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Electronic structure and electron-phonon interactions in layered Li_xNbO_2 and Na_xNbO_2

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Results of full-potential linear-muffin-tin-orbital calculations for the new intercalated niobium oxide phases Li_xNbO_2 and Na_xNbO_2 are presented. It is shown that alkali atoms are ionized, and their valence electrons completely fill the hybridized Nb d–O $2p$ conduction band in $M_{1.0}NbO_2$ crystals making them semiconducting. In the nonstoichiometric M_xNbO_2 phases, the Fermi level is located well inside the conduction band of predominant Nb $4d$ nature with significant contributions from O $2p$ states. Estimates of electron-phonon interaction parameters and T_c in the scope of the rigid-ion approximation result in $T_c \sim 12$ K for $Li_{0.5}NbO_2$ and $T_c \sim 9$ K for Na_xNbO_2 in reasonable agreement with the experimental data—and show that superconductivity observed in these materials is of the usual electron-phonon type, similar to that in cubic $Li_{0.5}TiO_2$. It is shown that the density of states at the Fermi level and T_c for Na_xNbO_2 should be more critically dependent on stoichiometry than for Li_xNbO_2. Since the electronic-structure peculiarities obtained in the calculations are very different than those typical for superconducting cuprates, it does not appear likely that any high-T_c superconductors should be expected in this class of compounds.

I. INTRODUCTION

Among complex oxides of transition metals which are considered of interest in the search for new superconductors, hopefully with T_c's comparable to those of the cuprates, niobium oxides are believed to be among the most promising. They possess a wide variety of different crystal structures, distinct Jahn-Teller distortions, variable metal atom valencies, and reveal unusual electrical resistivity and magnetic susceptibility anomalies.[1] All this is very true for layered oxides of the general formula MNbO$_2$ with M an alkali metal, which can be rather easily intercalated to or removed from the basic hexagonal crystal lattice with trigonal-prismatic coordination of Nb atoms.[2,3] The layered structure of these compounds makes them very suitable for detailed studies of two-dimensional interactions, layer ordering phenomena, and ion transfer in two-dimensional planes. The layered structure is not their only interesting feature. Rather unusual and intriguing is that a formal oxidation state cannot be realized and charge compensation takes place through oxygen sublattice. These phenomena are very typical for cuprate high-temperature superconductors (HTSC).

Superconductivity was observed recently in these layered niobium-oxide phases for two-phase samples with composition $Li_{0.45}NbO_2$ and with $T_c = 5.5$ K; T_c decreased, however, down to 5.0 K for $Li_{0.5}NbO_2$. According to Meissner-effect measurements, the superconducting phase was about 15% of the whole sample,[4] so resistivity measurements were not possible for this two-phase system. Using different solid-state synthesis techniques, samples containing up to 100% superconducting phase in Li_xNbO_2 were obtained and characterized.[5] Their measurements confirmed the existence of superconductivity with $T_c = 5$ K in lithium deficient Li_xNbO_2, for x up to $Li_{0.71}NbO_2$. Later on, similar onsets of superconductivity were obtained for Na_xNbO_2 samples[6] with somewhat lower T_c values (the superconducting phase was 60% of the sample volume). Hall-effect measurements[5,6] showed that these superconductors studied were of the hole type, similar to the case of the cuprates. All this provided the basis for the authors of Ref. 6 to declare that a new class of layered niobium-oxide superconductors was discovered, and that despite their very low critical temperatures, the phenomenon observed might be similar to HTSC.

In this paper, we present results of detailed studies of the electronic structure and chemical bonding in stoichimetric layered $LiNbO_2$ and $NaNbO_2$, and alkali deficient $Li_{0.5}NbO_2$ and $Na_{0.5}NbO_2$ making use of the full potential linear-muffin-tin-orbital (FLMTO) method.[8] Estimates of electron-phonon coupling constants and T_c values are given in the scope of the conventional rigid-ion

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approximation[13–15] and some conclusions are made on the nature of superconductivity in these materials.

