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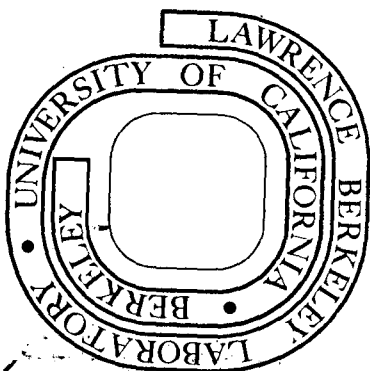
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Electronic Band Structures and Charge Densities of NbC and NbN\*

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Abstract

We present non-local pseudopotential calculations of the electronic band structures and charge densities of NbC and NbN. The major contribution to the charge density of the bands near the Fermi energy  $\lambda$  comes from C or N 2p-states. The charge density for the first partially filled Nb 4d-band and the shape of the Fermi surface for this band are also discussed.

I. Introduction

Transition metal compounds have been the object of much research for some time because of their unusual physical properties. Some of these compounds are high temperature superconductors with superconducting transition temperatures that vary appreciably with composition.<sup>1</sup> Despite the great practical and theoretical interest in these compounds, the electronic structure of many transition metal compounds have not been studied in detail as yet.

In this paper we apply the empirical pseudopotential method (EPM) to the study of two transition metal compounds: NbC and NbN. The band structure and density of states of NbN have been recently calculated by the APW<sup>3,4</sup> and the EPM<sup>5</sup> methods. The band structure and density of states of NbN presented in this paper are the same as those of Ref. 5. For NbC only the density of states has been presented previously (calculated using the APW method<sup>6</sup>).

Usual EPM calculations are based on experimental data such as optical reflectivity spectra, which provide information on critical point energy gaps, and on photoemission data which give information on the density of states. Such experimental information is lacking for NbN and some other transition metal compounds. The EPM band structure calculation<sup>5</sup> for NbN was therefore fitted to a self-consistent<sup>4</sup> APW calculation and the results indicated that the non-local EPM method could be used to obtain accurate band structures for transition metal compounds of interest. Our calculations on NbC are an extension of the EPM calculation<sup>5</sup> on NbN. We find the band structures of NbC and NbN to be very similar. The important difference between the two compounds appears to be the position of the Fermi energy which determines the occupancy and electronic charge distribution in the partially filled Nb 4d-bands. The band structures, charge density distributions and Fermi surfaces of NbC and NbN are discussed in the Section II in more detail.

The pseudopotentials used in the NbC calculation were obtained from previous EPM calculations on NbN<sup>5</sup> and C.<sup>7</sup> The non-local d-pseudopotential of the NbN calculation<sup>5</sup> was used in NbC to treat the Nb 4d-states. The non-local p-pseudopotential needed for the C 2p-states was obtained from a previous EPM calculation on C<sup>7</sup> and adjusted for the lattice constant change. All the relevant pseudopotential parameters for NbC are listed in Table I and their significance is discussed in Ref. 5 which also includes the NbN pseudopotentials.

The energy band structure of NbC was calculated on a grid of 46 points in 1/48 of the irreducible part of the Brillouin zone. To obtain sufficient convergence for the charge density calculation the wavefunctions for NbC and NbN were expanded in a basis set of about 150 plane waves. The band structure, charge density and Fermi surface results are discussed in the next Section.

## II. Results

The band structures and densities of state of NbC and NbN are shown in Figs. 1-4. In discussing the band structures and charge densities of these compounds we will number the bands according to their energies. This can cause a band (such as band 3 in NbC and NbN) to be mostly p-like in some part of the Brillouin zone and d-like in another part of the zone, as can be seen by following band 3 from  $\Gamma$  to X.

The lowest valence band in NbC arising from C 2s-states is not shown in Fig. 1. This band is separated by a large energy difference

from the higher bands and does not mix with them. This is consistent with other APW<sup>3,4</sup> calculations on NbN; however the precise energy of this band relative to the higher bands does not seem to be well established. High energy photoemission experiments would be very useful in determining the position of this band. The next three higher bands with  $\Gamma_{15}$  symmetry at  $\vec{k} = 0$  arise mainly from C or N 2p-states together with some Nb 5p-states. In addition, there is a small overlap and mixing between these bands and Nb 4d-states as can be seen in going from  $\Gamma$  to X in the Brillouin zone. This type of overlap is also present in the self-consistent APW calculation of Schwarz<sup>4</sup> for NbN but is absent in the APW calculation of Mattheiss.<sup>3</sup> Some measurements of NbC valence band X-ray emission spectra<sup>8,9</sup> indicate that the Nb 4d-states overlap with the C 2p-states more than our calculation<sup>10</sup> indicates. To obtain better agreement with these experimental results the C 2p-states would have to be moved closer to the Fermi energy.

The band structures and band orderings for NbC and NbN shown in Figs. 1-2 are seen to be very similar in the region below the Fermi energy  $E_F$ . The partially filled bands at  $E_F$  come from a mixture of Nb 4d-states and C or N 2p-states. The Nb 5s state is high in energy and lies above the Fermi energy in both NbC and NbN. The electronic charge in this state has been transferred to the Nb 4d-levels while some Nb 4d-electrons have dropped into the C 2p-states. The position of the Nb 5s level relative to the 5d-levels is seen to be lower in NbC than in NbN (Figs. 1-2). This tends to make the dispersion of the bands above  $E_F$  somewhat different in NbC and NbN because of interactions between the bands. Other calculations on NbN<sup>3,4</sup> and TiC<sup>11,12</sup> also reveal the transition metal s-states to be above the Fermi energy.

The densities of states,  $N(E)$ , of NbC and NbN (Figs. 3-4) are also seen to be very similar. The Fermi energy,  $E_F$ , measured relative

to the energy of  $\Gamma_{25'}$  state, is higher in NbN than in NbC because of the extra electron in NbN. In both crystals  $E_F$  lies in a dip of  $N(E)$  and NbN has a larger density of states at  $E_F$  than NbC. This could, perhaps, be related to the higher superconducting transition temperature found in NbN. The large peak on the low energy side of  $N(E)$  comes mainly from C or N 2p-states. The lowest lying C or N 2s-states are not shown in Figs. 3-4.

The charge densities for several bands in NbC and NbN are shown for the (100) and (110) planes in Figs. 5-13. The charge densities for the lowest bands are strongly concentrated on the non-metal ions and are not shown in these Figures. The charge densities for the p-like bands (i.e. bands 2, 3, and 4) are very similar in NbC and NbN. The charge densities of the three bands are also very similar to one another. In Figs. 5 we show the charge density in the (100) plane for one of these bands in NbC. The charge density is p-like around C; it rises to a maximum as we go away from C and then gradually decreases. This is similar to the behavior of the p-like charge densities in semiconductors<sup>13, 14</sup> although the shape of the contours depends on crystal symmetry. The d-states of Nb contribute to the small charge density around Nb. The outermost closed contour around C contains approximately 60% of the total charge in band 3 while the corresponding contour around Nb contains only about 15% of the total charge. The remaining 25% of the charge is spread out almost uniformly in the rest of the unit cell.



The higher bands in NbC and NbN are each only partially filled. The first partially filled band (i. e. band 5 with symmetry  $\Gamma_{25'}$  at  $\vec{k} = 0$ ) contains nearly all the remaining electron in NbC and over 80% of the two remaining electrons in NbN. The charge density of this band in the (100) and (110) planes are shown in Figs. 6-9. The interesting feature of these figures are the local maxima in the charge density occurring along the Nb-Nb direction. The magnitude of the charge in the maxima is strongly dependent on the number of electrons per unit cell and is twice as large in NbN (with 10 electrons) than in NbC (with 9 electrons). These maxima arise from the Nb 4d-states and have  $d_{xy}$  symmetry about the Nb atoms. The charge density of band 5 is not purely d-like. There is a large mixture of C 2p-states in the wavefunction which gives the p-like charge distribution around C.

