Strong depression of superconductivity in VN by spin fluctuations

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In this paper we argue that spin fluctuations prevent VN from being a superconductor with a transition temperature of about 30 K instead of the experimental value of 8.6 K. Thus, besides V and Nb for which similar results have been reported recently, VN provides a further and even more pronounced example for spin-fluctuation-limited high-T_c superconductivity. Our results are obtained from microscopic calculations of T_c for the refractory compounds TiN, ZrN, VN, and NbN and from magnetic susceptibility data. Among these four compounds VN is exceptional in exhibiting both a large theoretical overestimate of T_c, if spin fluctuations are omitted, and a high magnetic susceptibility. Incorporating spin fluctuations within the theory of Berk and Schrieffer, the theoretical value of T_c can be brought into agreement with experiment. Calculations of the magnetic susceptibility and of T_c in nonstoichiometric VN_x ($0.75 \leq x \leq 1.0$) and their comparison to experimental results of Ajami and MacCrone provide further support for our ideas.

I. INTRODUCTION

Since the discovery of superconductivity a huge effort has been put into the search for materials having high transition temperatures T_c. But in spite of the wealth of different alloys and compounds investigated at low temperatures success has remained very modest: Until now T_c has never exceeded 23 K, and for almost all known superconductors it is below 20 K. Within this context the immediate question has arisen whether there is a mechanism limiting T_c inherent in superconductivity. There are several answers to this question,[1] the most common being that the electron-phonon interaction underlying superconductivity is limited: An increase of this coupling (caused, e.g., by changes in the electronic configuration) will be accompanied by lattice softening. As a consequence, there will be a maximum coupling strength at which any attempt of a further increase will result in a collapse of the crystal into a structure which is more stable but has a lower T_c.[2,3]

Most of the high-T_c superconductors are either compounds of $A15$ structure (e.g., Nb_3Ge with $T_c \sim 23$ K) or refractory compounds with NaCl structure (e.g., NbN with $T_c \sim 17$ K). If lattice instabilities are essential in limiting high T_c superconductivity then they should show up especially in materials belonging to these two classes. Now, some of the $A15$ compounds show indeed tendencies towards lattice instabilities. So, V_3Si and Nb_3Sn undergo a martensitic phase transition from cubic to tetragonal at low temperature. On the other hand, it is known[4,5] that T_c differs only little in the different phases and it seems doubtful that these martensitic transformations impose a limit on T_c. A clear answer could be given if one were able to calculate the electron-phonon coupling strength and to find out what T_c it allows. Unfortunately, due to the complicated lattice dynamics and electronic structure of the $A15$, such calculations can hardly be performed at present.

Let us now turn to the refractory compounds. Many among them obviously exhibit high electron-phonon coupling strength which is manifest in soft-phonon anomalies and high T_c.[6] Nevertheless, they are stable against structural transitions and one may ask again why in this class T_c does not exceed 18 K? In contrast to the $A15$, for the refractory compounds we are able to calculate the coupling strength and to find out whether the limit in T_c is due to a limit in the coupling. We shall show below that for the refractory compound VN the electron-phonon coupling would allow $T_c \sim 30$ K in contrast to the experimental value of 8.6 K. Thus, at least in this case T_c is not limited by a maximum coupling strength.

In a recent letter,[7] it has been shown that in the superconductors V and Nb spin fluctuations ("paramagnons") as a precursor of band ferromagnetism lead to considerable depression of T_c and may possibly be considered as the main limitation of high T_c values.[8] In this paper we want to corroborate this idea by presenting VN as a further and still more pronounced example for these effects. For this purpose we perform microscopic T_c calculations for the refractory compounds ZrN, TiN, NbN, and VN and analyze their magnetic susceptibilities. Within this group of compounds we find VN to be exceptional in two respects: T_c calculated *omitting* spin fluctuations is much higher (32 K) than the experimental value (8.6 K), simultaneously the magnetic susceptibility, χ, is about eight times that of the other three compounds. We consider this coincidence between a large theoretical overestimate of T_c and an unusually high magnetic susceptibility to be a strong hint for paramagnon depressed superconductivity. A convenient measure for the influence of paramagnons on superconductivity[7] is the Stoner enhancement factor S of the magnetic spin susceptibility χ_{spin}. It is defined by $S=\chi_{\text{spin}}/\chi_0$, where the Pauli spin susceptibility χ_0 is given by $\chi_0=2\mu_B^2 N(\epsilon_F)$ [$N(\epsilon_F)$ is the electronic band-structure density of states at the Fermi level]. We calculate the influence of spin fluctuations on T_c by solving the Eliashberg equations including the q- and ω-dependent particle-hole t matrix $t(q,\omega)$ which depends on S. S is evaluated in the frame of the local density functional formalism and leads to susceptibilities which compare favorably to experiment. Furthermore, the same S causes a large reduction of T_c compared to the calculation without spin fluctuations, and reconciles theory with experiment. In addition, the exploitation of T_c and susceptibility measurements performed on understoichiometric samples of composition VN_x ($0.75\leq x\leq 1.0$) by Ajami and MacCrone[9] will provide further strong evidence for the importance of spin fluctuations in the superconductor VN.