II. CRYSTAL STRUCTURE AND CALCULATIONAL METHOD

The crystal structure of $LiNbO_2$ and $NaNbO_2$ was reported in Refs. 2 and 3 to consist of layers of NbO_6 trigonal prisms shifted relative to one another. The compounds are isostructural to MoS_2, in which alkali atoms occupy octahedral holes between trigonal-prismatic Nb-O layers. The other way to describe the structure is to present the lattice as hexagonal planes of Nb atoms, separated by hexagonal layers of oxygens (cf. Fig. 1). The space group is $P6_3/mmc$, and the unit cell contains two nonequivalent Nb atoms, both in trigonal-prismatic coordination. The lattice parameters depend essentially on the alkali-metal radius: for $LiNbO_2$, $a=2.905$ Å, $c=10.46$ Å; for $NaNbO_2$, $a=2.958$ Å, $c=11.58$ Å.[6] As shown in Ref. 7, Li_xNbO_2 is a variable composition phase with a wide stoichiometry region, $0.51<x<0.93$. These limits are corrected in Ref. 4, where it was shown that x may be as low as 0.45, and that this composition reveals the highest $T_c=5.5$ K. The decrease of lithium content results in an increase of the lattice parameters and to the concentration-type "semiconductor-metal" transition. The superconducting state appears at the same critical concentration point, similar to the case of $YBa_2Cu_3O_{6+x}$. Hall coefficient measurements showed the concentration of carriers (which appear to be holes) to be about 0.2 holes/molecule or $1/R_e=4.3\pm0.4\times10^{21}$ holes/cm^3.[5] For $X<1$, removal of Li in Li_xNbO_2 results in some increase of Li-O distances with a simultaneous decrease of Nb-O bond lengths, so that the thickness of the LiO_6 layer grows, but NbO_6 layers become more compressed.[5]

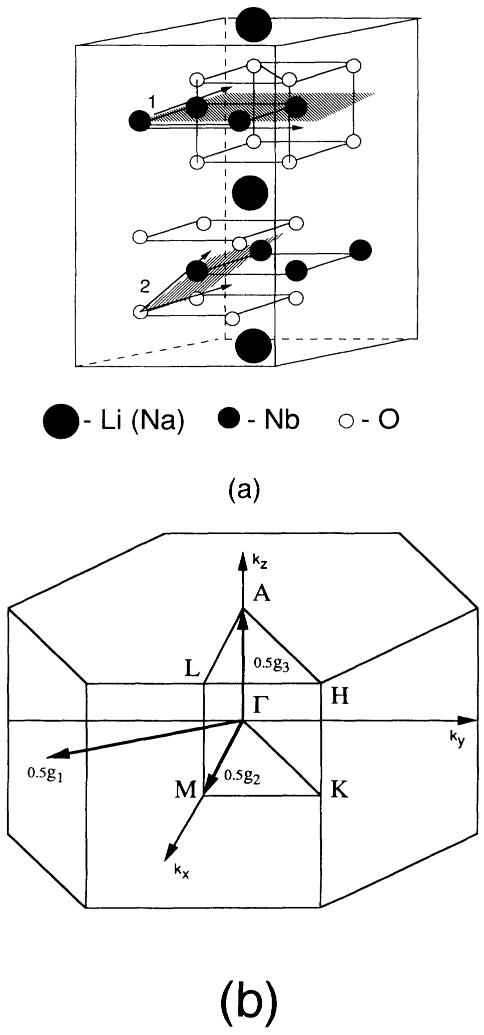


FIG. 1. (a) Crystal structure and (b) the first Brillouin zone for M_xNbO_2 ($M=$Li,Na).

