in Purdue's Tandem Van de Graaff Accelerator Laboratory. Sb^{+3} ions could fit into Nb sites very well since the crystal ionic radius of Sb^{+3} (0.76 Å) is very close to that of Nb^{+4} (0.74 Å). The involvement of different cation pairs in the lowest- and highest-T σ_c peaks would provide a very natural way of accounting for the different (larger) values of W_D and Q associated with highest-T peaks than with the lowest-T peaks.

VI. CONCLUSIONS

Our admittance measurements on monocrystalline samples of NbO_2 between 196 and 4.2 K have revealed that the electrical conductivity σ increases with frequency and goes through one or more relaxation-type peak as a function of temperature due to polarization conduction by small electronic polarons. The set of peaks at lowest and highest temperatures were subjected to quantitative analysis using relaxation time expressions from reaction rate theory for adiabatic transitions of polarons between two nonequivalent centers. Reasonable values are obtained for the energy parameters involved. It is inferred that the conducting centers are Nb-Nb or Nb-Sb pairs onto which an electron has to be thermally activated, probably from an oxygen-ion vacancy. Additional work is needed to account for the two sets of σ_c peaks at intermediate temperatures.

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