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SUPERCONDUCTIVITY OF NIOBIUM NITRIDE OF VARIABLE COMPOSITION

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ABSTRACT

The wide range of stoichiometry and the accompanying uncertainty in specimen composition have led to confusing results in previous investigations of the superconductivity of cubic NbN. A preparative technique involving different nitriding temperatures and pressures has led to compounds of relatively low oxygen content which span the range N/Nb = 0.87 - 0.97. The critical temperature (T_c) is dependent on both lattice parameter and stoichiometry. The maximum T_c (17.3°K) found in this study occurs for a composition slightly below stoichiometry ($NbN_{0.93-0.96}$) and for a lattice parameter near 4.390Å. A maximum upper critical field (H_{c_2}) of 118 kG was found. These values of T_c and H_{c_2} are considerably higher than those previously reported for this compound.

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INTRODUCTION

Much effort has been expended in the study of critical temperatures (T_c) and upper critical fields (H_{c_2}) for metals and alloys (including solid solutions and intermetallic compounds). Another whole class of materials showing interesting superconductive properties consists of transition metal-interstitial compounds. One of the highest critical temperatures known is for such a material, i.e., 70 mole % NbN-30 mole % NbC.[1] These compounds have not been investigated as much as metals and alloys because of the difficulty of preparation and because of the suspected dependence of properties on interstitial impurities.

A totally unambiguous determination of critical temperature of these compounds is quite difficult if not impossible, although excellent work has been done on the compounds of niobium carbide and tantalum carbide.[2] By careful techniques of preparation coupled with the best available chemical analyses and lattice parameter measurements it is possible to characterize the structure and define the properties of this important class of compounds. Such is the case with cubic niobium nitirde. Previous investigators have established the importance of stoichiometry;[3] however, there still remains doubt as to the absolute value of the critical temperature of this compound because of the uncertain effect of the principal impurities (oxygen and carbon) whose content, in many instances, was not reported. Furthermore, it would appear that the preparation techniques employed were not such to span the entire composition range over which NbN_{1-x} exists.

In the present investigation a range of nitriding temperatures and pressures was utilized in an effort to bracket the optimum conditions for superconductivity. The nitrogen content of the compounds so prepared was determined from precision lattice parameter data, using the correspondence established by Brauer and coworkers.[4,5] Carbon and oxygen contents were determined by chemical analyses of both the raw materials and at different processing stages. It is important to emphasize that with available raw materials and known processing techniques it is impossible to eliminate completely the problem of impurities; however, the degree of their influence can be established and the properties of the pure material obtained by extrapolation.

PREPARATION PROCEDURE

Available niobium powder contains varying amounts of carbon and oxygen. In general the combined content of carbon plus oxygen is high, i.e., about 0.3-0.4 wt.% (~2-3 at.%) with oxygen usually predominating. However, the ratio of these elements can vary with source and history. In those few instances where carbon and oxygen contents have been reported,[6,7] it appears that the starting material was high in oxygen. Fine niobium powder exposed to air will typically have a high oxygen content (up to 0.4 wt.%).

Pickus and Wells[8] found that vacuum sintering of high-carbon material resulted in a reduction of both oxygen and carbon levels, presumably by carbon deoxidation. Thus a high carbon processing treatment was selected because if afforded an opportunity for purification in processing.

Niobium powder* of -325 mesh was mixed with a solution of styrene in toluene, and the solvent was evaporated to leave the powder coated with

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* Kawecki Chemical Co., Boyertown, Pa. Nominally 99.9% niobium (with respect to metallics); analyses indicated 0.11 wt.% (0.85 at.%) carbon and 0.43 wt.% (2.5 at.%) oxygen.

styrene binder.[8] In this form the mixture could be treated as a thermoplastic and extruded under very little pressure as 1/8" diameter rods. After being broken into 2" lengths, the rods were placed on a niobium support in a horizontal tube furnace with a flowing purified argon atmosphere. The argon was dried by molecular sieves and deoxygenated by hot Ti-Zr alloy chips. Heating was programmed to allow complete volatilization of the styrene at 400°C before initiating partial sintering of the niobium at 1400°C. Final sintering was accomplished in a graphite tube furnace where the rods, supported by tungsten hooks, were fired at 1900-1950°C for one hour in high vacuum (10^{-6} Torr). The resulting rods (0.34 wt.% carbon and less than 10 ppm oxygen) were sufficiently porous to facilitate rapid nitriding.

