Second, one would like to know if the two main lines are connected by Nb-Mo alloys in the region of low $N(0)$. The work of Geballe and Matthias[16] on pure Mo suggests that these alloys may also be superconducting if they can be made free from iron. The presence of a small amount of iron in the Nb-Mo samples represented by the lowest data points may have depressed T_c and obscured a trend connecting the two lines. The vertical dotted line in Fig. 4 at $1/N(0) = 2.9$ represents the probable minimum in $N(0)$ through which a connecting line must go. It is to be noted that in this region, the $N(0)$ for the s band is probably about one-third of the total $N(0)$. Therefore $1/V$, as well as the intercept, might be expected to change due to s-s or s-d interaction. Thus, superconductivity will be discontinuous in this region if these interactions cause V to change sign. A third area for investigation is the region of high $N(0)$

where one finds the compounds. Since the metals on the upper line of Fig. 4 have a value of T_c/θ_D about five times that of the lower line for a given $N(0)$ it seems reasonable to suppose that one can move up along the upper line to very high values of T_c by appropriate compound formation. The idea is to narrow the d band by compound formation and increase $N(0)$ while maintaining the Fermi level in the center of the third peak. The limit in T_c probably has been reached in compound formation involving the second peak because in V_3Ga, $N(0) = 7.1$ and there are only 10 states in the band. This is far from being the case in the compounds involving the third peak.

ACKNOWLEDGMENTS

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X-Ray Scattering Factor of Nitrogen in Fe₄N†

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A comparison of the x-ray intensities of the superlattice reflections of Fe₄N with the normal lattice reflections shows that nitrogen is negatively charged in this compound and is probably in the N^{3-} state.

THE iron nitride, Fe₄N, has been shown by x-ray[1,2] and neutron diffraction[3] to be cubic. The space group is probably $O_h^1 - Pm3m$ with

1 Fe   at   (0,0,0);

3 Fe   at   (0,1/2,1/2), (1/2,0,1/2), (1/2,1/2,0);

1 N   at   (1/2,1/2,1/2).

Guillaud[4] found Fe₄N to be ferromagnetic with a saturation magnetization per gram, $\sigma = 208.5$. From this value the net number of Bohr magnetons is calculated to be 8.86 per unit cell. A magnetic structure in which the three face-centered irons donate electrons to the nitrogen in the center of the cell, making it N^{3-}, has been proposed by Zener[5] to account for the observed magnetism. But more recently Wiener and Berger[6] have

suggested a model in which electrons are either transferred in the opposite direction, making nitrogen N^{3+}, or are used in covalent bonding between the central nitrogen and the nearest iron neighbors. This model has been confirmed by the neutron diffraction work of Frazer[3]. The question of charge distribution in Fe₄N and similar compounds is only partially answered by these experiments, however, and an x-ray investigation of Fe₄N was undertaken in this laboratory in the hope of obtaining further information.

The x-ray powder diffraction pattern of Fe₄N contains several lines of low intensity which are due almost entirely to scattering by nitrogen.[7] Two of these, the (100) and (110), occur at values of $\sin\theta/\lambda$ for which the calculated intensities are markedly dependent on the nitrogen scattering factor used in the calculation, and thus on the electronic charge. For example, the (100) reflection is roughly five times stronger if nitrogen is in the N^{3-} state than if it is in the N^{3+} state. A comparison of these weak reflections with the more intense reflec-

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[3] B. C. Frazer, Phys. Rev. 112, 751 (1958).
[4] C. Guillaud, Compt. Rend. 222, 1170 (1946).
[5] C. Zener, Phys. Rev. 85, 324 (1952).
[6] G. W. Wiener and J. A. Berger, J. Metals 7, 360 (1955).

[7] The contribution by iron in different oxidation states in nonequivalent sites is less than 1% of the intensity.

tions of the diffraction pattern, therefore, should give information about the distribution of charge between iron and nitrogen.

Powder diffraction intensity data were obtained on a Norelco spectrometer, using Fe $K\alpha$ radiation. The Fe₄N sample[8] was ground to pass through a 325 mesh seive. Samples were mounted in the powder holder by a method described by McCreery[9] and examined under the microscope before being used. Integrated intensities of reflections were measured on a relative scale by recording the total counts as the counter passed through the Bragg angle regions at the rate of $\frac{1}{8}°$ per min. Background was determined 2°–3° from each maximum and subtracted.

A test for extinction was made using a method suggested by Vand.[10] None was observed.

After some preliminary observations on the reproducibility of strong reflection intensities, three samples were mounted on the spectrometer and complete sets of data taken. In addition to the (100) and (110) reflections the (210) and (211) were also observed but were too weak for intensity measurement. The intensities of the strong reflections were reproducible to ±4%, the weaker (100) and (110) reflections to ±12%.

The observed and calculated intensities are given in

TABLE I. Comparison of observed and calculated intensities.

hkl	I_{obs}	N³⁺	N⁰	N³⁻	$I_{obs}/e^{-1.9\ sin^2\theta/\lambda^2}$
			I_{calc}		
100	8.8	2.13	4.9	10.5	9.1
110	4.6		3.0	4.6	4.9
111	331			331	340
200	180			190	190
220	105			123	127
311	133			181	178
222	49			71	67

[8] The sample of Fe₄N was kindly sent to us by Dr. W. J. Takei, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania.
[9] G. L. McCreery, J. Am. Ceram. Soc. 32, 141 (1949); H. P. Klug and L. E. Alexander, X-Ray Diffraction Procedures (John Wiley & Sons, Inc., New York, 1955), p. 300.
[10] V. Vand, J. Appl. Phys. 26, 1191 (1955).
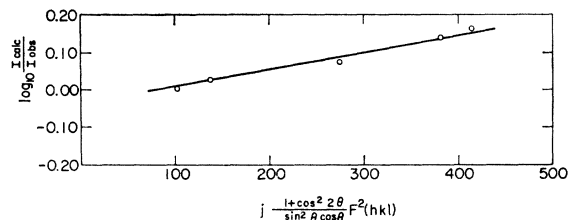
FIG. 1. Logarithm of the ratio of calculated to observed intensities plotted as a function of $sin^2\theta/\lambda^2$.

Table I. For the (100) and (110) reflections calculated intensities are shown for different ionization states of nitrogen. The scattering factor for the N³⁻ ion was obtained by extrapolation of published form factors combined with the results of some unpublished work on TiN done in this laboratory. The scattering factor used for iron is that of Watson and Freeman.[11]

Intensities were calculated using the formula[12]

$$I \propto j \frac{1+\cos^2 2\theta}{\sin^2\theta\ \cos\theta} F^2(hkl).$$

For the strong reflections a plot of $\log_{10}(I_{calc}/I_{obs})$ against $sin^2\theta/\lambda^2$ is a straight line, as shown in Fig. 1. From the slope one obtains the temperature factor, $B=1.9$. This is appreciably larger than the value 1.13 found by Frazer.[3]

A comparison of the observed intensities, corrected for temperature, and those calculated for nitrogen in the N³⁻ state show good agreement. The calculated intensities of the (100) and (110) reflections for the N⁰ and N³⁺ states of nitrogen, however, are much too weak. The results of this experiment together with the magnetic measurements suggest that covalent bonds are formed between the nitrogen atom and its nearest iron neighbors, and that the electrons donated by the iron to these bonds are close enough to the nitrogen to contribute appreciably to its scattering factor at small angles.

[11] R. E. Watson and A. J. Freeman, Acta Cryst. 14, 27 (1961).
[12] See reference 9, p. 157.