The sum of the charge densities of all occupied states in NbC and NbN are shown in Figs. 10-13. The strong concentration of charge on C or N evident in these Figures arises from the first s-like valence bands in NbC and NbN. The C or N 2s-bands could be too low in energy in our calculation and this would tend to make the charge localization on C or N stronger than it should be. Since the Nb 5s-state lies above the Fermi energy there is no charge localization on Nb; the charge contours around Nb coming from the Nb 4d and 5p states have much lower values than the combination of s, p-contours around C or N. Figures 10-13 show the charge distribution of NbC and NbN to be strongly ionic in character. A spread

out metallic-like charge distribution outside the closed contours around the ions can also be seen in these Figures. This seems to indicate that bonding in NbC and NbN results mainly from a combination of ionic and metallic charge distributions. The C-C, N-N and Nb-Nb metal and non-metal nearest neighbor distances are too large for the formation of localized covalent bonds as in the case of the diamond or zincblende crystals where the bonding is characterized by a peak in the magnitude of the charge density on the line joining the nearest neighbor atoms. The overlap between the bonding orbitals on the ions in NbC and NbN are small and do not produce a maximum in the charge density. The overlap results, instead, in a region, centered halfway between like atom nearest neighbors, with a slowly varying charge distribution which appears metallic-like. The bonding configuration for NbC and NbN (and probably in other transition metal compounds as well) can be described as having ionic, covalent and metallic components.

A very interesting property of NbC, NbN and some other transition-metal carbides is the occurrence of anomalies in the phonon dispersion curves of those compounds and the association of these with a high superconducting<sup>15, 16</sup> transition temperature,  $T_c$ . These phonon anomalies have been interpreted by Weber, Bilz and Schröder<sup>17</sup> as resulting from resonances in the  $\vec{q}$ -dependent polarizability of the metal ions. They attribute the coupling between the metal ions as arising from a charge density with  $d_{xy}$  symmetry. This is consistent with the charge

density of band 5 in NbC and NbN (Figs. 6-9) which we have obtained. Because of the extra electron in NbN compared to NbC the magnitude of the charge in the  $d_{xy}$  peak is larger in NbN than in NbC. The coupling between the Nb atoms is therefore expected to be larger in NbN than in NbC. If the number of valence electrons is reduced from 9 to 8 (as in going from NbC to NbC<sub>0.75</sub>) the magnitude of the charge in the  $d_{xy}$  peak becomes nearly zero. It is interesting to note that no phonon anomalies are observed in <sup>15</sup>NbC<sub>0.75</sub>. If the phonon anomalies and high values of  $T_c$  are related to resonances in  $\vec{q}$ -dependent polarizability of the metal ions than it appears that it is band 5 which is most important in determining the superconducting properties of NbC, NbN and other transition-metal carbides.

A cross-section of the Fermi surface of NbC for band 5 is shown in Fig. 14. The Fermi surface of NbN for various bands at the Fermi energy is given in Ref. 5. An interesting feature of the NbC Fermi surface is the magnitude of wavevectors separating the occupied and empty states. The wavevectors AD and BC (Fig. 14) with  $\vec{q} \cong \frac{2\pi}{a} (\frac{2}{3}, 0, 0)$  and the wavevector GH with  $\vec{q} \cong \frac{2\pi}{a} (0.5, 0.5, 0)$  are in good agreement with the  $\vec{q}$  values at which the anomalies in the phonon dispersion curves have been observed.<sup>15</sup> The shape of the Fermi surface in NbC (and NbN) can lead to resonances in the wavevector dependent dielectric function  $\epsilon(\vec{q})$  for wavevectors in the vicinity of which the phonon anomalies occur. Experimentally it is observed that the phonon anomalies disappear without any shift in their

position when the number of valence electrons is diminished.<sup>15</sup> The shape of the Fermi surface and the wavevectors at which resonance behavior may occur can change with the number of valence electrons. Therefore, there may not be a direct relation between the phonon anomalies and the shape of the Fermi surface.

### III. Acknowledgement

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Table Caption

Table I. Pseudopotential parameters for NbC. Non-local d and p-pseudopotentials were used in addition to the local pseudopotentials in calculating the band structure of NbC.

Table I

Local Pseudopotentials	Parameters for non-local d-pseudopotential (See Ref. 5)	Parameters for non-local p-pseudopotential (See Ref. 7)
$V^A(G^2 = 3) = 0.444$	$V_{NL} = \begin{cases} A_2 & r \leq R_s \\ 0 & r > R_s \end{cases}$	$V_{NL} = \begin{cases} A r e^{-\alpha r} & r \leq R_s \\ 0 & r > R_s \end{cases}$
$V^A(11) = 0.06$	$R_s = 1.18 \text{ \AA}$	$R_s = 0.20 \text{ \AA}$
$V^S(4) = -0.14$	$A_2 = -4.65 \text{ Ry}$	$A = -0.19 \text{ Ry}$
$V^S(8) = -0.11$	$\alpha = 0.118$	$\alpha = 1.10 \text{ \AA}^{-1}$
$V^S(12) = -0.066$	$\kappa = 1.74$	
$a = 4.47 \text{ \AA}$		



Figure Captions

- Fig. 1. Electronic energy band structure of NbC along principal symmetry directions. The lowest C 2s-band is not shown. The zero of energy is at the  $\Gamma_{25'}$  level.
- Fig. 2. Electronic energy band structure of NbN. This band structure was obtained from Ref. 5. The zero of energy is at the  $\Gamma_{15}$  level.
- Fig. 3. Density of states of NbC. The density of states of the lowest band is not shown.
- Fig. 4. Density of states of NbN. The density of states of the lowest band is not shown.
- Fig. 5. Electronic charge density of band 3 in the (100) plane of NbC. The charge density arises mainly from C 2p-states with the Nb 4d-state making a small contribution. Charge density is normalized to  $2e/\Omega$  where  $\Omega$  = primitive cell volume.
- Fig. 6. Charge density of the first partially filled band in NbC for the (100) plane.
- Fig. 7. Charge density of the first partially filled band in NbC for a (110) plane. The "empty" region in the middle with no contours has a nearly uniform charge density of about  $0.7 (e/\Omega)$ .
- Fig. 8. Charge density of the first partially filled band in NbN for a (100) plane.
- Fig. 9. Charge density of the first partially filled band in NbN for a (110) plane.

Fig. 10. Total charge density of occupied states in NbC for a (100) plane.

Fig. 11. Total charge density in NbC plotted for a (110) plane.

Fig. 12. Total charge density of NbN for a (100) plane.

Fig. 13. Total charge density of NbN for a (110) plane.

Fig. 14. A cross section of the Fermi surface for the first partially filled band in NbC.