II. THEORY

We calculate the superconducting transition temperature T_c by solving the linearized Eliashberg equations including the influence of spin fluctuations. On the imaginary axis they read[7,10]

$$\begin{aligned}
&\Delta(\omega_i)=T_c\sum_j[\lambda^-(\omega_i-\omega_j)-\mu^*]\frac{\pi}{|\tilde{\omega}_j|}\Delta(\omega_j)\ ,\\
&\tilde{\omega}_j=\omega_j+\pi T_c\sum_l \mathrm{sgn}\omega_l\lambda^+(\omega_j-\omega_l)\ ,\\
&i\omega_j=\pi i(2j+1)T_c\ ,\\
&\lambda^{\pm}(\omega_i-\omega_j)=2\int_0^\infty d\omega\frac{\omega[\alpha^2F(\omega)\pm P(\omega)]}{\omega^2+(\omega_i-\omega_j)^2}\ .
\end{aligned}\tag{1}$$

Here, the Eliashberg function $\alpha^2F(\omega)$, the unretarded Coulomb repulsion μ^*, and the paramagnon spectral weight function $P(\omega)$, reflect normal-state properties and represent the ingredients which determine T_c. In all calculations, we set $\mu^*=0.13$ with a cutoff at $5\omega_D$. $P(\omega)$ is related to the particle-hole t matrix $t(q,\omega)$ by[10]

$$P(\omega)=\frac{3N(\epsilon_F)}{2\pi}\int_0^{2k_F}\frac{qdq}{2k_F^2}\,\mathrm{Im}t(q,\omega)\ .\tag{2}$$

For $t(q,\omega)$ we use the RPA (random-phase approximation) ansatz of Schrieffer[11] allowing for a q-dependent interatomic interaction $J(q)$ in addition to the contact potential U,

$$\begin{aligned}
t(q,\omega)&=\frac{1}{3}\frac{U+J(q)}{1-[U+J(q)]N(\epsilon_F)u(q,\omega)}\\
&\quad+\frac{2}{3}\frac{U}{1-UN(\epsilon_F)u(q,\omega)}\ ,\\
J(q)&=J_0(1-C^2q^2)\ ,
\end{aligned}\tag{3}$$

where $u(q,\omega)$ is the Lindhard function and $c=1/\sqrt{2}k_F$. We are aware of the fact that Eqs. (3) represent an oversimplified description of $t(q,\omega)$. However, as already discussed in Ref. 7, for medium Stoner enhancements ($S\sim 2$–3) the physical conclusions do not depend critically on details in the calculation of $t(q,\omega)$ in contrast to situations where S is so large that the system is near a ferromagnetic instability.

Introducing the quantities

$$\begin{aligned}
S&=1/[1-N(\epsilon_F)I]\ ,\\
\kappa&=J_0/I\ ,
\end{aligned}\tag{4}$$

where $I=U+J_0$ is energy dependent and taken at ϵ_F, $I=I(\epsilon_F)$, we study T_c as function of S considering κ as a parameter. κ is a measure for the nonlocality of the electron-electron Coulomb interaction and paramagnon effects are weakened for increased κ. $\kappa=0$ reduces the Coulomb interaction to a contact potential, and this leads to an overestimate of the paramagnon effects.[7,11] Since at present we are unable to calculate $t(q,\omega)$ microscopically, we perform our calculations for two different κ values, namely, $\kappa=0$ and 0.3. $\kappa=0.3$ has proved to describe the right electron mass enhancement in the strongly-Stoner-enhanced Pd,[11] and we expect κ to be not too different in other d-electron metals.

Besides the calculation of T_c, $\alpha^2F(\omega)$ and $P(\omega)$ can be used to evaluate the phonon and paramagnon contributions λ_{ph} and λ_{spin} to the electron mass

enhancement factor m^*/m

$$m^*/m = 1 + \lambda_{ph} + \lambda_{spin} ,$$

$$\lambda_{spin} = 2\int_0^\infty d\omega P(\omega)/\omega , \qquad (5)$$

$$\lambda_{ph} = 2\int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} ,$$

which determines the electronic specific-heat coefficient γ through the relation

$$m^*/m = 3\gamma/2\pi^2 k_B^2 N(\epsilon_F) . \qquad (6)$$

The Eliashberg function $\alpha^2 F(\omega)$ has been calculated using a nonlocal version of the Gaspari-Gyorffy theory[12]

