Superconductivity of VN under pressure

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The superconducting transition temperature (T_c) for VN has been determined as a function of hydrostatic pressure up to 17 kbar. Similar to V metal, T_c increases monotonically in this pressure range, except the rate of increase $\partial T_c/\partial P$ for VN is even stronger. The upper critical field of VN has also been measured. The results are discussed in conjunction with the effects due to spin fluctuation.

INTRODUCTION

VN belongs to the group of refractory compounds with NaCl structure. It is also a superconductor with transition temperature (T_c) ranging from 2–9 K depending on the nitrogen content.[1,2] Recently, a phenomenological theory pointed out that VN might be a spin-fluctuation system because of the high value of its spin susceptibility.[3,4] The theory contended that, had the spin-fluctuation not existed, the T_c of stoichiometric VN would have been much higher.

In this article, we report the effect on T_c of VN under hydrostatic pressure up to ~ 17 kbar and the results of upper critical field (H_{c2}) measurements. Similar to other transition-metal carbides and nitrides, VN with NaCl structure can be formed readily. However, achieving full stoichiometry is a difficult proposition. Despite the literature report that the NaCl structure of VN_x existed for $x = 0.7$–1.0,[1,2] we were only successful, after many attempts, in preparing single-phase samples with x up to 0.93.

EXPERIMENTAL PROCEDURES

Specimens of VN_x were prepared from high-purity V ribbon (Materials Research Corporation Marz grade) and research-grade N_2 in a diffusion-pump evacuated quartz furnace system, which was capable of providing a vacuum in the low 10^{-6}-Torr range. The formation of VN_x was complete after the V ribbon was heated in a W boat at $\sim 1100\,^{\circ}C$ and ~ 600 Torr of N_2 pressure for ~ 10 h. Under such preparation conditions, a minute amount of oxygen contamination seemed inevitable although its content was not easily determined.

With the use of x-ray diffraction techniques, the lattice parameters of the single-phase VN_x material were accurately measured. The well-established linear relationship between the lattice parameter and the x value[2,5,6] was used to determine the N content.

The pressure experiments were carried out in the usual manner with a beryllium-copper cell of the self-clamping design. The pressure was generated in a 1:1 fluid mixture of n-pentane and isoamyl alcohol contained inside a 4.8-mm-diam Teflon cup which was capable of producing pressures up to ~ 20 kbar. A four-probe arrangement was utilized to measure the specimen resistance (R) and a Pb manometer was used to monitor the pressure. The critical-field experiments were performed with a Bitter magnet (for fields up to 17 T) at the Naval Research Laboratory High Field Facility. Throughout the measurements, the transition midpoints were designated to be T_c and H_{c2} in the R vs T and R vs H curves, respectively.

RESULTS

From all the data collected, we judge that among the samples we prepared, the best was $VN_{0.93}$ with lattice constant $4.127\,A$. The results reported here are exclusively of this sample.

The T_c of $VN_{0.93}$ increases with applied pressure as shown in Fig. 1. Among the many superconductors tested under high-pressure conditions, positive values of dT_c/dP are common only for V metals[7,8] and V-based compounds.[9] For comparison, the pressure dependence of T_c, together with Debye temperature Θ_D and electronic specific heat γ, are

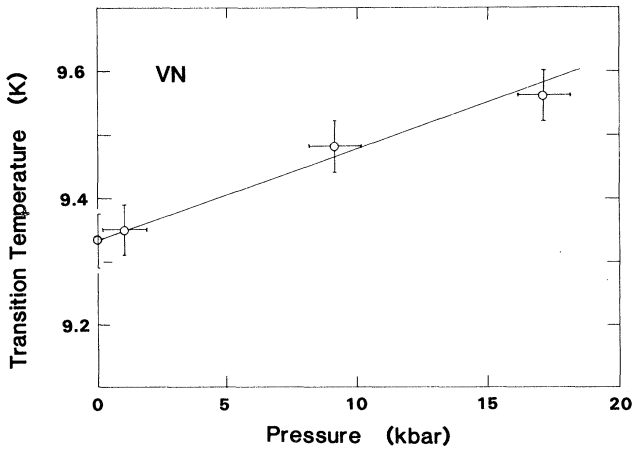

FIG. 1. Transition temperature of $VN_{0.93}$ as a function of applied pressure. The horizontal bars indicate the uncertainty in pressure readings and the vertical bars show the transition widths.

