Electronic Structure and Low-Temperature Properties of $V_xNb_{1-x}N$ Alloys

M. Dacorogna,* T. Jarlborg, A. Junod, M. Pelizzone, and M. Peter

Département de Physique de la Matière Condensée, Université de Genève, Geneva, Switzerland

(Received March 9, 1984; revised June 8, 1984)

The vanadium and niobium nitrides $V_xNb_{1-x}N$ are studied theoretically and experimentally for varying compositions $x$. Self-consistent linear muffin-tin orbital band calculations are performed for various ordered supercells corresponding to $x = 0.0, 0.25, 0.50, 0.75,$ and $1.0$. The band results are used to calculate electron-phonon coupling and spin susceptibility enhancement factors in order to study the variations of specific heat and superconducting transition temperatures with composition. A relative localization of, in particular, the V 3d states is found for the mixed compositions. The superconducting temperatures are found to be more reduced for intermediate compositions than what is expected from a simple interpolation between pure VN and NbN. Effects of spin fluctuations are important for the alloys containing vanadium, but are probably larger than what has been found in our theoretical study, and also containing $q \neq 0$ contributions. A small peak in the density of states near the Fermi energy is associated with a flat band near the W point, and causes a shoulder in density of state-dependent properties for $x$ near 0.9.

1. INTRODUCTION

The rocksalt structure (B1) niobium and vanadium nitrides are of technological interest because of their relatively high superconducting transition temperature $T_c$, which is 15.6 K for NbN and 8.7 K for VN. In addition, they are of interest due to phonon anomalies and possible spin fluctuations. Numerous calculations of the band structure and electron-phonon coupling $\lambda$ for the pure compounds (and the corresponding carbides) all give quite similar results for the electronic structure, 1-5 so that the density of states (DOS) near the Fermi energy $E_F$ is quite large, at least in VN, but there is no pronounced peak in the DOS near $E_F$. The details in the Fermi surfaces (FS) have not been compared to the experimental

*Present address: Department of Physics, University of California, Berkeley, California.
ones, due to the difficulties in obtaining high-quality single crystals for de Haas–van Alphen and positron annihilation measurements. Calculated large values of $\lambda$ and $T_c$ for VN, using a semiempirical model for the phonon spectrum,\(^6\) suggest that $T_c$ is limited by spin fluctuations in this compound.\(^7\,^8\) Stoichiometry plays an important role, and the $V_xNb_{1-x}N$ system shows lower $T_c$ values than expected from the pure compounds. Thus, although these compounds have long been well known, there remain several interesting questions about their properties. However, recent measurements have provided additional information concerning phonon spectra,\(^9\) electronic specific heat $\gamma$, and magnetic susceptibility $\chi$, especially for the intermediate compositions $V_xNb_{1-x}N$.

Motivated by the recent experimental work on the pseudobinary compounds $V_xNb_{1-x}N$, we have reinvestigated the electronic structure not only for the pure compounds, but also for intermediate compositions by the use of supercell calculations. Electron–phonon coupling and Stoner factors are calculated as a function of composition, in order to relate the results to the recent specific heat and superconductivity measurements; as well as to examine the importance of spin fluctuations. In particular we want to understand the mechanism for the drop in $T_c$ for intermediate compositions relative to the pure alloys. Similar low intermediate $T_c$ values have been observed in other V–Nb systems, such as $V_xNb_{1-x}$,\(^11\) and Au-based $\mathrm{Al}_5$ compounds,\(^12\) where the behavior cannot be ascribed to only structural effects. Furthermore, we study the small differences in the band structure in the isoelectronic pure alloys VN and NbN and their relation to their physical properties.

The electronic structures have been determined by using the self-consistent linear muffin-tin orbital (LMTO) band method\(^{13,14}\) with supercells containing up to eight atoms per unit cell. This method has been used in studies of several ordered compounds,\(^{14-17}\) and here we extend it to study substitutionally disordered alloys by the use of supercells. Some details of the calculations are given in Section 2 together with various physical parameters. Results and a discussion, including a comparison with experimental data, are presented in Section 3.

**2. DETAILS OF THE CALCULATIONS**

In addition to the pure compounds VN and NbN, we present results for intermediate compositions $V_xNb_{1-x}N$, where it is assumed that the particular compositions can be described by an ordered supercell. The pure compounds have the B1 (NaCl) structure with two atoms per unit cell. For moderately large supercells we can study the compositions $x = 0.33$ and $0.67$ (six atoms/cell) and $x = 0.25$, $0.50$, and $0.75$ (eight atoms/cell). In the