$$\alpha^2(\omega)F(\omega) = \frac{N(\epsilon_F)}{16\pi k_F^2} \sum_{\alpha,\alpha'} \int \frac{d^3q}{q} \Theta(2k_f - q)\tilde{V}_\alpha(q)\tilde{V}_{\alpha'}(q) e^{i\vec{\tau}\cdot(\vec{\rho}_{\alpha'} - \vec{\rho}_\alpha)} \times \frac{1}{\omega}\sum_\nu \frac{[\vec{e}_{\vec{q}\nu}(\alpha)\cdot\vec{q}][\vec{e}_{\vec{q}\nu}(\alpha')\cdot\vec{q}]}{(M_\alpha M_{\alpha'})^{1/2}} \delta(\omega - \omega_{\vec{q}\nu}) , \qquad (7a)$$

$$\tilde{V}_\alpha(q) = -\frac{1}{\pi k_f N(\epsilon_F)} \left(\frac{2m\epsilon_F}{\hbar^2}\right)^{1/2} \sum_l \left(\frac{n_l^\alpha n_{l+1}^\alpha}{n_{0l}^\alpha n_{0l+1}^\alpha}\right)^{1/2} \sin(\delta_l^\alpha - \delta_{l+1}^\alpha) \sum_{l'=0}^{l} (2l'+1) P_{l'}\left(1 - \frac{q^2}{2k_F^2}\right) . \qquad (7b)$$

Here, $\vec{e}_{q\nu}(\alpha)$ is the amplitude of a phonon with wave vector $\vec{q}$ of the νth branch and at the αth ion with position $\vec{\rho}_\alpha$ in the unit cell, $\omega_{\vec{q}\nu}$ is the corresponding frequency, and $\vec{\tau}$ is the reciprocal-lattice vector which reduces $\vec{q}$ to the first Brillouin zone. The n_l^α are the contributions to the crystalline density of states with angular momentum l at site α and the n_{0l}^α are the corresponding single scatter quantities. δ_l^α denotes the phase shifts for the partial wave with angular momentum l scattered from site α. The n_l and δ_l are taken at $\epsilon = \epsilon_F$, the δ_l are restricted to the interval $[0, \pi]$. In order to ensure correct counting of states in $\vec{k}$ space, $k_F = (3\pi^2 n)^{1/3}$ has to be used where n is the number of conduction electrons per unit volume.

The electronic quantities entering Eqs. (7) have been obtained using the self-consistent cluster approach described extensively in Ref. 13. Exchange and correlation have been treated according to the ansatz of Hedin and Lundqvist.[14] Scattering up to angular momentum $l = 2$ has been taken into account for both metal and nonmetal atoms, whereas for the metal atoms $l = 3$ was treated by perturbation theory. Self-consistency was reached after 6 to 8 iterations. 7 shells of atoms have been used in order to obtain the potentials and 15 shells for the final calculation of the electronic parameters entering the Eliashberg function. In this way, boundary effects could be eliminated even in energy regions where phase shifts and densities of states vary rapidly. The self-consistent electronic densities and radial wave functions have also been used to calculate the Stoner enhancement S in the frame of the spin-density formalism (see Ref. 15 and references therein) according to Eqs. (4).

As a model for the lattice dynamics providing the phonon frequencies and amplitudes which enter Eqs. (7) we chose the double-shell model of Weber.[16] For the different refractory compounds, this model has been fitted to phonon dispersion curves measured in inelastic neutron scattering experiments on single crystals. Details and the model parameters for TiN, ZrN, VN, and NbN can be found in Refs. 17–20.

III. NUMERICAL RESULTS AND DISCUSSION

The electronic quantities resulting from the cluster calculations are given in Table I. Together with the lattice dynamics model they have been used to generate via Eqs. (7) the Eliashberg functions $\alpha^2 F(\omega)$ which are shown in Fig. 1. Examples of the paramagnon spectral weight function $P(\omega)$ for $S = 2.5$ and several κ values are shown in Fig. 2. The Fermi energy ϵ_F which enters the Lindhard function $u(q, \omega)$ in Eqs. (3) has been put equal to the energy separation between the Fermi edge and the lower bottom of the d band (2.9 eV for VN). As can be seen from Fig. 2, $P(\omega)$ is long ranged in energy and one has to sum over a large number of Matsubara frequencies ω_j in Eqs. (1). We overcame this difficulty by replacing the gap function $\Delta(\omega_j)$ by a series of 30 step functions in the region where $P(\omega)$ is slowly varying (i.e., for $\omega \gtrsim 0.5$ eV). A further increase in the number of steps had little effect on the results. The numerical solution of Eqs. (1) was then performed by the use of the iterative algorithm of Culetto and Rainer[21] which is particularly suited for the case of a strong Coulomb (and paramagnon) repulsive kernel.

First we calculated T_c without consideration of spin fluctuations, i.e., for $P(\omega) \equiv 0$. These values are denoted by T_c^{theor} and listed in Table II[22,23] together with their experimental counterparts T_c^{expt}. In the same table, λ_{ph} and the specific-heat coefficient γ^{theor} as calculated from Eqs. (5) and (6) (with $\lambda_{spin} = 0$) and the experimental value γ^{expt} can be found. The last column lists measured magnetic susceptibilities χ_{tot}.