TABLE I. Comparison of parameters among some known superconductors.

	T_c (K)	Θ_D (K)	γ (mJ/g atom K^2)	dT_c/dP (10^{-5} K/bar)	References
V	5.4	380	8.8	+0.62	7,10
Nb	9.2	280	7.6	−0.20	7,10
Ta	4.5	220	5.8	−0.26	7,10
V_3Si	17.1	330	19.4	+3.7	9,11
V_3Ga	16.5	310	25.5	+1.05	9,11
V_3Au	2.8	330	13.1	+1.3	9,12
V_3Ge	6.1	405	7.6	+8.1	9,11
Nb_3Sn	18.0	290	15.7	−1.4	9,11
Nb_3Al	18.5	370	7.6	−0.7	9,13
VN	9.2	450	9.1	+1.4	

listed in Table I for a number of well-known superconductors.

The upper critical field (H_{c2}) of $VN_{0.93}$ is shown in Fig. 2. The initial slope $[dH_{c2}/dT]_{T_c}$ is ~ 17.5 kOe/K, which is comparable with the values of Nb_3Sn and V_3Si but much smaller than that of V_3Ga.[14]

DISCUSSION

An important argument in favor of the spin-fluctuation theory for VN is its unusually high spin susceptibility (χ_0). This point is demonstrated in Table II together with other refractory nitrides and carbides of the NaCl structure. It is clear that the χ_0 values of VN and VC are correspondingly much higher. In particular, the T_c's of VN and VC do not scale with their electronic specific heat γ.

For VN_x, T_c and χ_0 depend sensitively on the N content; both reach the respective highest values at full stoichiometry ($x=1$). An apparent inconsistency exists since spin fluctuation is supposed to depress T_c, while χ_0, hence spin fluctuation, and T_c reach maxima simultaneously. However, inelastic neutron scattering results[18] revealed considerable phonon softening in VN_x as x approached 1. Thus the observed T_c of VN was the result of two competing factors: the strong spin fluctuations and the softening of acoustic phonons.

The pressure dependence of T_c of VN and, more generally, all other V-based compounds, can be explained on the basis of competing mechanisms. Under pressure, the mean square of the phonon spectrum, $\langle\omega^2\rangle$, is expected to increase. But the steep rise of the Hopfield "electronic" factor η (Ref. 19) more than compensated for the effect of $\langle\omega^2\rangle$. Thus the overall effect as a result of pressure resulted in a net increase of the electron-phonon enhancement factor. This explanation is based on the assumption that the pressure enhancement of T_c in all V-based material is not substantially influenced by the effects which were observed for individual compounds such as the martensitic transformation in V_3Si, the sensitive dependence on long-range ordering in V_3Au, etc.

In considering the H_{c2} result, the empirical approach recently published[14] is adopted for the purpose of comparison. In this approach the Pauli limiting field $H_{\mathscr{P}}$ is modified as a result of the electron-phonon enhancement factor $\lambda_{e\text{-ph}}$:

$$H_{\mathscr{P}} = H_{\mathscr{P}}^{\mathrm{BCS}}(1+\lambda_{e-\mathrm{ph}}) \ ,$$

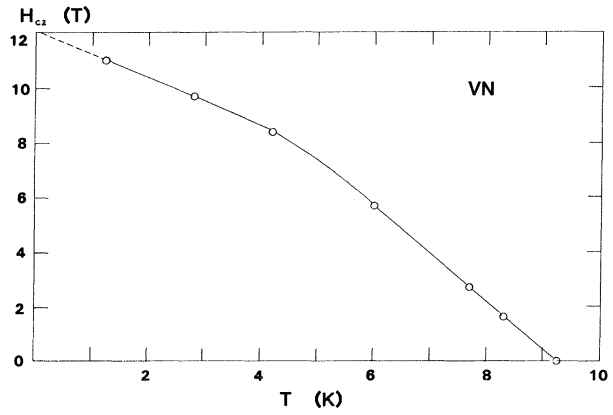

FIG. 2. Upper critical field of $VN_{0.93}$ as a function of temperature. $H_{c2}(0)$ is extrapolated to be ~ 120 kOe.

TABLE II. Comparison of parameters among superconductors with the NaCl structure.