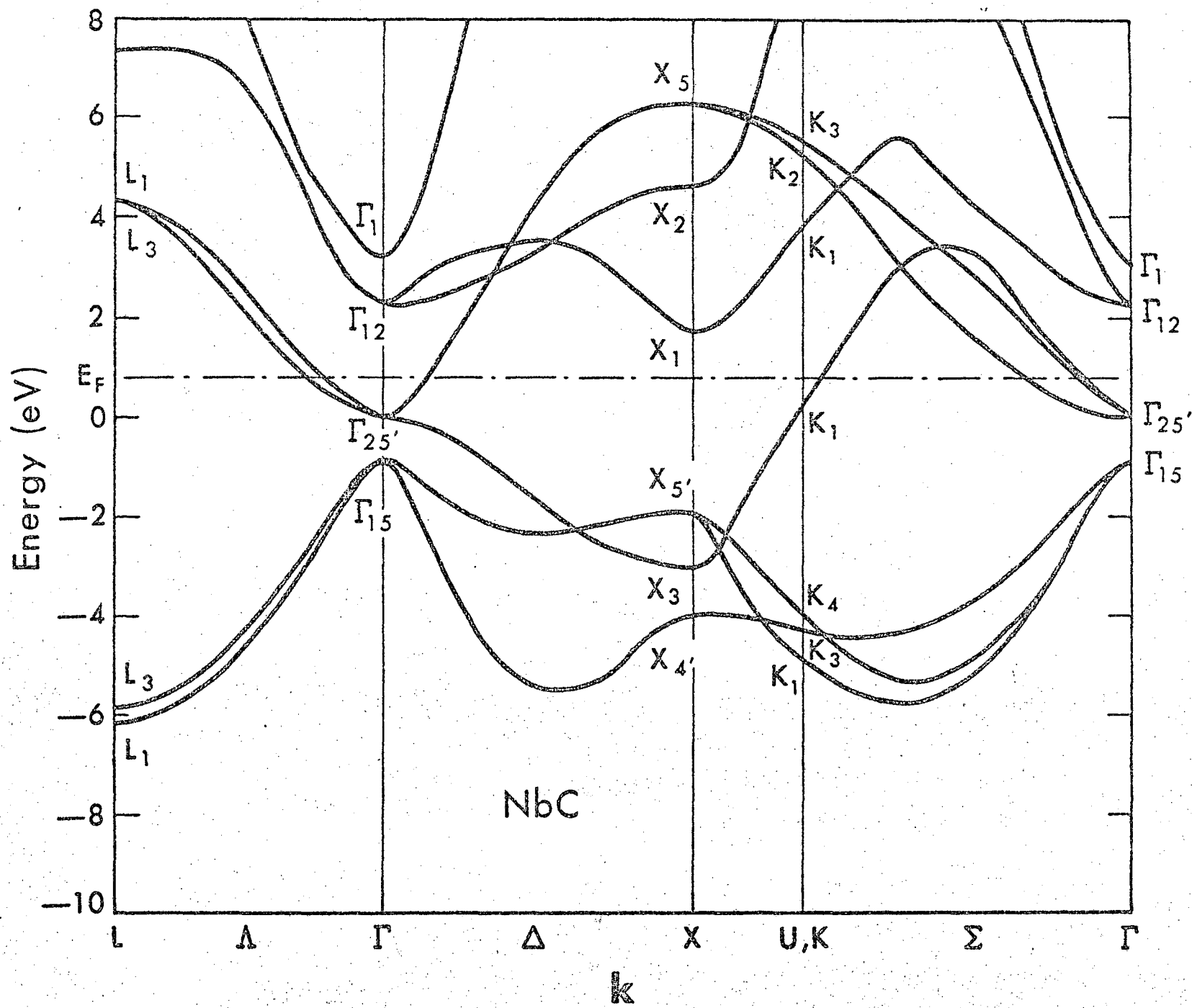


Figure 1

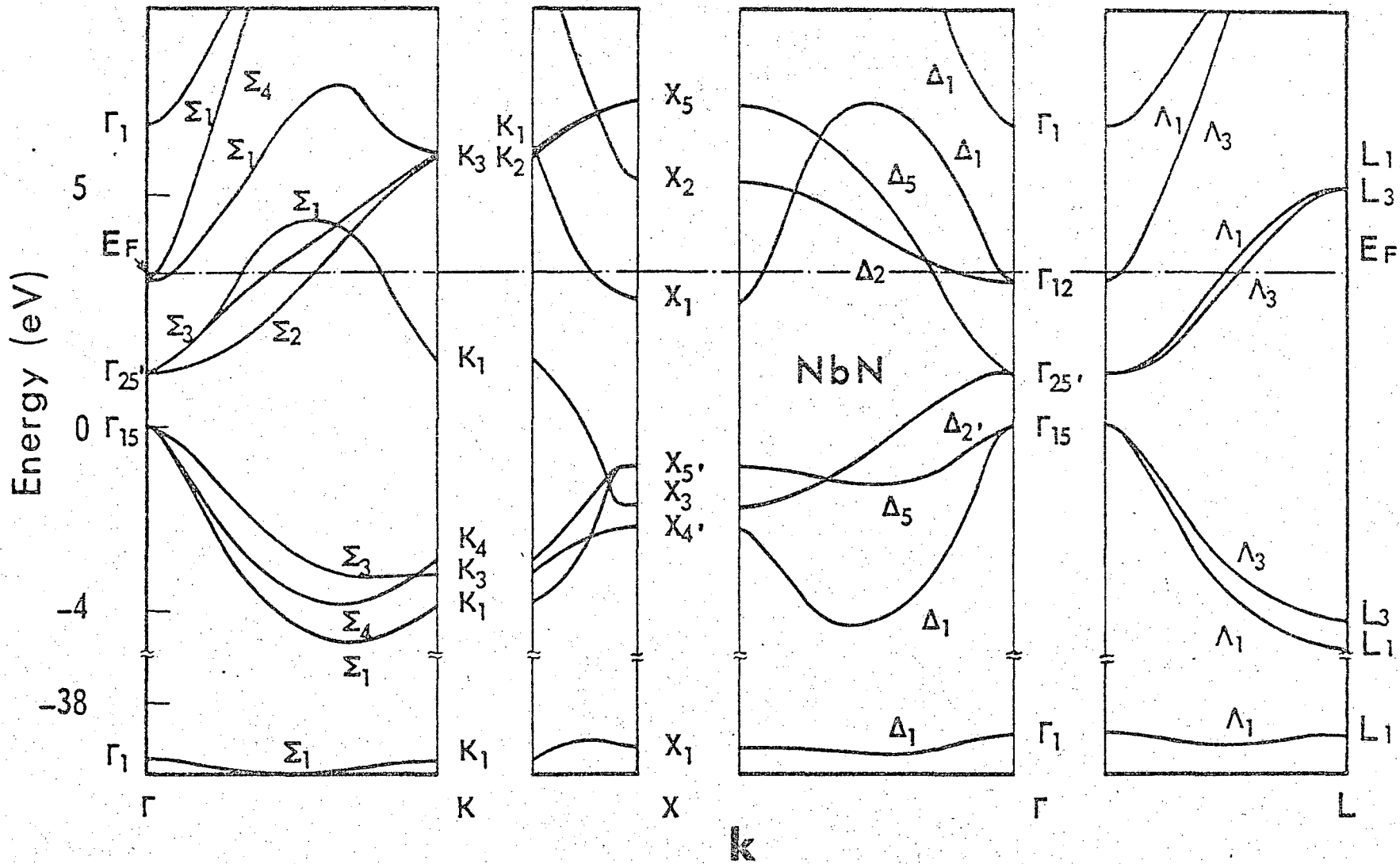


Figure 2