Calculations of the electronic structure of Li_xNbO_2 and Na_xNbO_2 were carried out by the FLMTO method[8] with the Hedin-Lundqvist form of exchange-correlation potential.[9] We used the triple-κ basis set for each type of atom and each angular momentum l channel (l up to 3) with kinetic energies -0.7, -1.0, and -2.3 Ry. The muffin-tin sphere radii were chosen as $R(\mathrm{Nb})=1.79$, $R(\mathrm{O})=2.20$, and $R(\mathrm{Li})=1.80$ a.u. for Li_xNbO_2 and $R(\mathrm{Nb})=1.88$, $R(\mathrm{O})=2.20$, and $R(\mathrm{Na})=2.16$ a.u. for Na_xNbO_2. The Brillouin-zone integrations were carried out using a 170 k points in the irreducible zone mesh by the tetrahedron method for stoichiometric compounds and 260 k points for the crystal with alkali vacancies.

III. RESULTS AND DISCUSSION

A. Stoichiometric $LiNbO_2$ and $NaNbO_2$

Figures 2 and 3 presents the energy bands and the total and partial densities of states (DOS) calculated for stoichiometric $LiNbO_2$ and $NaNbO_2$. The lowest bands in Fig. 2(a) correspond to the upper part of a wide (more than 4 eV in width) hybridized Nb 4d-O 2p band. Two highly dispersed bands in the energy interval from 0 down to -1.8 eV are completely occupied in the

TABLE I. Total and l-projected charges inside the muffin-tin spheres.

	$LiNbO_2$	$Li_{0.5}NbO_2$	$NaNbO_2$	$Na_{0.5}NbO_2$
Li(Na)*s*	0.05	0.05	0.06	0.07
p	0.10	0.10	0.09	0.10
Q	0.17	0.17	0.22	0.22
Nb *s*	0.05	0.05	0.06	0.06
p	0.06	0.06	0.07	0.07
d	1.48	1.41	1.60	1.53
Q	1.59	1.54	1.75	1.69
O *s*	1.92	1.94[a]	1.92	1.92[a]
p	4.71	4.52[a]	4.66	4.46[a]
Q	6.79	6.61[a]	6.71	6.51[a]

[a]Numbers for oxygen atoms close to a vacancy.

stoichiometric compound, but form the conduction bands in Li_xNbO_2 with $x > 0$ that contain holes, in agreement with experiment data.[5] The type of holes is obvious from the DOS curves in Fig. 3(a) these bands are composed mainly of Nb 4*d* with some significant contributions of O 2*p* states. Lithium appears to be completely ionized (see also Table I), and its states are negligibly admixed with the Nb 4*d*-O 2*p* hybridized band. The unoccupied part of the conduction band is well separated from the lower one by 1.5 eV. This energy diagram is surprisingly close to the qualitative model suggested earlier[10] from semiempirical extended Hückel calculations of an isolated NbO_2 layer, according to which trigonal-prismatic coordinated niobium oxide should be a nonmagnetic semiconductor with a gap of 1.4 eV. The experimentally observed antiferromagnetism was attributed[10] to the effects of impurities or nonstoichiometry. We cannot add more to this interpretation.

Similar results were also obtained for ideal $NaNbO_2$ [Figs. 2(b) and 3(b)]. The larger lattice parameters in this phase lead to a noticeable narrowing of both the valence and conduction bands. The energy interval between the upper part of the O 2*p* band and Nb 4*d* conduction band increases up to 2.3 eV, and the width of the latter is now 1.25 eV as compared with 1.8 eV in the $LiNbO_2$ case. The shape of the DOS peak formed by hybridized Nb 4*d*-O 2*p* states in the vicinity of E_F is rather close to that in $LiNbO_2$, but is much higher. Total and *l*-projected charges in muffin-tin spheres (Table I) confirm that Na atoms are completely ionized also, do not give any contributions [Fig. 3(b)] to the conduction band, and all the increase of the DOS near E_F is due to the changes of lattice parameters when Na is substituted for Li.

The main types of chemical bonding in $LiNbO_2$ are illustrated in Figs. 4 and 5; where charge-density maps in two planes are given. Figure 4 corresponds to the plane of metal atoms (cf. Fig. 1) and shows the clear formation of rather strong metal-metal bonding. Figure 5 shows the formation of Nb-O bonding in the plane connecting the nearest metal and oxygen atoms (cf. Fig. 1).