Nitriding was conducted in the same graphite tube furnace used for the final sintering. The temperatures selected, 1280, 1360 and 1470°C were chosen on the basis of the results of Brauer and Kirner.[4] They found that temperatures near 1300°C favored the formation of the cubic niobium nitride near stoichiometric composition. In our work the temperature was raised while the sample was under vacuum (10^{-6} Torr). Nitrogen was bled into the furnace after having passed through molecular sieves for water removal and overheated copper turnings for oxygen removal. The pressure was regulated automatically to within 10% at 1 Torr and to better than 1% at 10, 100, and 760 Torr. After a firing period of either 4 or 8 hours, the samples were cooled at constant nitrogen pressure. The cooling process was rapid because a cold wall furnace was employed. Carbon contamination due to the graphite furnace in the sintering and nitriding operations is highly unlikely since the specimens were not in contact with the graphite and even at 1900-1950°C the vapor pressure of the graphite is less than the operating pressure (as determined by an ionization gauge) by more than an order of

magnitude; furthermore, the graphite tube has been previously outgassed at high temperatures while under vacuum.

SPECIMEN COMPOSITIONS

Specimen compositions were determined through chemical analyses and lattice parameter measurements. Chemical analyses for carbon and oxygen were found to be reproducible within ±10%. The final oxygen content after nitriding tended to be higher than that in the sintered niobium (Table I). The total impurity level (mainly due to carbon and oxygen) of the specimens reported here is as low as or lower than the impurity levels which have been reported for niobium nitride in the literature (Table II). Rögener,[3] who did not report oxygen or carbon levels, did consider the effect of oxygen. He found that when two specimens were nitrided the same way, one in pure nitrogen gas and one in nitrogen gas containing 0.1 vol.% oxygen, that the latter had a critical temperature more than one degree lower than the former.

The amount of nitrogen in the specimens was determined from precision lattice parameter measurements in conjunction with the lattice parameter-composition data of Brauer and coworkers (Fig. 1).[4,5] Although lattice parameter corrections for carbon and oxygen contents were not made, the error introduced is generally less than the experimental uncertainty in the lattice parameter.

X-RAY RESULTS

X-ray powder patterns were obtained from a Picker diffractometer with nickel filtered copper radiation. Debye-Scherrer powder patterns were used to determine the lattice parameters of the predominantly cubic specimens. Nickel filtered copper radiation ($\lambda_{CuK\alpha_1}$ = 1.54051Å) was used in a 57.3 mm diam. camera with Straumanis mounting. Tetragonal parameters were deter-

mined from the (131), (113) lines on the diffractometer trace and from the (151), (115) lines on the Debye-Scherrer film.

All samples nitrided at or above 100 Torr were cubic, although there were trace amounts of either the tetragonal niobium nitride[5] or a second cubic phase in four of the samples prepared at 1470°C.

At 10 Torr all samples contained large amounts of the tetragonal phase, and at 1 Torr the crystal structure was predominantly hexagonal, corresponding to Nb_2N. The results of the x-ray investigation are summarized in Table III.

SUPERCONDUCTIVITY RESULTS

Critical temperatures were measured by the method of Merriam and Von Herzen.[10] The technique involved monitoring the voltage across a coil to which was supplied an ac signal at a low audio frequency of 5000 Hz. The sample, placed in the center of the coil, caused an impedance change in the coil when the superconducting transition took place. A calibrated germanium resistance thermometer with an accuracy of ±0.1°K and a precision of better than ±0.05°K was used to detect the temperature.