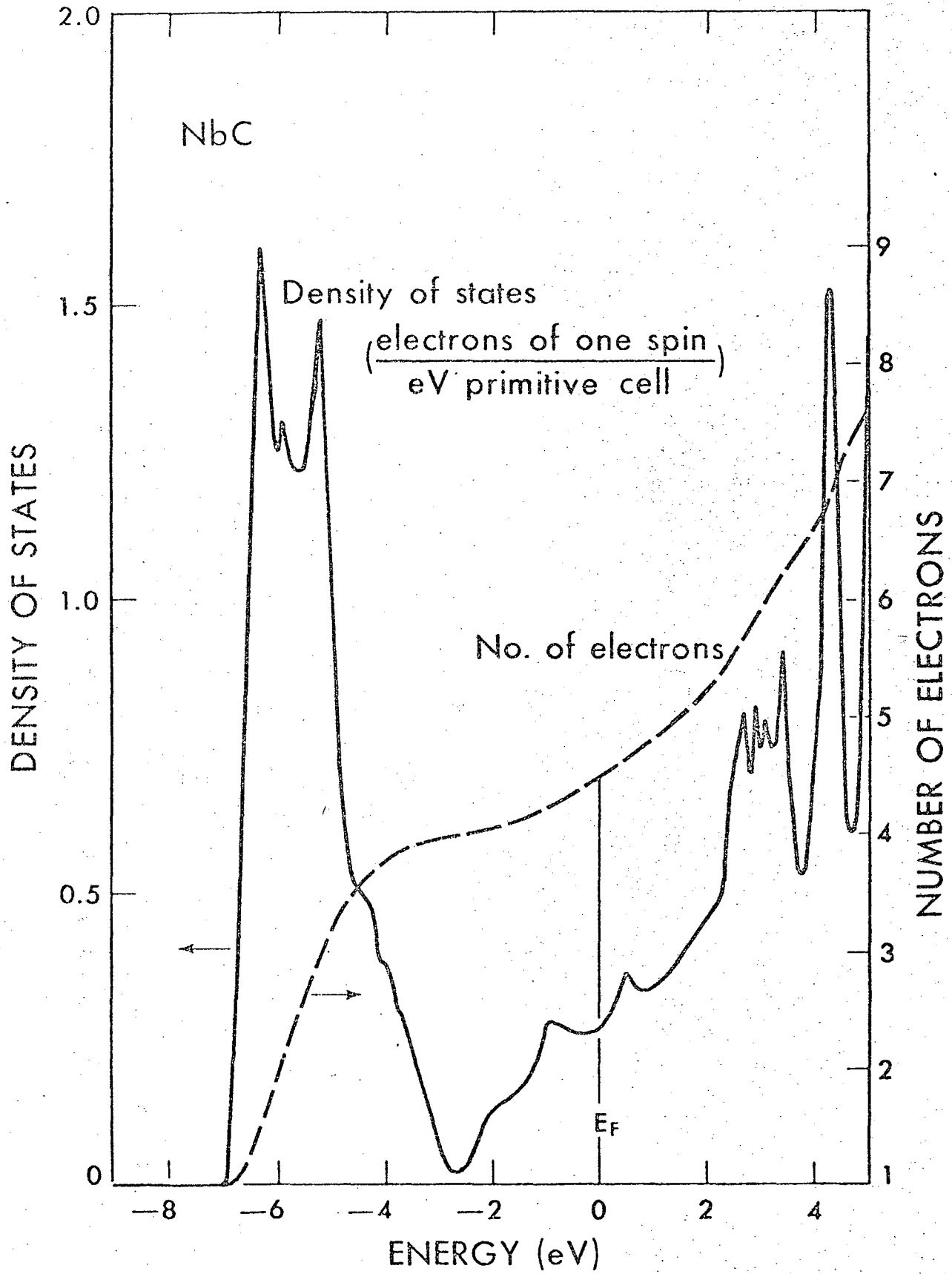


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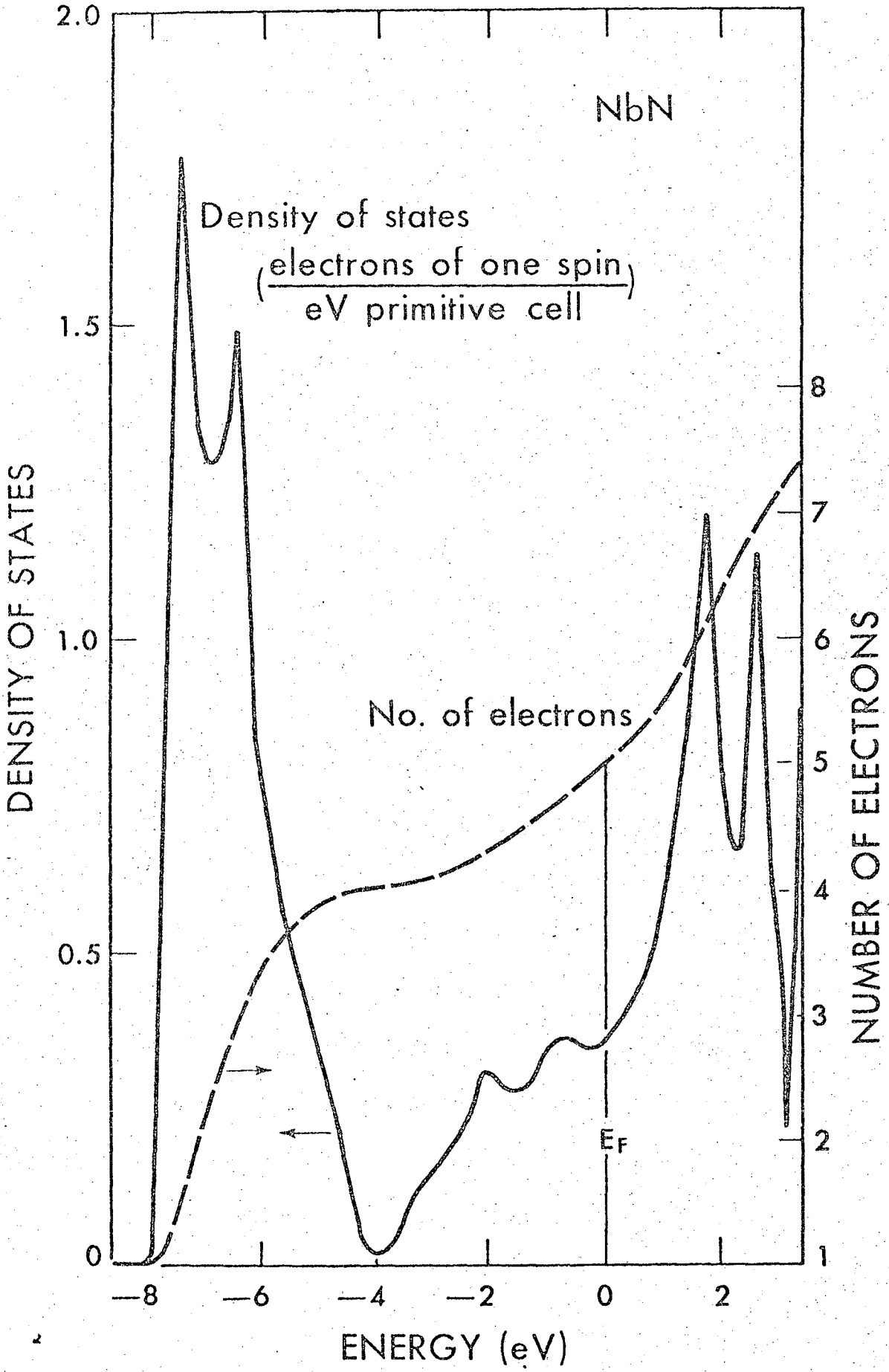