TABLE I. Electronic quantities resulting from the self-consistent cluster calculations for TiN, ZrN, VN, and NbN.

	Ti	N	Zr	N	V	N	Nb	N
δ_0	2.19	1.37	2.0	1.41	2.26	1.34	2.01	1.35
δ_1	2.81	1.72	2.6	1.76	2.86	1.44	2.62	1.75
δ_2	1.32	0.016	0.97	0.018	1.92	0.016	1.55	0.02
δ_3	0.005	0.0	0.01	0.0	0.004	0.0	0.013	0.0
n_0/n_{00}	0.18	0.17	0.13	0.2	0.12	0.54	0.15	0.6
n_1/n_{01}	0.1	0.33	0.07	0.4	0.17	0.61	0.09	0.61
n_2/n_{02}	0.36	1.8	0.33	2.3	0.78	3.0	0.53	1.98
n_3/n_{03}	2.1	. . .	1.72	. . .	4.1	. . .	3.0	. . .
ϵ_F (eV)	11.8		11.1		12.2		12.2	
$N(\epsilon_F)$ (spin at eV)$^{-1}$	0.404		0.28		0.79		0.44	
$I(\epsilon_F)$ (eV)	0.71		0.69		0.83		0.69	
S	1.4		1.24		2.9		1.44	

The best agreement between T_c^{expt} and T_c^{theor} is obtained for NbN and would possibly be even better if the experimental T_c were determined on stoichiometric samples for which our calculation actually holds. Unfortunately, T_c values for NbN samples without an appreciable amount of vacancies on Nb and/or N sites are not available. In any case, the difference between T_c^{expt} and T_c^{theor} is not significant and spin fluctuations should be, if at all, only of minor importance in NbN. This is in accordance with the low magnetic susceptibilty, χ_{tot}, and low Stoner enhancement, S.

For TiN and ZrN, T_c^{theor} is too small, for TiN by a factor of 2. Both compounds are weak coupling superconductors in the sense that they have λ_{ph} significantly below one. In that case T_c depends exponentially on λ_{ph} and just a small increase of λ_{ph} (0.45 to 0.53 for TiN and 0.60 to 0.69 for ZrN) would be sufficient to raise T_c^{theor} to the experimental value. In other words, the relatively large errors in T_c^{theor} may arise from small errors (less than 20%) in λ_{ph} and therefore in $\alpha^2F(\omega)$. This can be considered as satisfactory, especially in view of the remaining uncertainties in lattice dynamics, electronic quantities, and electron-phonon coupling. Because of the low susceptibilities and Stoner enhancements we believe that in TiN and ZrN there is only a small influence of spin fluctuations on T_c. We note that we have al-

TABLE II. Theoretical values for T_c(K), λ_{ph}, and γ(mJ/K^{2}mole) calculated with omission of spin fluctuations together with experimental data for T_c, γ, and x_{tot} (10^{-6} emu/mole).

	T_c^{theor}	T_c^{expt}	λ_{ph}	γ^{theor}	γ^{expt}	χ_{tot}^{expt}
TiN	2.8	5.5[a]	0.45	2.7	3.3[a,b]	38[a]
ZrN	7.4	10.0[a]	0.60	2.1	2.7[a,b]	22[a]
VN	32.3	8.6[c]	1.54	9.5	8.6[a,b]	240[c]
NbN	23.0	17.3[d]	1.23	4.8	4.1[e]	31[a]

[a]Reference 23.
[b]Reference 22.
[c]Reference 10.
[d]M.W. Williams, K. M. Ralls, and M. R. Pickus, J. Phys. Chem. Solids 28, 333 (1967).
[e]P. Roedhammer, E. Gmelin, W. Weber, and J. P. Remeika, Phys. Rev. B 15, 711 (1977); a more recent evaluation of the same specific-heat data lead to a γ appreciably above 4.1 [P. Roedhammer (private communication)], thus underlining the difficulties in extrapolating $C(T)$ to $T=0$.