Critical temperature data including those of Rögener,[3] Horn and Ziegler,[11] and Pessall et al.[12] are shown as a function of lattice parameter (Fig. 2) and as a function of nitrogen content (Fig. 3) for cubic niobium nitride. As the lattice parameter increases T_c increases. Increasing nitrogen content, however, causes T_c to go through a maximum. Figures 3a and 3b result because composition is not a single-valued function of lattice parameter (Fig. 1); since Rögener[3] prepared many of his compounds at nitrogen pressures significantly greater than 760 Torr and Brauer and Kirner[4] have shown that this will result in compositions beyond the stoichiometric limit, Fig. 3b is more likely correct

than Fig. 3a. Nitriding pressure significantly influences the critical temperature. The optimum pressure for producing a high T_c seems to be in the vicinity of 760 Torr (Fig. 4).

Upper critical field was determined inductively at 4.2°K with a pulsed field technique (8 msec rise time).[13] A few samples were checked by resistive measurements to confirm the consistency of the two techniques. The results agreed within 2 or 3 kG (i.e., ~2% of the critical field). The critical field (averaged over the three temperatures and two firing times) is plotted in Fig. 4 as a function of nitriding pressure. The maximum critical field was found for samples nitrided at 760 Torr. This value is considerably higher than has been reported previously for niobium nitride.[14] Tabulated T_c and H_{c_2} data are presented in Table III.

DISCUSSION

Reported values of T_c for cubic niobium nitride range from 11 to 16°K.[3,6,7,11,12,14-18] From the present study on materials of relatively low oxygen content, it is apparent that T_c for cubic niobium nitride extends up to 17.3°K; this value is rather close to the T_c predicted by Geballe et al.[9] for slightly substoichiometric NbN. The maximum T_c occurs below stoichiometry (Fig. 3b) although the exact composition for the maximum is uncertain due to, in part, the uncertainties in the lattice parameters. This is the first case to our knowledge in which critical temperature is strongly composition dependent with the best composition slightly off stoichiometry. The form of the curve is similar to that for niobium carbo-nitrides near stoichiometry. A direct comparision of the NbN_{1-x} data with those of the NbN-NbC system is appropriate. Two points are of interest: $NbN_{0.8}$, where T_c is close to the T_c value for stoichiometric NbC,[19] and $NbN_{0.93}$-$NbN_{0.96}$, where T_c is a maximum. A comparison of

valence-electron-to-niobium-atom ratios* is given in Table IV. Further comparision with other NbN-NbC solid solution compositions leads us to conclude that deviation from stoichiometry for NbN results in virtually the same T_c as does solid solution addition of NbC to NbN, for the same number of valence electrons per niobium atom, and that the peak in T_c occurs at about 9.7 - 9.75 valence electrons per niobium atom. From this comparision it appears that the interstitial ingredient does not matter; what does matter is only the (fcc) niobium d band and the conduction electron density.

In the NbC and TaC systems T_c increases as a_o increases when composition is varied. Similarly, the critical temperature for NbN of variable composition generally increases with increasing lattice parameter. Indeed, T_c vs a_o follows a single curve for compositions above and below stoichiometry (Fig. 2).

The rapid upward trend of H_{c_2} with increasing nitriding pressure in comparision to the slow increase in T_c (Fig. 4) might appear to be surprising,** particularly since the normal state electrical resistivity ought to decrease rapidly as stoichiometry is approached. However, these data are indicative of phase stability as well as stoichiometry variation within a single phase. It is apparent that the cubic niobium nitride is favored for superconductivity. The maximum values of H_{c_2} (117-119 kG) occur for materials with the highest critical temperatures (17.1-17.3°K) and are significantly higher than those reported by Pessall et al.[14] for a

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*Valence-electron-to-atom ratio, based on all atoms, seems to be an inappropriate variable since for all Nb-N compositions this would be constant at 5.0. Valence-electron-to-niobium-atom ratio, on the other hand, varies with stoichiometry and is equivalent to twice the valence-electron-to-atomic site ratio for substoichiometric compositions.

**The superconductivity for specimens prepared at 1 Torr is due to a small amount of tetragonal or cubic phase.

material of apparently lower nitrogen content. Slight interstitial impurity additions would be expected to raise H_{c_2} even further due to increased normal state resistivity. We have found that an addition of about 1 at.% oxygen raises H_{c_2} to 132 kG but lowers T_c to 16°K.