Figure 4

NbC  
Band 3

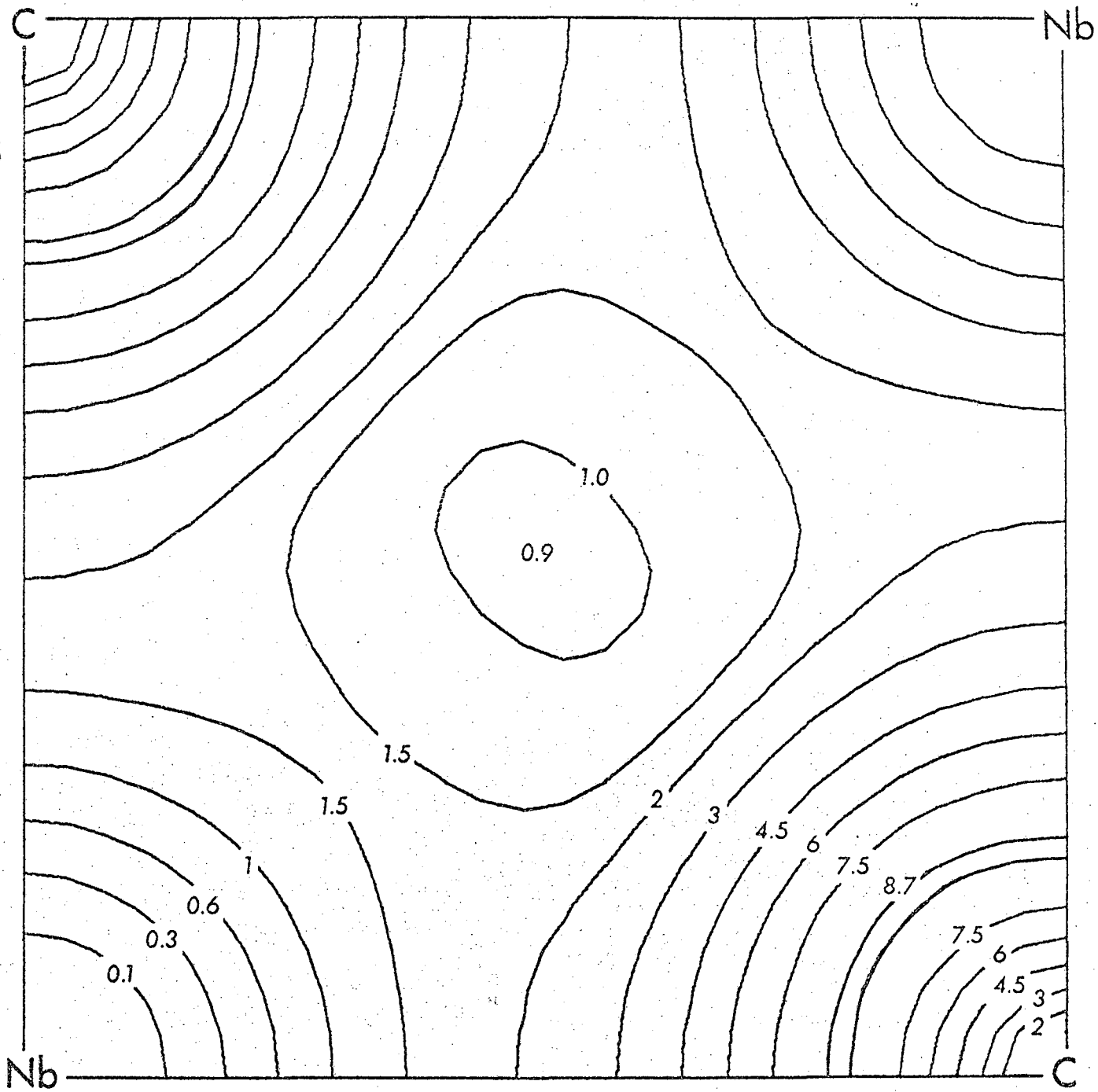


Figure 5

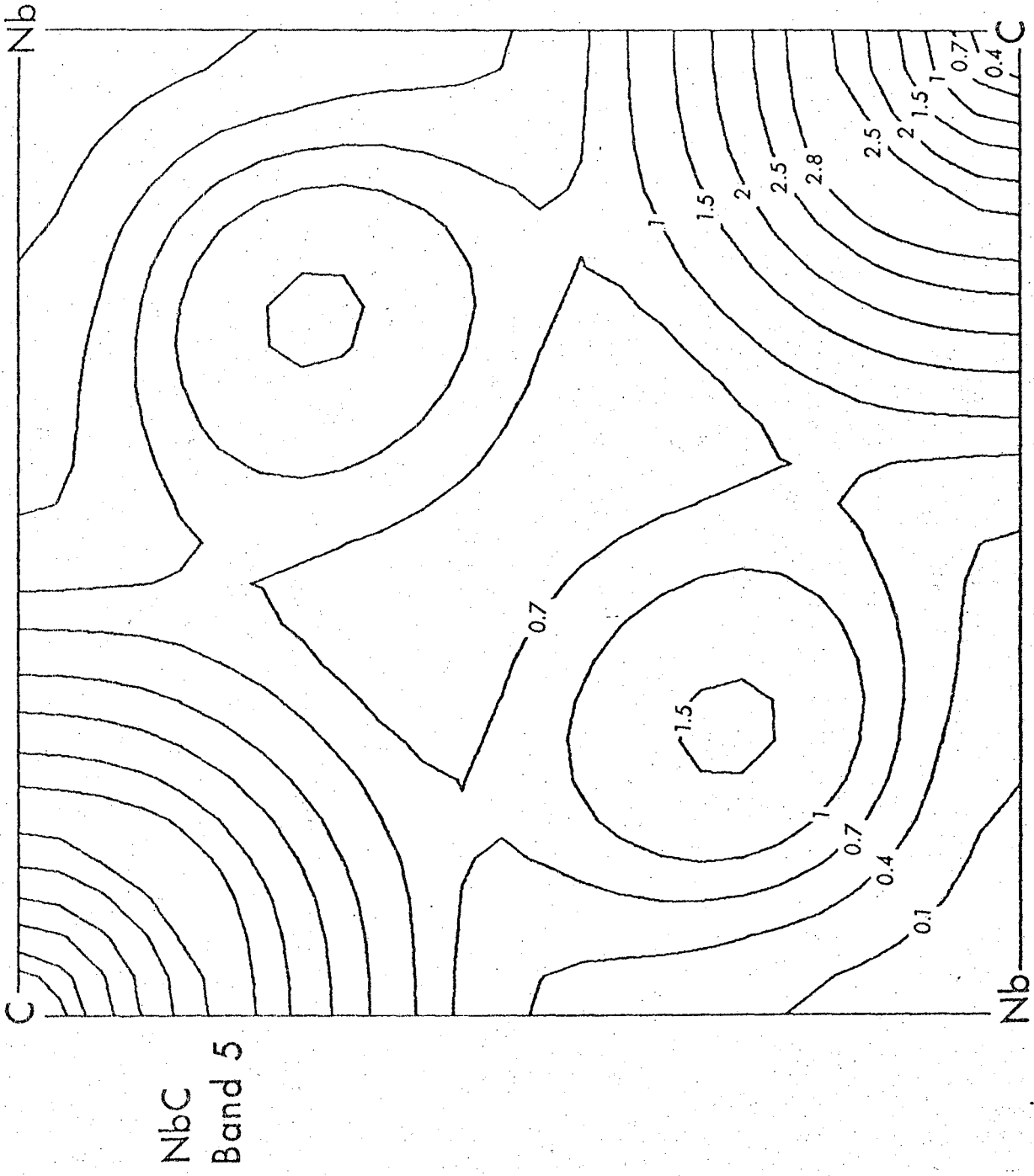


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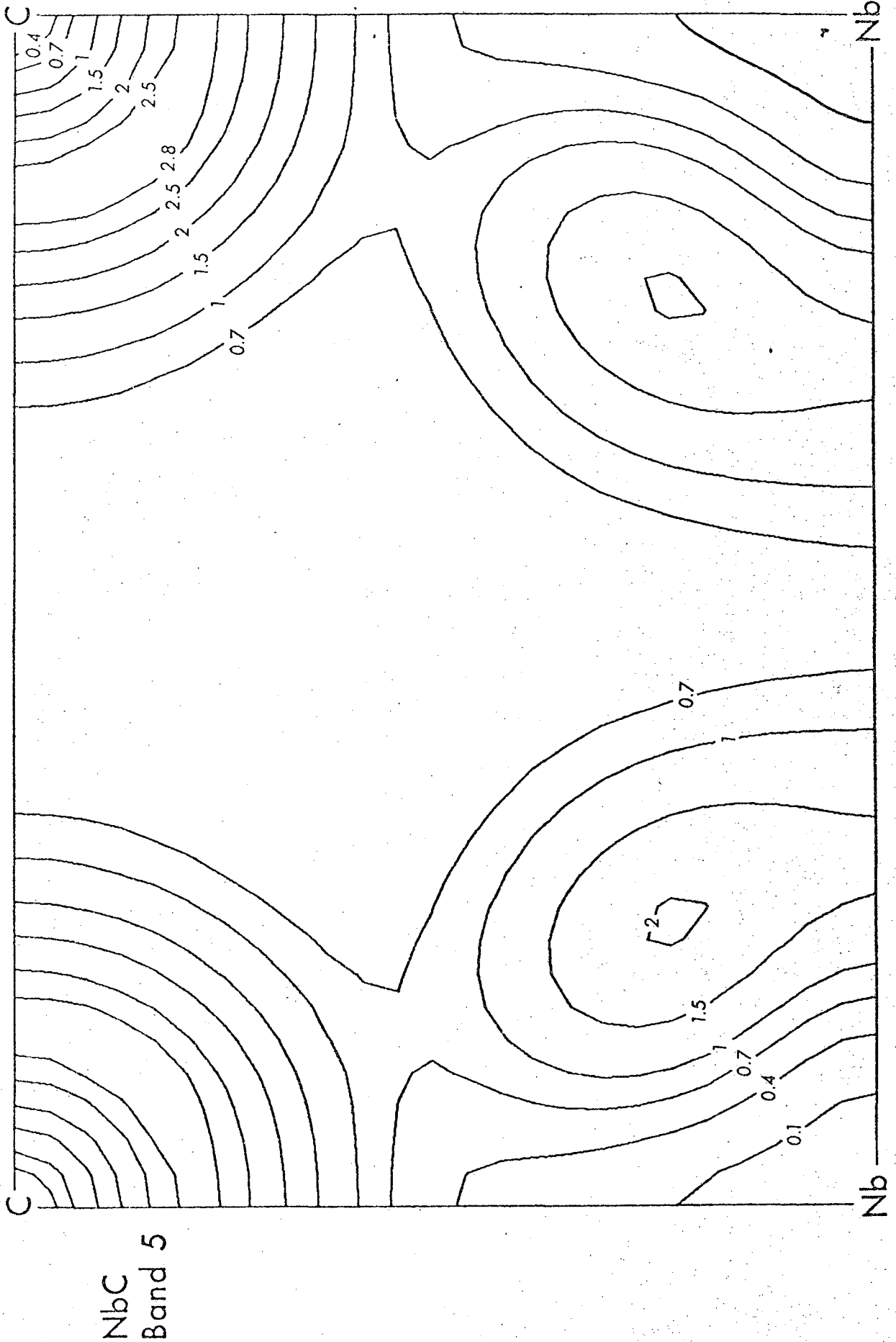