Let us consider now the changes in electronic spectra of nonstoichiometric M_xNbO_2. As suggested in Ref. 4,

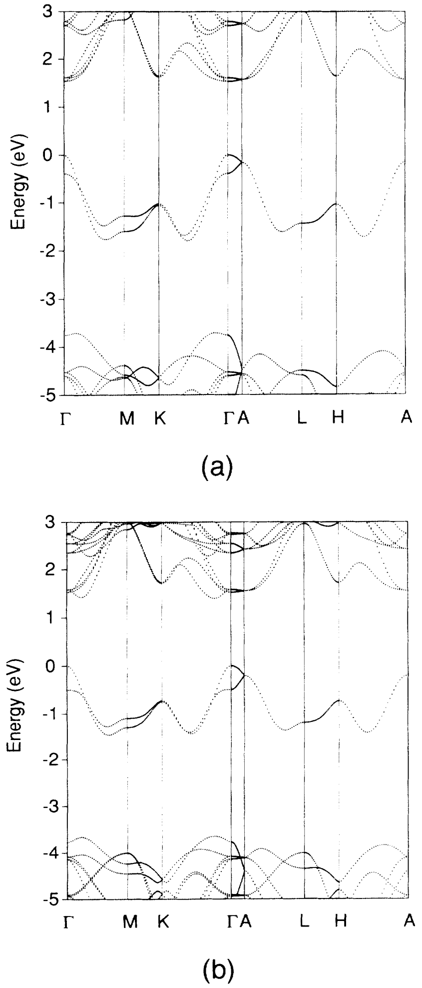


FIG. 2. Energy bands for (a) $LiNbO_2$ and (b) $NaNbO_2$.

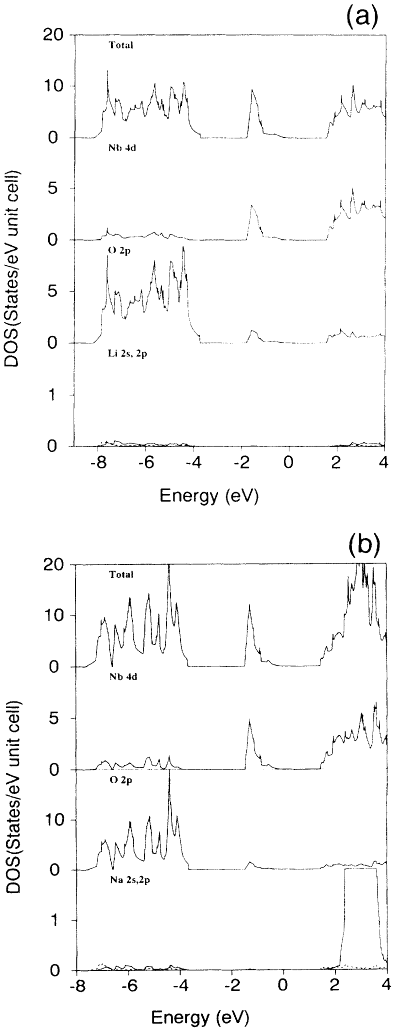


FIG. 3. Total and partial densities of states for (a) $LiNbO_2$ and (b) $NaNbO_2$.