CONCLUSIONS

This investigation extends previous work on the superconductivity of niobium nitride. The correlation of critical temperature with lattice parameter and with nitrogen content for relatively low oxygen materials suggests that the optimum conditions for preparation of a high T_c material were never before reached.

Critical temperature is a function of lattice parameter, increasing to a maximum value of 17.3°K when a_o = 4.390Å. The optimum composition for a high T_c is in the range $NbN_{0.93}$-$NbN_{0.96}$. The variation of T_c with electrons per atom in a number of alloy systems and series of compounds has long been known. Presumably this reflects a rigid band model for the density of states, particularly d band density of states. The optimum nitrogen content corresponds to an electron per niobium atom ratio of 9.65 - 9.8; the maximum T_c in the NbN-NbC psuedo-binary system (at stoichiometry) occurs at a composition having 9.7 electrons per niobium atom. It is also noteworthy that both $NbN_{0.8}$ and $NbC_{1.0}$, which have the same electron to niobium atom ratio, have almost identical critical temperatures. This correlation is further evidence of the relevance of electrons per atom as a descriptive parameter in the superconductivity of these interstitial-niobium compounds.

Values of H_{c_2} in the range 117-119 kG occur for substoichiometric cubic niobium nitride specimens which have the maximum critical temperatures. Samples with low impurity levels (~150 ppm carbon and ~170 ppm

oxygen) were found to have H_{c_2} = 118 kG and T_c = 17.3°K, which presumably then is characteristic of pure niobium nitride near $NbN_{0.95}$. Suitable small additions of oxygen can raise H_{c_2} up to 132 kG, yet lower T_c.

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REFERENCES

1. B. T. Matthias, Phys. Rev., 92, 874 (1953).
2. A. L. Giorgi, E. G. Szklarz, E. K. Storms, A. L. Bowman, and B. T. Matthias, Phys. Rev. 125, 837 (1962).
3. H. Rögener, Z. Physik, 132, 446 (1952).
4. G. Brauer and H. Kirner, Z. Anorg. Allgem. Chem. 328, 34 (1964).
5. G. Brauer and R. Esselborn, Z. Anorg. Allgem. Chem. 309, 151 (1961).
6. G. Aschermann, E. Friederich, E. Justi, and J. Kramer, Phys. Z. 42, 349 (1941).
7. T. H. Courtney, J. Reintjes and J. Wulff, J. Appl. Phys. 36, 660 (1965).
8. M. R. Pickus and M. Wells, Powder Metallurgy 8, 351 (1965).
9. B. T. Matthias, private communication, and T. H. Geballe, B. T. Matthias, J. P. Remeika, A. M. Clogston, V. B. Compton, J. P. Maita and H. J. Williams, Physics 2, 293 (1966).
10. M. F. Merriam and M. Von Herzen, Phys. Rev. 131, 637 (1963).
11. F. H. Horn and W. T. Ziegler, J. Am. Chem. Soc. 69, 2762 (1947).
12. N. Pessall, C. K. Jones and H. A. Johansen, Westinghouse Reasearch Laboratories, Res. Sci. Paper 65-9J00-HTTRA-P2. Presented at the International Symposium on Magnet Technology at Stanford University, September 1965.
13. M. Suenaga and K. M. Ralls, to be published in J. Appl. Phys 37 (October 1966).
14. N. Pessall, C. K. Jones, H. A. Johansen and J. K. Hulm, Appl. Phys. Letters 7, 38 (1965).
15. D. B. Cook, M. W. Zemansky and H. A. Boorse, Phys. Rev. 79, 1021 (1950).
16. G. Lautz and E. Schröder, Z. Naturforsch. 11a, 517 (1956).
17. E. Schröder, Z. Naturforsch. 12a, 247 (1957).

18. G. K. Gaulé, J. T. Breslin, R. L. Ross, J. R. Pastore and J. R. Shappirio, Proc. IXth International Conference on Low Temperature Physics, Columbus, Ohio, (1964) (Prenum Press, New York, 1965) p.612.