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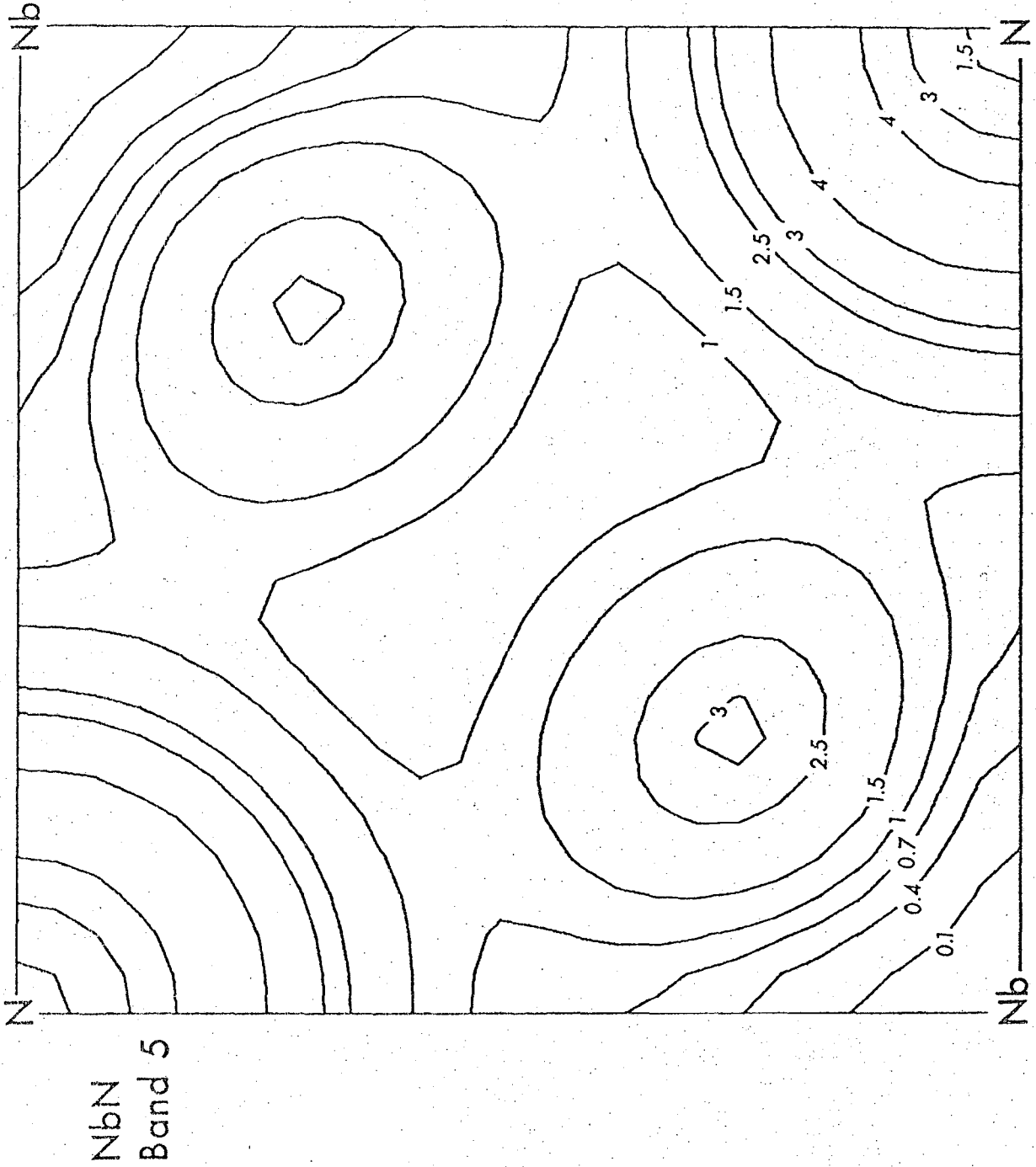