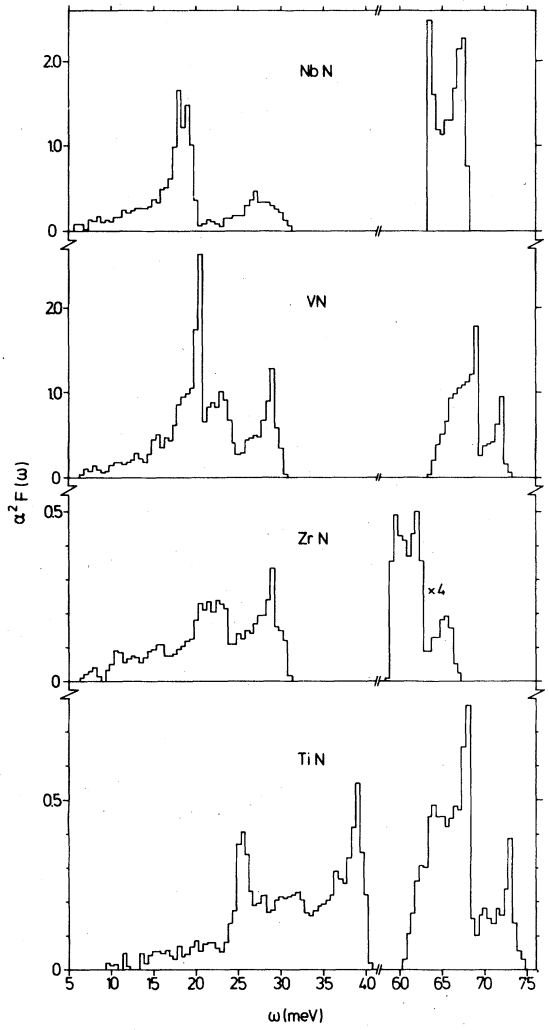

FIG. 1. Histogram of the Eliashberg function $\alpha^2F(\omega)$ for TiN, ZrN, VN, and NbN as calculated from Eqs. (7); note that for ZrN the optical part has been reduced before plotting and must be multiplied by 4.

ready calculated T_c for the refractory compounds ZrC, NbC, and YS without consideration of spin fluctuations and have obtained fairly good agreement with experiment.[24] This is in accordance with our present results for TiN, ZrN, and NbN since all of these compounds have low magnetic susceptibilities.[23]

In VN, T_c^{theor} is more than three times the experimental value. We believe this large discrepancy to be significant and inexplicable by errors in λ_{ph} [i.e., in $\alpha^2F(\omega)$], since a reduction of λ_{ph} from 1.54 to 0.72(!) would be required in order to make T_c^{theor} agree with T_c^{expt} (see Sec. IV). In addition, the magnetic susceptibility of VN (see Table II) is about eight times larger than for the other three compounds. Moreover, we calculate a Stoner factor $S = 2.9$ for VN, whereas $S < 1.5$ for TiN, ZrN, and NbN (see

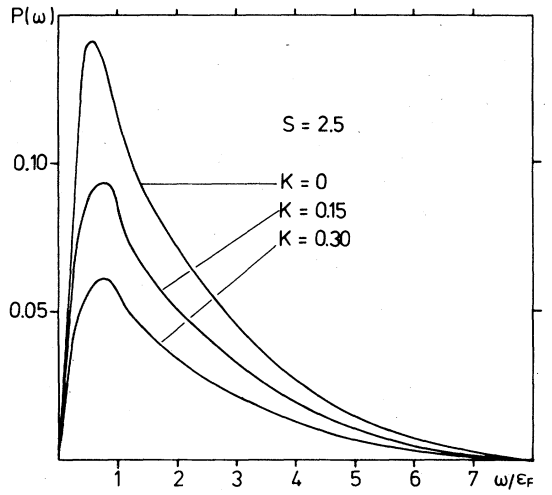

FIG. 2. The paramagnon spectral weight function $P(\omega)$ for a Stoner enhancement $S = 2.5$ and several κ as calculated from Eqs. (2) and (3).

Table I). This suggests that the high susceptibility in VN is at least partly due to a high spin susceptibility, an assumption which will be confirmed in Sec. IV by analyzing susceptibility data of understoichiometric VN. These results lead us to recalculate T_c for VN under consideration of spin fluctuations via Eqs. (1)–(3). In Fig. 3 T_c is shown as a function of the Stoner enhancement, $T_c = T_c(S)$, for $\kappa = 0$ and $\kappa = 0.3$. From $T_c(S) = T_c^{\text{expt}}$ we obtain $S = 2.2$ for $\kappa = 0$ and $S = 3.3$ for $\kappa = 0.3$, respectively. The calcu-

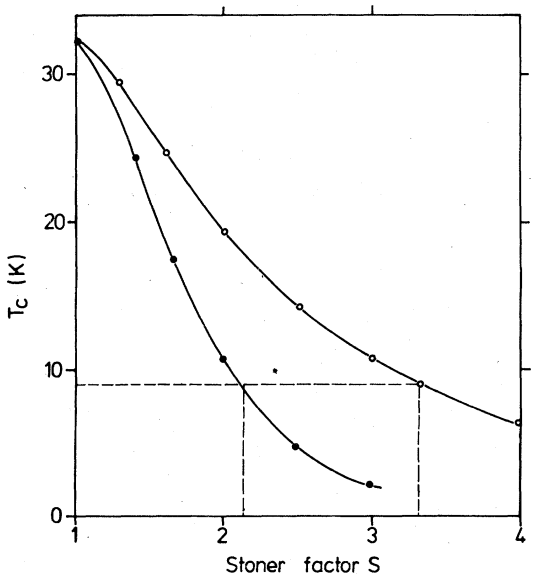

FIG. 3. The superconducting transition temperature T_c as a function of the Stoner enhancement S for VN. Closed circles, contact model of Ref. 9 ($\kappa = 0$); open circles, $\kappa = 0.3$; solid line, guide to the eye; broken line, $T_c(S) = T_c^{\text{expt}}$.

lated Stoner factor $S = 2.9$ fits into this scheme thus demonstrating that spin fluctuations are able to account for the large difference between T_c^{theor} and T_c^{expt}.