19. J. Piper, Nuclear Metallurgy, 10, 29 (1964).

TABLE I. Chemical Analyses of Selected Specimens

Specimen and (Nitriding Conditions)	C(wt.%)*	O(wt.%)**	Analyses Performed by
Sintered Nb; not nitrided	0.34	< 0.001	a
1280°C, 4 hrs. 10 Torr	0.58-0.59	0.086-0.096	a
1280°C, 8 hrs. 100 Torr	0.28-0.30	0.025-0.030	a
1280°C, 4 hrs. 760 Torr	0.015	0.017	a
1360°C, 4 hrs. 760 Torr	0.266	0.031	b
1470°C, 4 hrs. 760 Torr	0.75 ± .01	0.036	a

* C determined by combustion.

** O determined by vacuum fusion.

a. Anamet Laborabories, Inc., Berkeley, Calif.

b. Oak Ridge National Laboratory

TABLE II. Impurity Levels for Niobium Nitride

Reference	C(wt.%)	O(wt.%)	Other (wt.%)
This work	0.3*	0.03*	Metallics < 0.1
6	0.68-1.47	**	**
7	1.1	0.18	Hydrogen 0.18 Metallics < 0.1
9	0.01	0.34	Metallics ~ 0.14

* Averaged over all specimens reported.

** The starting niobium contained 4.27 w/o O and 5 w/o Ta.

TABLE III. X-Ray and Superconductivity Results for Niobium Nitrides

Temperature	Nitrogen Pressure	Time	Crystal Structure	T_c	H_{c_2}
1280°C	1 Torr	4 hrs.	hexagonal + trace 2 cubic	10.7±1°K	
		8 hrs.	hexagonal	11.0±.6°K	
	10 Torr	4 hrs.	tetragonal a=4.38Å c=4.32Å; c/a=0.986 + trace cubic	15.0±1°K 16.2±1°K	25kG
		8 hrs.	tetragonal a=4.38Å c=4.34Å; c/a=0.992 + trace cubic	12.9±.1°K	28 kG
	100 Torr	4 hrs.	cubic a=4.381±.001Å	16.5±.1°K	92 kG
		8 hrs.	cubic a=4.386±.001Å	16.7±.1°K	108 kG
	760 Torr	4 hrs.	cubic a=4.390±.001Å	17.3±.1°K	118 kG
		8 hrs.	cubic a=4.391±.001Å	17.3±.1°K	119 kG
1360°C	1 Torr	4 hrs.	hexagonal + trace cubic	10.9±.2°K	
		8 hrs.	hexagonal	11.2±.1°K	
	10 Torr	4 hrs.	tetragonal a=4.38Å c=4.32Å; c/a = 0.986	11.0±.1°K	30 kG
		8 hrs.	tetragonal a=4.38Å c=4.32Å; c/a = 0.985 + trace cubic	14.8±.4°K	63 kG
	100 Torr	4 hrs.	cubic a=4.387±.002Å	16.7±.1°K	87 kG
		8 hrs.	cubic a=4.383±.001Å	16.7±.1°K	94 kG

TABLE III. (Continued)

Temperature	Nitrogen Pressure	Time	Crystal Structure	T_c	H_{c_2}
	760 Torr	4 hrs.	cubic a=4.388±.0005Å	17.1±.1°K	118 kG
		8 hrs.	cubic a=4.384±.001Å	17.2±.2°K	117 kG
1470°C	1 Torr	4 hrs.	hexagonal	10.0±.1°K	
		8 hrs.	hexagonal	9.9±.1°K	
	10 Torr	4 hrs.	tetragonal a=4.39Å c=4.25Å; c/a = 0.967 + trace cubic	12.3±.3°K	47 kG
		8 hrs.	tetragonal a=4.39Å c=4.24Å; c/a = 0.966 + trace cubic	12.7±.2°K	48 kG
	100 Torr	4 hrs.	cubic a=4.388±.001Å + tetragonal a=4.46Å c=4.33Å	15.4±.2°K	91 kG
		8 hrs.	cubic a=4.391±.002Å + tetragonal a=4.46Å c=4.33Å	16.2±.2°K	93 kG
	760 Torr	4 hrs.	cubic a=4.387±.001Å + cubic	17.0±.1°K	100 kG
		8 hrs.	cubic a=4.388±.002Å + cubic	17.3±.1°K	118 kG

TABLE IV. Comparison of Transition Temperatures of Selected Compositions

	e/Nb atom	T_c(°K)
$NbN_{0.8}$	9	~12
$NbC_{1.0}$	9	12
$NbN_{0.93}$-$NbN_{0.96}$	9.65 - 9.8	17.3 (maximum)
0.7NbN-0.3NbC	9.7	17.8 (maximum)

FIGURE CAPTIONS

Fig. 1 The dependence of lattice parameter (a_o) on nitrogen to niobium atom ratio (N/Nb) according to Brauer and coworkers,[4,5] for cubic niobium nitride.