Figure 8

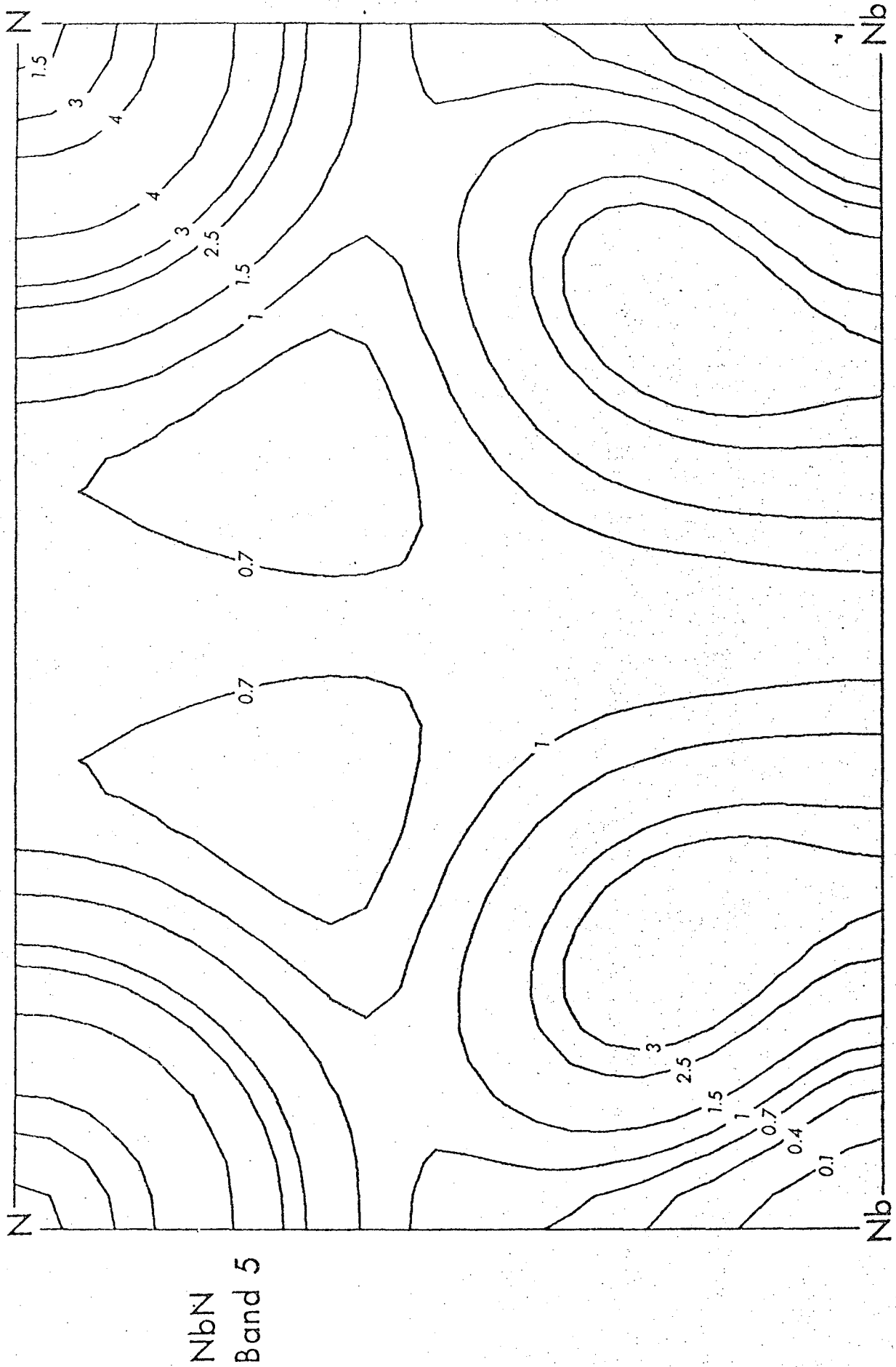


Figure 9

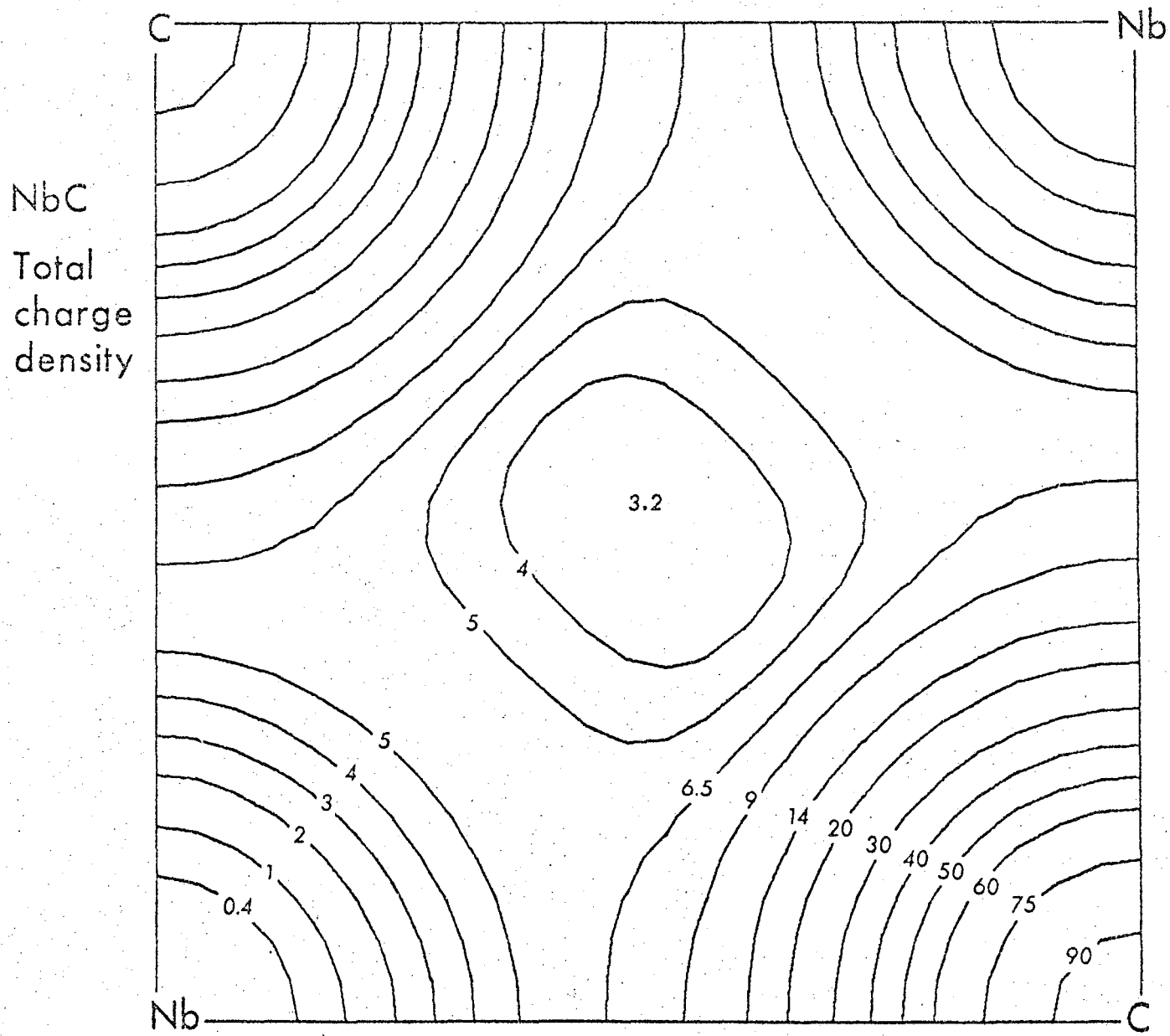


Figure 10

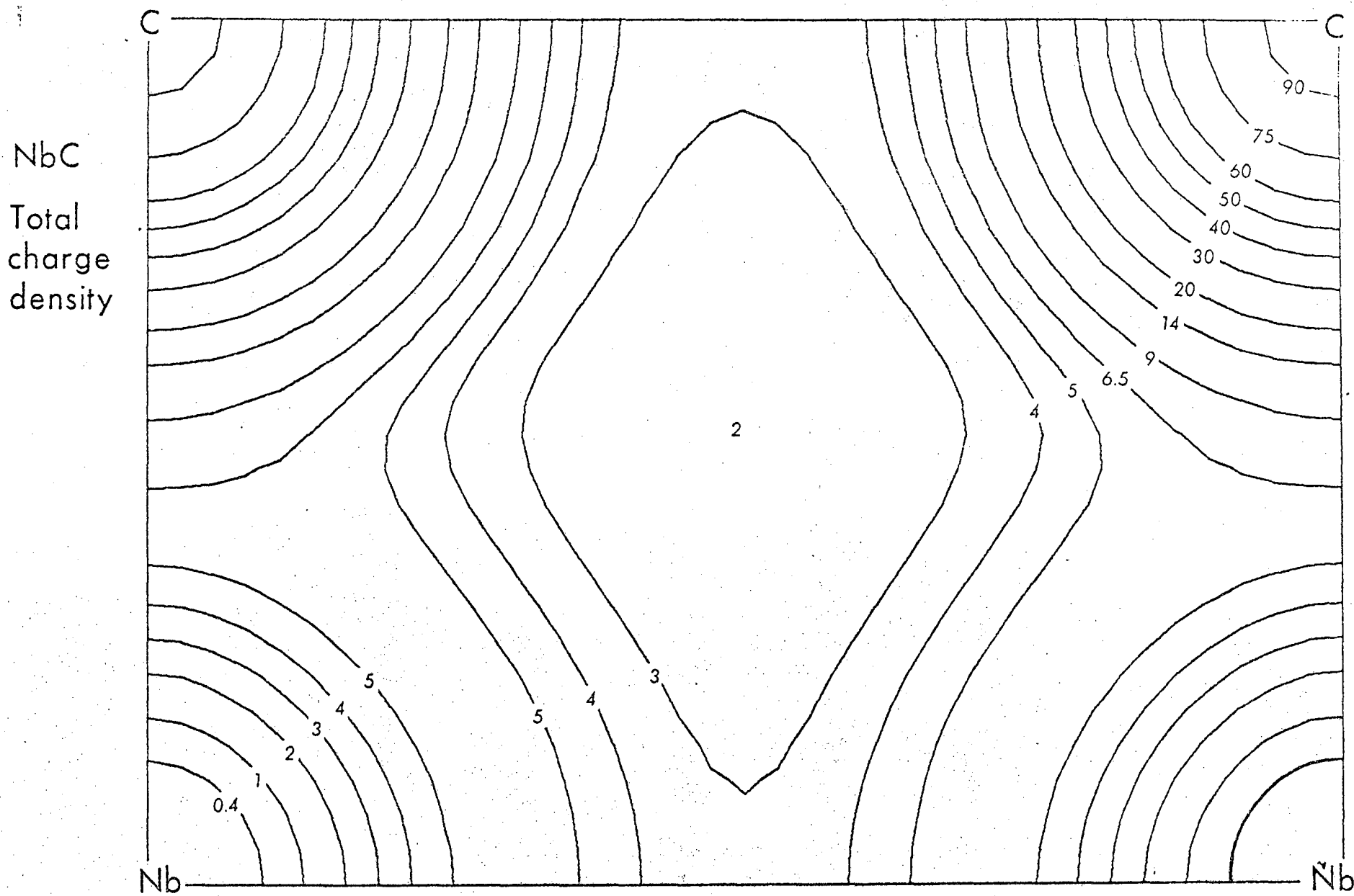