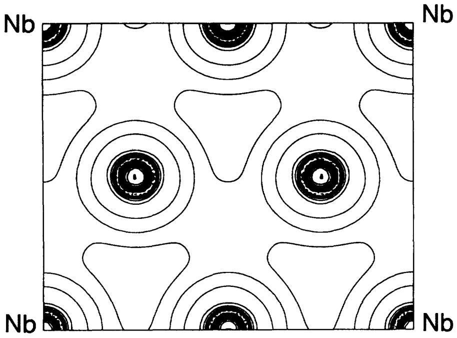


FIG. 4. Charge-density map for Nb-Nb plane (3) in Fig. 1.

the partial removal of alkali-metal atoms should result in the gradual oxidation of Nb atoms from the formal 3+ valence for $x = 1.0$ to formal 4+ valence for $x = 0.0$, and to the increase of E_F due to the loss of electrons from the conduction band of predominantly Nb 4*d* character (Figs. 2 and 3). Such a procedure was realized by the authors of Ref. 4, who obtained hexagonal layered Li_xNbO_2 for $0.45 < x < 1.0$ with the onset of superconductivity with $T_c = 5.5$ K at $x = 0.45$. Later, similar results were obtained for $NaNbO_2$ which showed $t_c = 4-5$ K.[6] For some samples, the detection of superconducting phases with T_c up to 12 K was claimed,[6] but unlike the samples with $T_c = 4-5$ K, these were not firmly reproducible.

B. $Li_{0.5}NbO_2$ and $Na_{0.5}NbO_2$

Again using the FLMTO method, we have carried out electronic structure calculations for $Li_{0.5}NbO_2$, i.e., with 50% lithium vacancies. The calculational parameters were kept the same as for the ideal crystal. Energy bands and total and partial DOS are given in Figs. 6(a) and 7(a). The Fermi level is now seen to cross the conduction band and is located at a high-energy shoulder. $N(E_F)$ is rather high (cf. Table II), the main contributions coming from Nb *d* and O 2*p* states: The latter is only two times less than the metal *d*-states contribution. Thus, oxygen states appear at E_F in $Li_{0.5}NbO_2$ as they do in the case of the superconducting cuprates, but their contribution is much smaller. It is worth noting that $N(E_F)$ for $Li_{0.5}NbO_2$ is comparable with that found in the full linear augmented-plane-wave calculations for $Li_{0.5}TiO_2$ (Ref. 11) with $T_c = 13.7$ K, which definitely corresponds to the conventional electron-phonon type of superconductivity.[11,12] Distinct similarities in the distribution of states and their nature near E_F for $Li_{0.5}NbO_2$ and $Li_{0.5}TiO_2$ imply that a similar superconductivity mechanism exists in both crystals. The difference is the location of the Fermi level. In $Li_{0.5}TiO_2$, E_F coincides with the maximum of a well-defined peak in the DOS curve. Since in electron-phonon superconductivity, higher $N(E_F)$ values correspond to higher T_c, one should not expect any increase of the T_c value with increase of lithium content. In $Li_{0.5}NbO_2$, a further shift of E_F to lower energy, which can be reached by further removal of lithium from this hexagonal phase, might result in a substantial increase of $N(E_F)$ and, consequently, of T_c. Using the rigid-band model, it is easy to show that E_F will be located at the

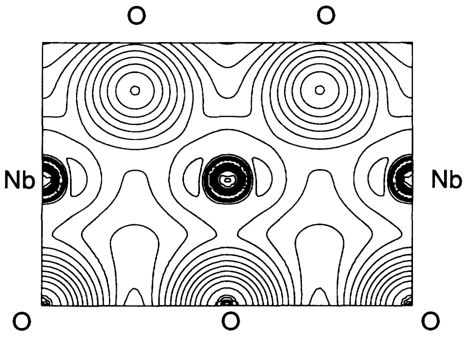
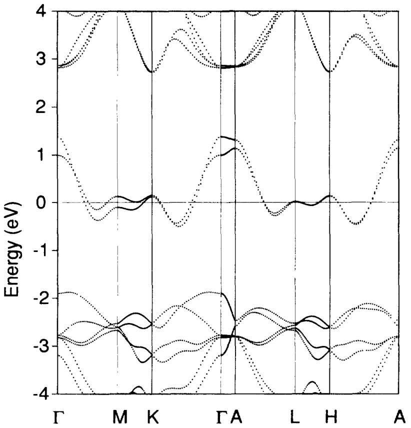
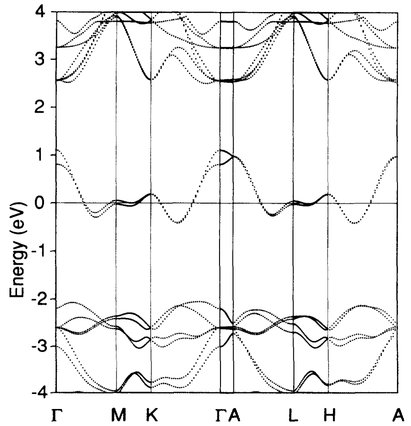