Fig. 2 The dependence of critical temperature (T_c) on lattice parameter (a_o) for cubic niobium nitride.

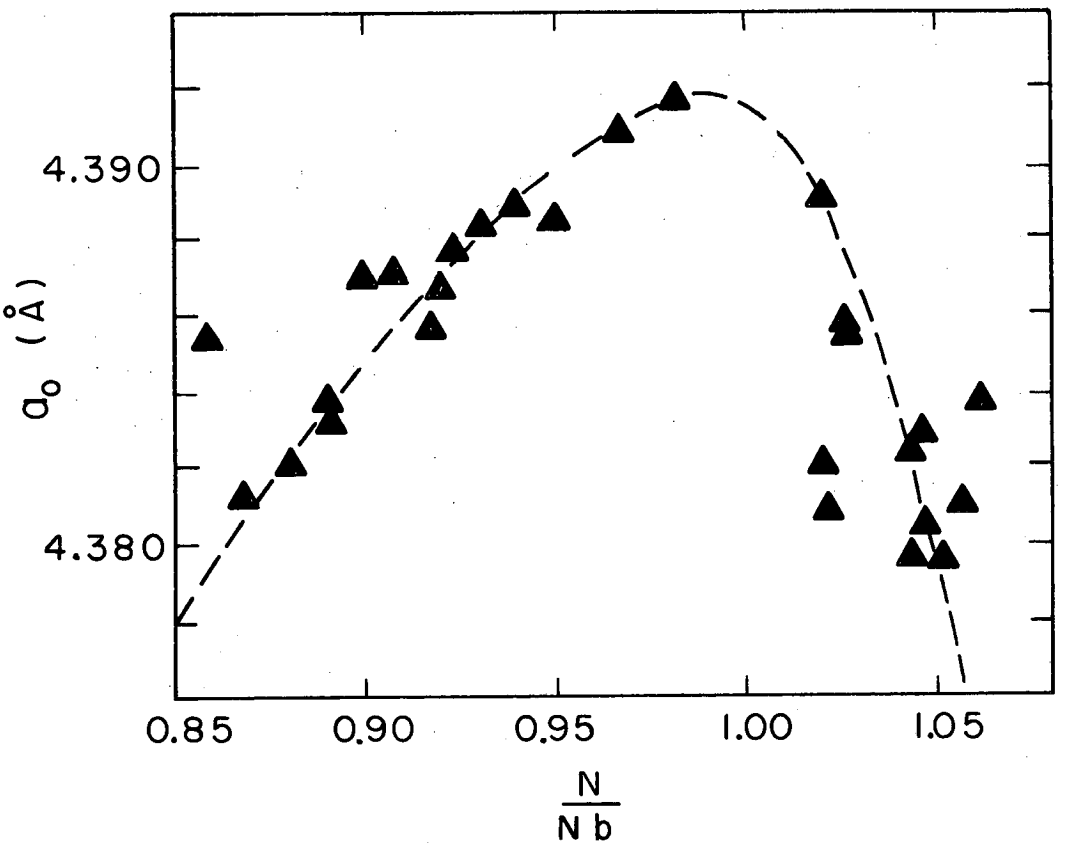
Fig. 3 The dependence of critical temperature (T_c) on nitrogen to niobium atom ratio (N/Nb) for cubic niobium nitride, (a) based on Rögener's compositions being below stoichiometry, (b) based on Rögener's compositions being above stoichiometry.

O present investigation; ● Rögener,[3]

■ Horn and Ziegler,[11] ▲ Pessallet al.,[12]

▼ Gaulé et al.[18]

Fig. 4 The variation of critical temperature (T_c) and upper critical field (H_{c_2}) with nitriding pressure.