	T_c (K)	Θ_D (K)	γ (mJ/g atom K^2)	χ_0 (10^6 emu/mole)
VN	9.2[a]	450[b]	9.1[b]	112 ~ 240[c]
NbN	17.3[d]	345[b]	4.2[b]	31[d]
ZrN	10.0[d]	510[d]	2.7[d]	22[d]
VC	< 0.05[d]	660[d]	3.2[d]	25 ~ 90[e]
NbC	11.1[d]	545[d]	2.8[d]	18[e]
TaC	10.4[d]	490[d]	3.2[d]	10[e]
TiN	5.5[d]	635[d]	3.3[d]	38[d]

[a]Present investigation.
[b]Reference 15.
[c]Reference 2.
[d]Reference 17.
[e]Reference 16.

TABLE III. Comparison between experimental H_{c2} of VN and calculated H_{c2} by parameter fitting.

(a) ($VN_{0.93}$) $(dH_{c2}/dT)\|_{T_c} = 17.5$ kOe/K, $H_{c2}^{*} = 112$ kOe, $H_{c2}^{expt} = 120$ kOe				
λ_{e-ph}[a]	λ_{sf}[a]	J	$H_{\mathscr{P}}$ (kOe)	$H_{c2}^{min\ b}$ (kOe)
1.54	0	0	435	105
0.92	0	0	329	100
1.54	0.54	0.5	264	95
0.92	0.24	0.5	185	85

(b) (VN_x films[c])						
			Clean $T_c = 8.7$ K, $(dH_{c2}/dT)\|_{T_c} = 12.4$ kOe/K $H_{c2}^{*} = 75$ kOe, $H_{c2}^{expt} = 82$ kOe		Dirty $T_c = 7.0$ K, $(dH_{c2}/dT)\|_{T_c} = 35.7$ kOe/K $H_{c2}^{*} = 173$ kOe, $H_{c2}^{expt} = 104$ kOe	
λ_{e-ph}[a]	λ_{sf}[a]	J	$H_{\mathscr{P}}$ (kOe)	$H_{c2}^{min\ b}$ (kOe)	$H_{\mathscr{P}}$ (kOe)	$H_{c2}^{min\ b}$ (kOe)
1.54	0	0	411	72	331	139
0.92	0	0	311	71	250	124
1.54	0.54	0.5	249	69	201	110
0.92	0.24	0.5	175	64	141	86

[a]Value taken from Ref. 3.
[b]Minimum allowed H_{c2}.
[c]Data taken directly from Ref. 20.

where $H_{\mathscr{P}}^{BCS} = 18.6 T_c$ kOe.

If the effect due to the electron-electron interaction is included, $H_{\mathscr{P}}$ is further modified:

$$H_{\mathscr{P}} = H_{\mathscr{P}}^{BCS}(1 + \lambda_{e-ph} + \lambda_{sf})(1 - J) \ ,$$

where λ_{sf} is the enhancement factor due to spin fluctuation and $(1 - J)$ is the Stoner factor.

Both equations can be applied to the case of VN, as compared in Table III, in which the available thin-film VN_x data are also included.[20] Apparently, the $VN_{0.93}$ sample in the present study showed very similar behavior as the "clean" film. From Table III, it can be seen that the effect due to the electron-electron interaction in VN is not as drastic as in V_3Ga.[14]

Also in this approach, the orbital critical field can be calculated:

$$H_{c2}^{*} = 0.693 T_c \left.\frac{dH_{c2}}{dT}\right|_{T \sim T_c} = 112 \text{ kOe}$$

which is within 10% of the extrapolated experimental H_{c2} value ($H_{c2}^{expt} \sim 120$ kOe), similar to V_3Si but in marked contrast to V_3Ga for which H_{c2}^{*} was substantially larger than H_{c2}^{expt}.[14]

For VN_x, it is difficult to attribute this observation to a large spin-orbit scattering since VN_x contains only elements of low atomic numbers, and the spin-orbit scattering effect should not be important. On the other hand, the reduction of Pauli-limiting field due to a strong electron-electron interaction would require a definite presence of spin-orbit scattering. Future work is necessary to clarify this point. It must be emphasized, however, because of the large spin susceptibility observed in VN, the spin-fluctuation effect needs to be considered seriously.

Overall, the spin-fluctuation theory, although purely phenomenological, is physically reasonable. While more evidence is being gathered, an important test of the theory lies in its generalization. Since the characteristics of V-metal and many V-based alloys and compounds are quite similar, the spin-fluctuation theory, if held true, would have to be applicable to all V-based materials.

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