FIG. 5. Charge-density map for Nb-O plane (2) in Fig. 1.



(a)



(b)

FIG. 6. Energy bands for (a) $Li_{0.5}NbO_2$ and (b) $Na_{0.5}NbO_2$.

TABLE II. Total and l-decomposed densities of states (1/Ry) at T_c for $Li_{0.5}NbO_2$ and $Na_{0.5}NbO_2$.

	$Li_{0.5}NbO_2$			$Na_{0.5}NbO_2$		
	Nb	O_1	O_2	Nb	O_1	O_2
s	0.03	0.12	0.04	0.04	0.10	0.04
p	0.50	10.72	4.15	0.55	9.58	3.46
d	29.85	1.10	1.60	24.05	0.90	1.28
f	0.23	0.63	0.64	0.20	0.40	0.40
total		81.9			73.6	

peak in the conduction band when one lithium atom is removed from the unit cell, i.e., for the hexagonal layered NbO_2 crystal with trigonal-prismatic coordination of Nb atoms. Indeed, such a phase, if it exists, has to be very unstable and has not, in fact, been observed.

Similar results were obtained in our calculations for ideal and nonstoichiometric $Na_{0.5}NbO_2$ crystals [Figs. 6(b) and 7(b)]. When half the Na atoms are removed, E_F is again located above the high-energy peak of the conduction band, so that $N(E_F)$ is rather high (Table II) but a little lower than in $Li_{0.5}NbO_2$. Hence one may expect that this phase should become superconducting too with a comparable value of T_c. The relative contribution of O $2p$ states at E_F is about the same as in $Li_{0.5}NbO_2$ and the states which form the Cooper pairs are of predominantly metal d type with a small oxygen contribution. From the absolute value of $N(E_F)$ one may expect that T_c for $Na_{0.5}NbO_2$ will be of the same order of magnitude as for $Li_{0.5}NbO_2$.

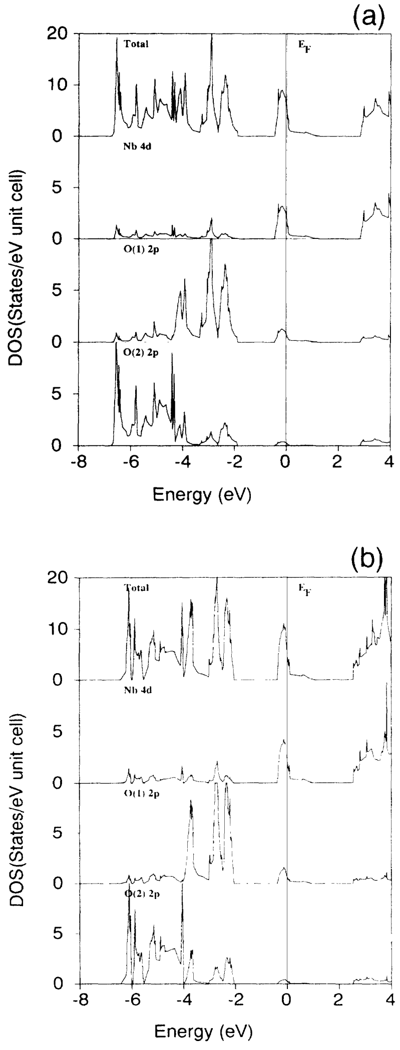


FIG. 7. Total and partial densities of states for (a) $Li_{0.5}NbO_2$ and (b) $Na_{0.5}NbO_2$.