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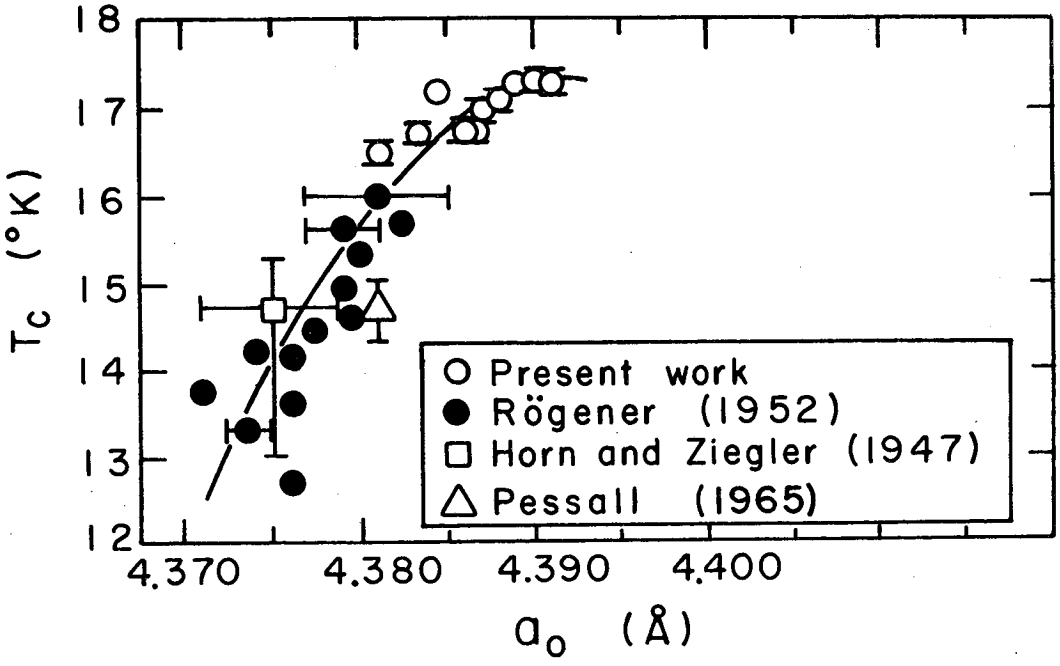
18
17
16
15
14
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12
T_c (°K)
4.370
4.380
4.390
4.400
a_o (Å)
Present work
Rögener (1952)
Horn and Ziegler (1947)
Pessall (1965)