Let us try to investigate the compatibility of our theoretical results with experimental specific-heat data and contrast two extreme assumptions:

(a) The overestimate in T_c^{theor} is completely due to errors in λ_{ph}, and spin fluctuations have no influence. Then, λ_{ph} must be reduced from 1.54 to 0.72 in order to get the right T_c which implies a reduction of γ^{theor} to 5.9 mJ/K^2 mole which is 32% below the experimental value.

(b) The overestimate in T_c^{theor} is completely due to the omission of spin fluctuations and $\lambda_{\text{ph}} = 1.54$ is correct. The correct T_c is now obtained including spin fluctuations. Then $\lambda_{\text{spin}} = 0.54$ (almost independent of κ), and γ^{theor} is increased [see Eq. (5)] to 11.5 mJ/K^2 mole which is now 34% above γ^{expt}.

If the experimental value $\gamma^{\text{expt}} = 8.6$ mJ/K^2 mole were reliable within few percents, neither (a) nor (b) could be true and we would have to assume some intermediary situation. [Solving Eqs. (1) with $\alpha^2F(\omega)$ reduced by a constant scale factor shows that then $\lambda_{\text{ph}} \sim 1.1$, $\lambda_{\text{spin}} \sim 0.3$, and $T_c^{\text{theor}} \sim 22$ K would give the right answer.] However, γ_{expt} has been derived by extrapolating the specific heat $C(T)$ for $T \to 0$ from experimental data *above* $T_c^{\text{expt}} = 8.6$ K. This may lead to large errors in γ, particularly in view of the unusually soft phonons which are typical for many refractory compounds and also present in VN.[25] Therefore, we estimate a 30% uncertainty in the quoted value of γ^{expt}. Assuming that our error in λ_{ph} for VN is comparable in size to that for the other three compounds (about 18%), the lower limit for λ_{ph} is about 1.3 resulting in $T_c^{\text{theor}} \sim 28$ K. In this case in order to bring down T_c^{theor} to T_c^{expt}, $\lambda_{\text{spin}} \sim 0.4$ would be needed implying $\gamma = 10$ mJ/K^2 mole. From these considerations it follows that additional specific-heat measurements under magnetic fields $> H_{c_2}$ are highly desirable in order to give a more precise answer.

IV. INFLUENCE OF STOICHIOMETRY

The physical properties of VN depend strongly on the nitrogen content of the sample. Ajami and MacCrone[9] have performed measurements of both the magnetic susceptibility χ_{tot} and the superconducting transition temperature T_c on samples of composition VN_x with $0.74 \leq x \leq 1.0$. The susceptibility data for $T = 77$ K are shown in Fig. 4 and the T_c data in Fig. 5. A remarkable feature is the drastic decrease of χ_{tot} for $0.85 \leq x \leq 1.0$ followed by a nearly constant behavior for $0.75 \leq x \leq 0.85$. At the same time, T_c decreases almost linearly with decreasing x, reaching $T_c = 2$ K for $x = 0.75$. One could be tempted to consider this decrease in T_c as contradictory to the conclusions of the preceding chapter since any drop in the magnetic susceptibility should be favorable for superconductivity due to a corresponding drop in spin fluctuations. However, not only the spin susceptibility changes with changing x but also the Eliashberg function $\alpha^2F(\omega)$, the latter in such a way that T_c is strongly depressed. We shall now show that it is just this combination of two counteracting effects which enables us to explain quantitatively the observed $T_c(x)$ in VN_x.

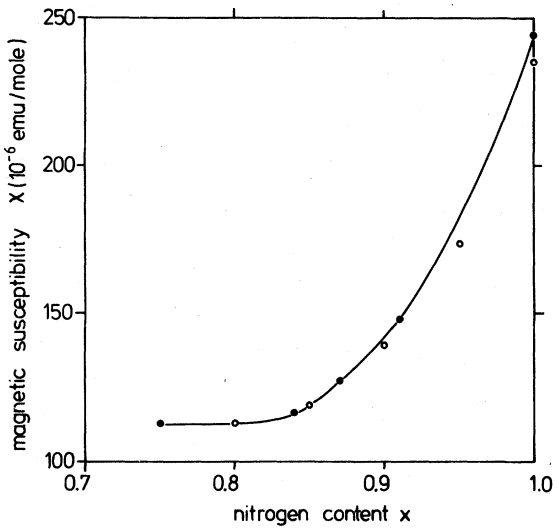

FIG. 4. The total magnetic susceptibility χ as a function of x in understoichiometric samples of composition VN_x. Closed circles, experimental values from Ref. 10; opened circles, rigid-band calculation assuming an x independent orbital contribution of 88×10^{-6} emu/mole.