C. Electron-phonon interaction and superconductivity

The structure of the electronic states at E_F and other peculiarities of the electronic distributions in Li_xNbO_2 and Na_xNbO_2 described above suggest that superconductivity in these compounds has the usual electron-phonon origin. In order to verify this and to clarify the role of the electron-phonon interaction, we have calculated T_c values for $Li_{0.5}NbO_2$ and $Na_{0.5}NbO_2$ making use of the simple rigid-ion approximation[13,14] with λ defined by the MacMillan formula:[15]

$$\lambda = \frac{N(E_F\langle I^2\rangle}{M\langle\omega^2\rangle} = \frac{\eta}{M\langle\omega^2\rangle} . \tag{1}$$

Here $\langle I^2\rangle$ is a mean-square electron-ion matrix element, M is the ionic mass, and $\langle\omega^2\rangle^{1/2}$ is the renormalized phonon frequency. The McMillan-Hopfield constant η depends on the electronic subsystem only and $\langle I^2\rangle$ can be estimated by making use of single-channel electron-ion matrix elements, $I_{i,i+1}$, and angular momentum-character functions, $f_l = N_l/N_{(E_F)}$, of the electronic states at E_F. The relevant expressions for $I_{i,i+1}$ can be found in Ref. 14, and calculated values are given in Table III. The $\langle I^2\rangle$ elements corresponding to Nb atoms give the dominant contributions to the partial Hopfield parameters η_α, and the value of the total $\eta = \sum_\alpha \eta_\alpha$ is mainly defined by Nb contributions, as in the well-known niobium carbide or nitride-based superconductors.

Unfortunately, estimates of the renormalized phonon frequency $\langle\omega^2\rangle^{1/2}$ for niobium-oxide systems are lacking. Thus, in our estimates of λ, we used the values extrapolated from the data on niobium carbide and nitride to obtain the calculated λ and T_c parameters given in Table III. The calculated T_c values overestimate the experimental values by about a factor of 2. While overestimates are typical of the rigid-ion approximation, we believe that most of this is due to a lack of knowledge of the

TABLE III. Mean-square electron-ion matrix elements $\langle I^2 \rangle$ (in eV/Å^2), MacMillan-Hopfield constants η (eV^2/Å^2), total density of states at the Fermi level $N(E_F)$ (1/eV), electron-phonon interaction parameter λ, and estimated critical temperature T_c (K) for $Li_{0.5}NbO_2$ and $Na_{0.5}NbO_2$.

	$\langle I^2 \rangle_{Nb}$	$\langle I^2 \rangle_{O1,2}$	η_{Nb}	$\eta_{O1,2}$	$N(E_F)$	λ	T_c
$Li_{0.5}NbO_2$	2.76	0.57(0.30)	8.31	1.71/0.90	6.02	1.55	12
$Na_{0.5}NbO_2$	2.29	0.49(0.24)	6.19	1.34/0.66	5.41	1.15	9

phonon spectrum. Nevertheless, the results obtained show that the usual electron-phonon mechanism can well explain the observed T_c values in Li_xNbO_2 and Na_xNbO_2, and it is very unlikely that any other mechanisms, play a prominent role for these materials. Finally, it is worth noting that as the peak at E_F for $Na_{0.5}NbO_2$ is more intense and steep, one may expect that the lowering of Na content could result in a more rapid increase of T_c compared with $Li_{0.5}NbO_2$. However, the range of T_c will hardly exceed the order of magnitude observed in recent experiments.

IV. CONCLUSIONS

The electronic structure calculations performed for Li_xNbO_2 and Na_xNbO_2 phases with trigonal-prismatic coordination of Nb atoms show that at the proper range of alkali-metal intercalation these phases reveal conventional electron-phonon-type superconductivity with $T_c$of the order of 10 K. The estimates made in the scope of the crude rigid-ion approximation allow one to get good agreement with the experimental data available—provided an adjustment is made for the phonon spectrum. Thus, it may be concluded that the classical BCS electron-phonon nature of superconductivity holds for these new phases.