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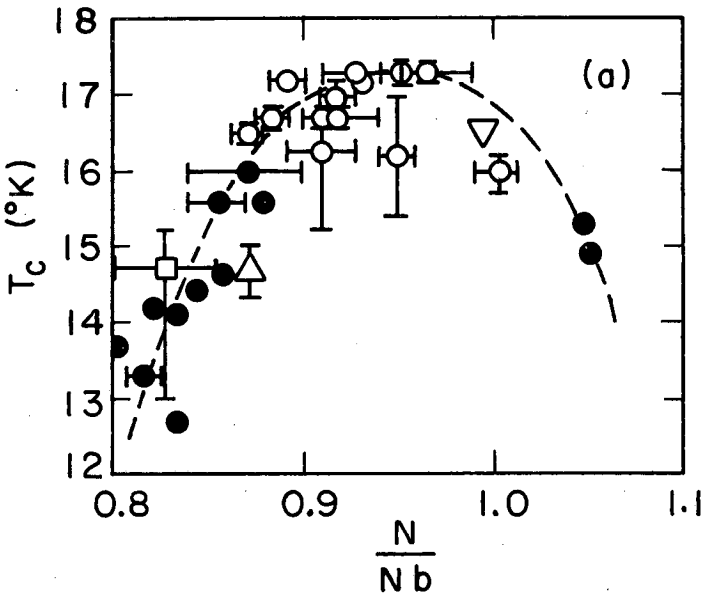
(a)
T_c (°K)
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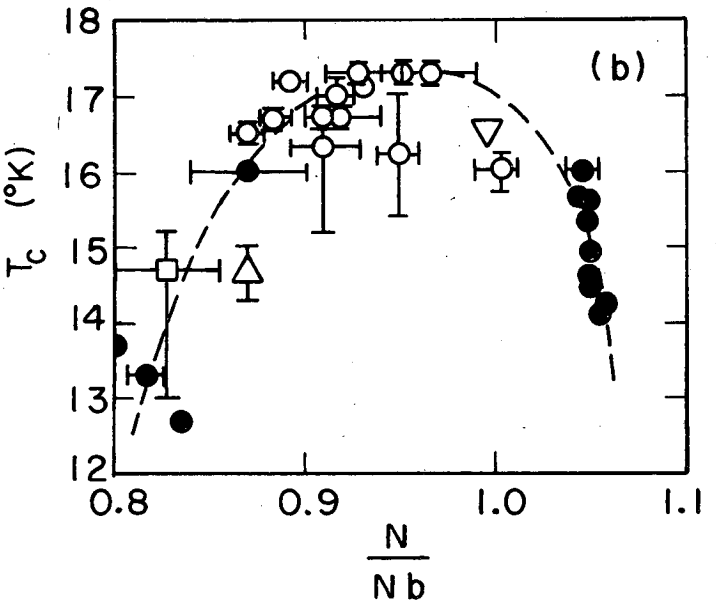
(b)
T_c (°K)
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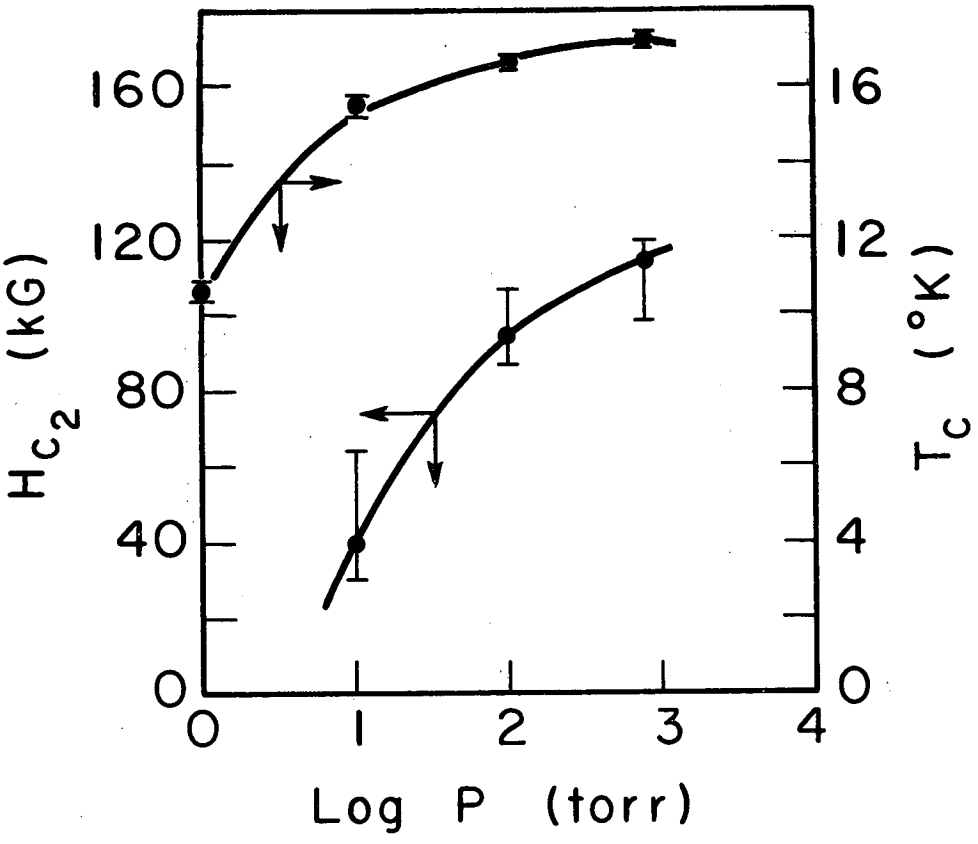

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