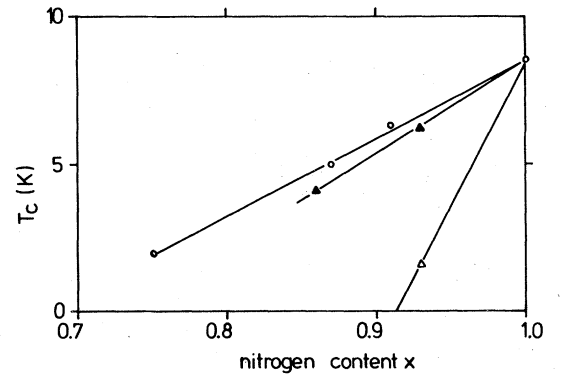

FIG. 5. The superconducting transition temperature T_c as a function of x in understoichiometric samples of composition VN_x. Circles, experimental values from Ref. 10; full triangles, rigid-band calculation taking account of spin fluctuations and their fast decay with decreasing x; open triangle, rigid-band calculation omitting spin fluctuations; solid lines, guides to the eye.

TABLE III. The quantities S, λ_{ph}, λ_{spin}, and T_c for different x in compounds of composition VN_x calculated in a rigid-band model; $\kappa = 0.22$ so that for $x = 1.0$ $T_c = T_c^{expt}$.

X	S	λ_{ph}	λ_{spin}	T_c(K)
1.0	2.9	1.54	0.54	8.6
0.93	1.9	0.92	0.24	6.2
0.86	1.4	0.62	0.085	4.1

For this purpose we need information on both the electronic structure and the lattice dynamics in VN_x for $x < 1$. Inelastic neutron scattering experiments[25] on samples of composition $VN_{1.0}$, $VN_{0.93}$, and $VN_{0.86}$ reveal a considerable hardening of the phonon frequencies for decreasing x. In terms of a mean-squared phonon frequency $\langle\omega^2\rangle$ it turns out that $\langle\omega^2\rangle_{0.93}/\langle\omega^2\rangle_{1.0} = 1.32$ and $\langle\omega^2\rangle_{0.86}/\langle\omega^2\rangle_{1.0} = 1.60$ for the acoustic-phonon spectrum while the optic frequencies are scarcely affected. Since the underlying lattice dynamics model was obtained by a fit to the phonon dispersion curves of a single crystal of composition $VN_{0.86}$ (the only available single crystal), we generated the corresponding models for $VN_{1.0}$ and $VN_{0.93}$ simply by rescaling the frequencies of the acoustic branches according to the above-mentioned ratios.

A more difficult problem is to obtain information about the x dependence of the electronic quantities. Strictly speaking, one has to recalculate the potentials $V_\alpha(q)$ occurring in Eqs. (7) for $x < 1$. Such calculations have been performed by Ries and Winter[26] in the limit of dilute nitrogen vacancies in VN but cannot be adopted for the finite concentrations $x = 0.93$ and 0.86 where the vacancies interact. Instead, we calculated $V_\alpha(q)$ for $x < 1.0$ within a rigid-band model. Omitting 5 valence electrons for each nitrogen defect, we determined the Fermi energy ϵ_F and the electronic quantities $N(\epsilon_F)$, $n_l(\epsilon_F)$, $\delta_l(\epsilon_F)$, and for $x < 1.0$, which allows the calculation of $V_\alpha(q)$ and χ_{spin}, respectively, via Eqs. (7) and (4), respectively. As a first test of this approximation, one may compare the x dependent change in the spin susceptibility χ_{spin} to experiment. Following Ref. 9 we assumed the orbital contribution, χ_{orb}, to the magnetic susceptibility to be roughly constant and put $\chi_{orb} = 88 \times 10^{-6}$ emu/mole independent of x. The resulting total susceptibility $\chi_{tot} = \chi_{spin} + \chi_{orb}$ as function of x is shown in Fig. 4. The agreement with the experimental data is excellent, and one may hope that the rigid-band approximation would also work well for the remaining quantities.

In order to calculate $T_c(x)$, we fixed $\kappa = 0.22$ which for $S = 2.9$ and $x = 1.0$ leads to the measured $T_c = 8.6$ K. We then calculated $\alpha^2F(\omega)$ and S for $x = 0.93$ and 0.86 and finally solved Eliashberg's equations (1) for T_c. Table III summarizes S, λ_{ph}, λ_{spin}, and T_c for different x, a comparison of $T_c(x)$ to $T_c^{expt}(x)$ is given by Fig. 5. There is excellent agreement between theory and experiment.