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[1] C. N. R. Rao, *New Directions in Sold State Chemistry* (Cambridge University, Cambridge, 1986).

[2] G. Meyer and R. Hoppe, Angew. Chem. **86**, 819 (1974).

[3] G. Meyer and R. Hoppe, Z. Anorg. Allg. Chem. **424**, 128 (1976).

[4] M. J. Geselbracht, Th. J. Richardson, and A. M. Stacy, Nature (London) **345**, 324 (1990).

[5] D. G. Kellerman, V. S. Gorshkov, A. P. Tyutyunik, V. G. Zubkov, V. A. Perelayev, T. V. Dyachkova, N. I. Kadyrova, A. S. Fedukov, S. A. Turzhevsky, V. A. Gubanov, G. P. Schveikin, A. E. Karakin, and V. I. Voronin, Superconductivity (to be published).

[6] D. G. Kellerman, V. G. Zubkov, A. P. Tyutyunik, V. S. Gorshkov, V. A. Perelayev, G. P. Shveikin, S. A. Turzhevsky, V. A. Gubanov, and A. E. Karakin, Superconductivity (to be published).

[7] N. Kumada, S. Muramatu, F. Muto, N. Kinomura, S. Kikkawa, and M. Koizumi, J. Solid State Chem. **73**, 33 (1988).

[8] M. Methfessel, Phys. Rev. B **38**, 1537 (1988).

[9] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[10] J. K. Burdett and T. Hughbanks, Inorg. Chem. **24**, 1741 (1985).

[11] S. Massidda, J. J. Yu, and A. J. Freeman, Phys. Rev. B **38**, 11 352 (1988).

[12] V. V. Moschalkov and B. A. Popovkin, Zh. Vses. Khim. Oya. **34**, 19 (1989).

[13] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. **13**, 801 (1972).

[14] W. E. Pickett, Phys. Rev. B **25**, 745 (1982).

[15] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

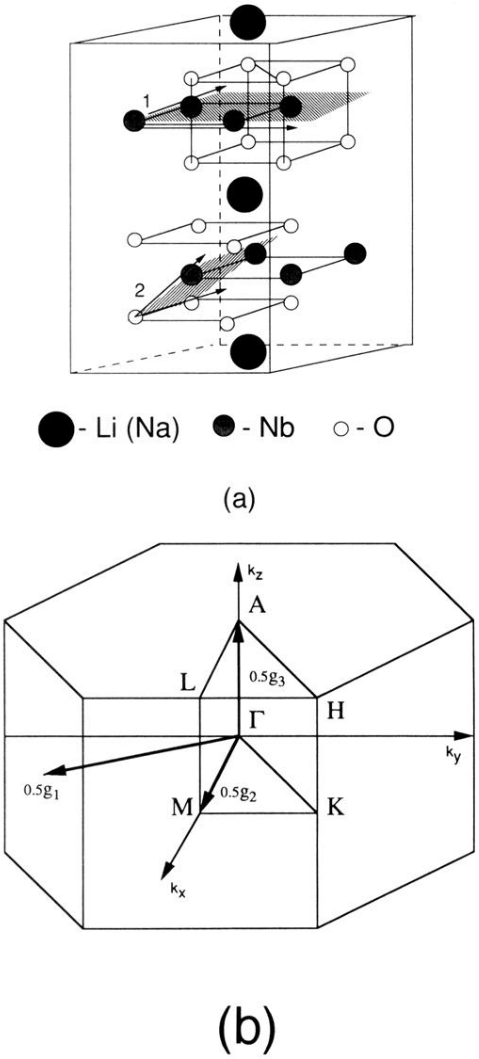

FIG. 1. (a) Crystal structure and (b) the first Brillouin zone for $M_x\mathrm{NbO}_2$ ($M=\mathrm{Li,Na}$).