One may again assume that the overestimate in T_c^{theor} is completely due to errors in λ_{ph} and ask whether then $T_c(x)$ could be equally well described. In other words, one may try to calculate the degradation in T_c under omission of spin fluctuations and only through the changes in $\alpha^2F(\omega)$. We did this in the following way. For $x = 1.0$, we multiplied the function $\alpha^2F(\omega)$ by the factor 0.47 which leads to $T_c = T_c^{expt}$ for $S = 1$. Reducing for $x = 0.93$ and 0.86 the functions $\alpha^2F(\omega)$ by the same factor we then got $T_c = 1.6$ K for $x = 0.93$ while for $x = 0.86$ no finite T_c could be found. In other words, if spin fluctuations are not taken into account, the relative change in $\alpha^2F(\omega)$ is sufficient to destroy superconductivity completely for $x \lesssim 0.9$, in contradiction to experiment (see Fig. 5).

V. EXCHANGE ENHANCEMENT OF T_c

Apart from pair breaking and reduction of T_c, spin fluctuations may imply changes in the phonon renormalization and vertex corrections of the electron-phonon coupling. Using a simple local exchange model, Kim[27] has shown that under favorable conditions those effects may give rise to an increase of λ_{ph} which even overcompensates the pair breaking thus leading to an enhancement of T_c. Let us recapitulate briefly some results of Ref. 27 and then discuss how relevant these considerations might be for our investigations. In short, we limit the discussion to the jellium model and adopt the notation of Ref. 27. Then, λ_{ph} is given by

$$\lambda_{ph} = N(\epsilon_F)\left\langle\!\!\left\langle \frac{2\Omega_p|\bar{\alpha}(q)|^2}{\omega_q^2} \right\rangle\!\!\right\rangle , \tag{8}$$

where the double brackets indicate a momentum average over the Fermi surface. Ω_p is the ion plasma frequency and ω_q the renormalized phonon frequency. $\bar{\alpha}(q)$ is the screened and vertex corrected electron-phonon coupling function. In terms of the static polarizability $F(q)$, the usual Coulomb interac-

tion $V(q)$, and an effective exchange and correlation potential $\tilde{V}(q)$, $\bar{\alpha}(q)$ can be written

$$\bar{\alpha}(q)=\alpha(q)/\{[1+2\tilde{F}(q)V(q)][1-F(q)\tilde{V}(q)]\}\ ,$$
$$\tilde{F}(q)=F(q)/[1-F(q)\tilde{V}(q)]\ , \tag{9}$$

where $\alpha(q)$ is a well-behaved function. ω_q is related to Ω_p by

$$\omega_q^2=\Omega_p^2/[1+2\tilde{F}(q)V(q)] \tag{10}$$

and the Stoner enhancement S is given by

$$S=1/[1-F(0)\tilde{V}(0)]\ . \tag{11}$$

Now, for $S\rightarrow\infty$ the system is at a ferromagnetic instability. This singular behavior is also reflected in ω_q leading to a vanishing velocity of sound and to an appreciable phonon softening for finite q. It is mainly this softening of ω_q which, through Eq. (8), gives rise to possible enhancement of λ_{ph}. Since in our calculations we have used lattice dynamics models fitted to experimentally determined phonon spectra, such effects have already been properly taken into account. A possible second source for enhancement of λ_{ph} may lie in an exchange enhancement of $\bar{\alpha}(q)$ due to vertex corrections. Within Kim's theory these corrections induce only minor changes since even for $S\rightarrow\infty$ $\bar{\alpha}(q)$ remains finite for all q. In addition, there is some tendency[28] for vertex corrections to cancel against a proper renormalization of the electron Green's function, though it can only be proven in the long-wavelength limit.

VI. SUMMARY

We have calculated the superconducting transition temperature T_c for the refractory compounds TiN, ZrN, NbN, and VN using self-consistent electronic cluster calculations and double-shell models in order to describe the lattice dynamics. For the compounds TiN, ZrN, and NbN the difference between theory and experiment is explainable by remaining errors in the electron-phonon coupling of at most 20%. However, the deviation for VN is much larger ($T_c^{\text{theor}}=32$ K compared to $T_c^{\text{expt}}=8.6$ K). This discrepancy could be removed by including the effect of spin fluctuations into the Eliashberg equations. The required Stoner enhancement S was found to agree well with measured susceptibilities and with the value $S=2.9$ calculated in the frame of the local density functional approach. The measured electronic specific-heat coefficient $\gamma^{\text{expt}}=8.6$ mJ/K^2 mole supports at least qualitatively our results. Further strong evidence for our ideas is provided by the x dependence of T_c and the magnetic susceptibility in compounds of composition VN_x ($x<1$) (Ref. 9): The relatively modest decrease in T_c for decreasing x can only be understood if, in addition to the degradation of the electron-phonon coupling, the rapid breakdown of spin fluctuations is taken into account. Thus, we have found VN to be a further and very characteristic example for paramagnon depressed superconductivity. We are convinced that it is only one member of a wide class of superconductors where spin fluctuations act as a drastic limitation for the occurrence of high T_c and that many other well-known superconductors belong to this same class.

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