Figure 11

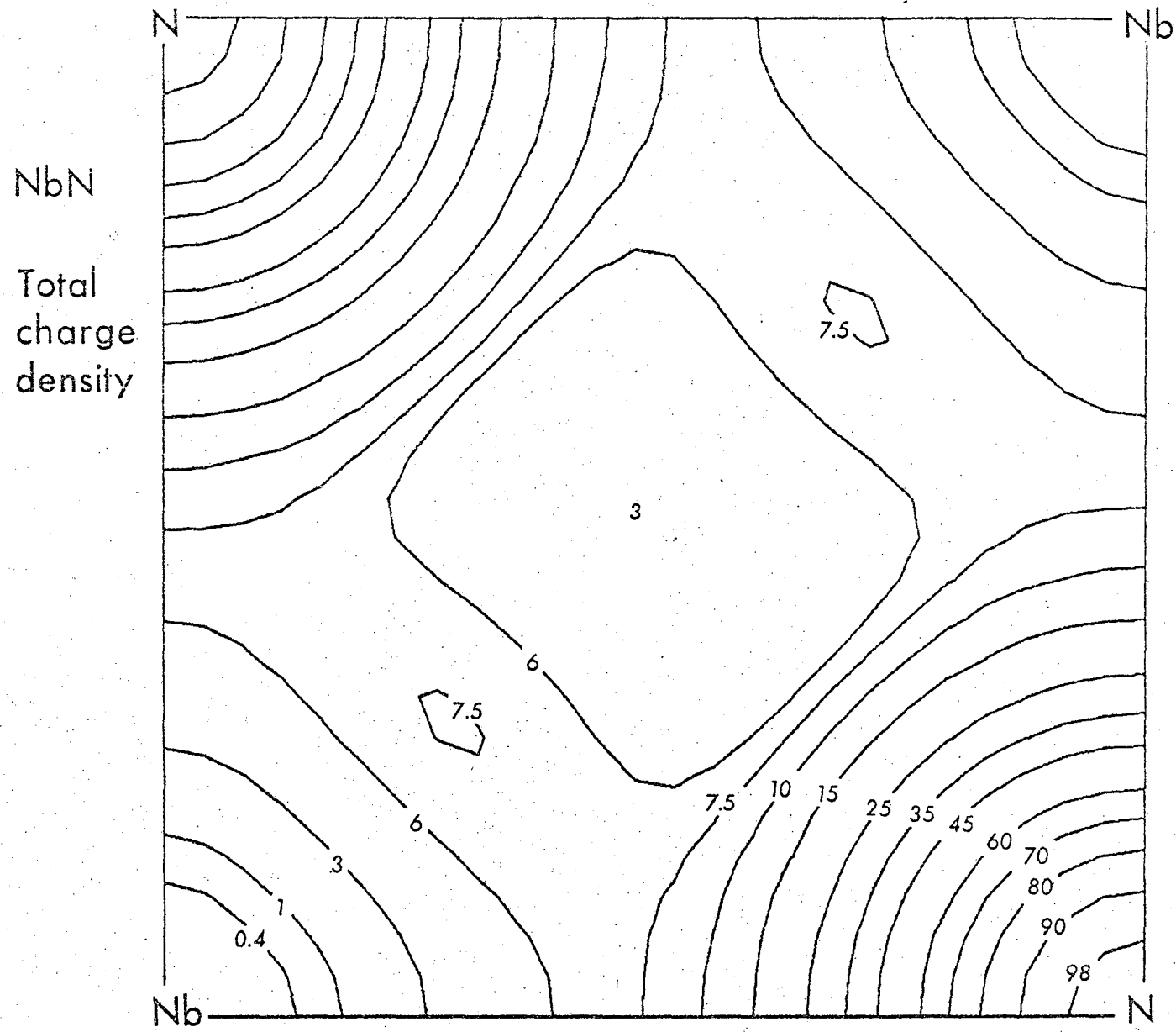


Figure 12

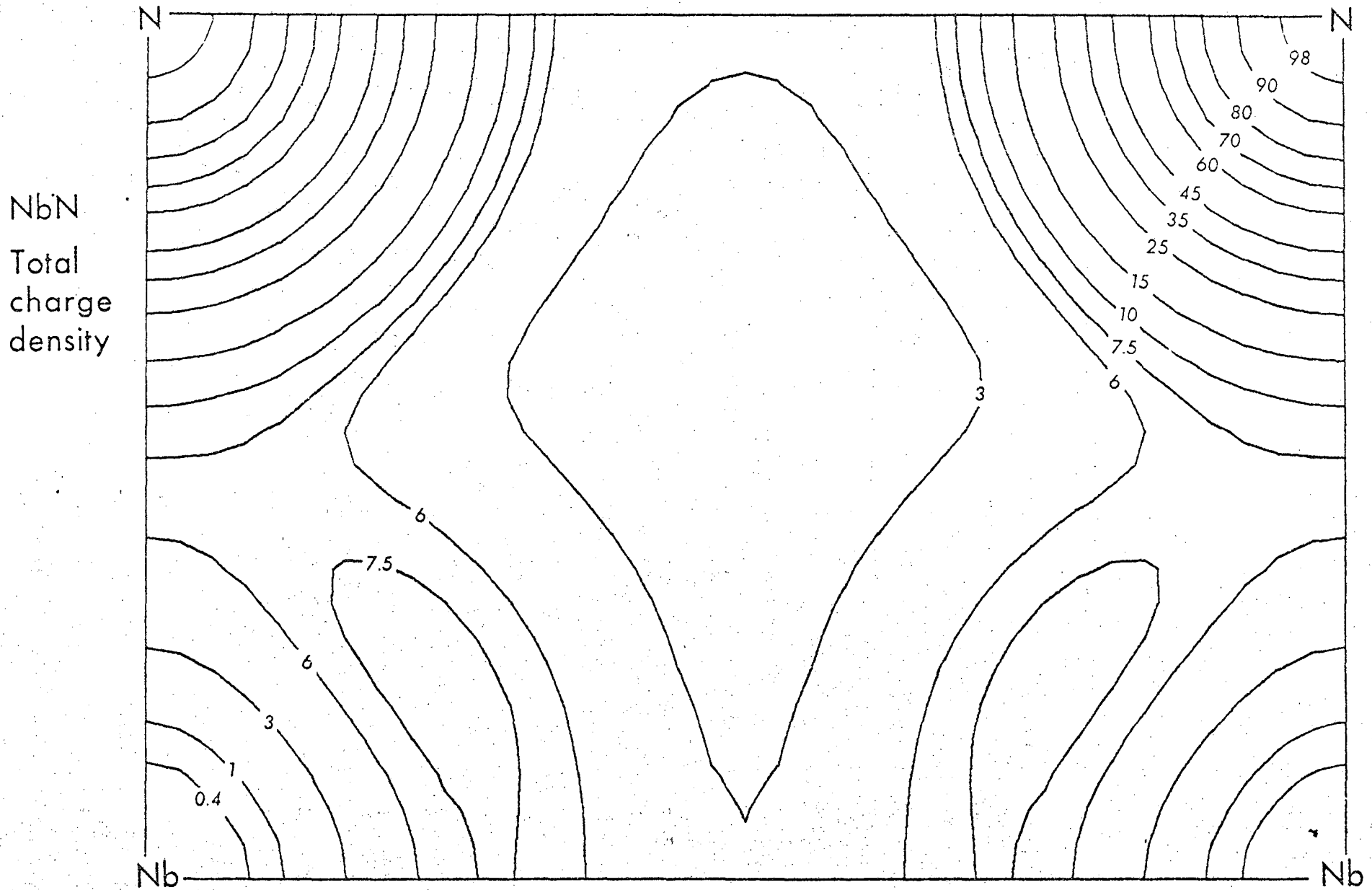


Figure 13

### NbC BAND 5 FERMI SURFACE

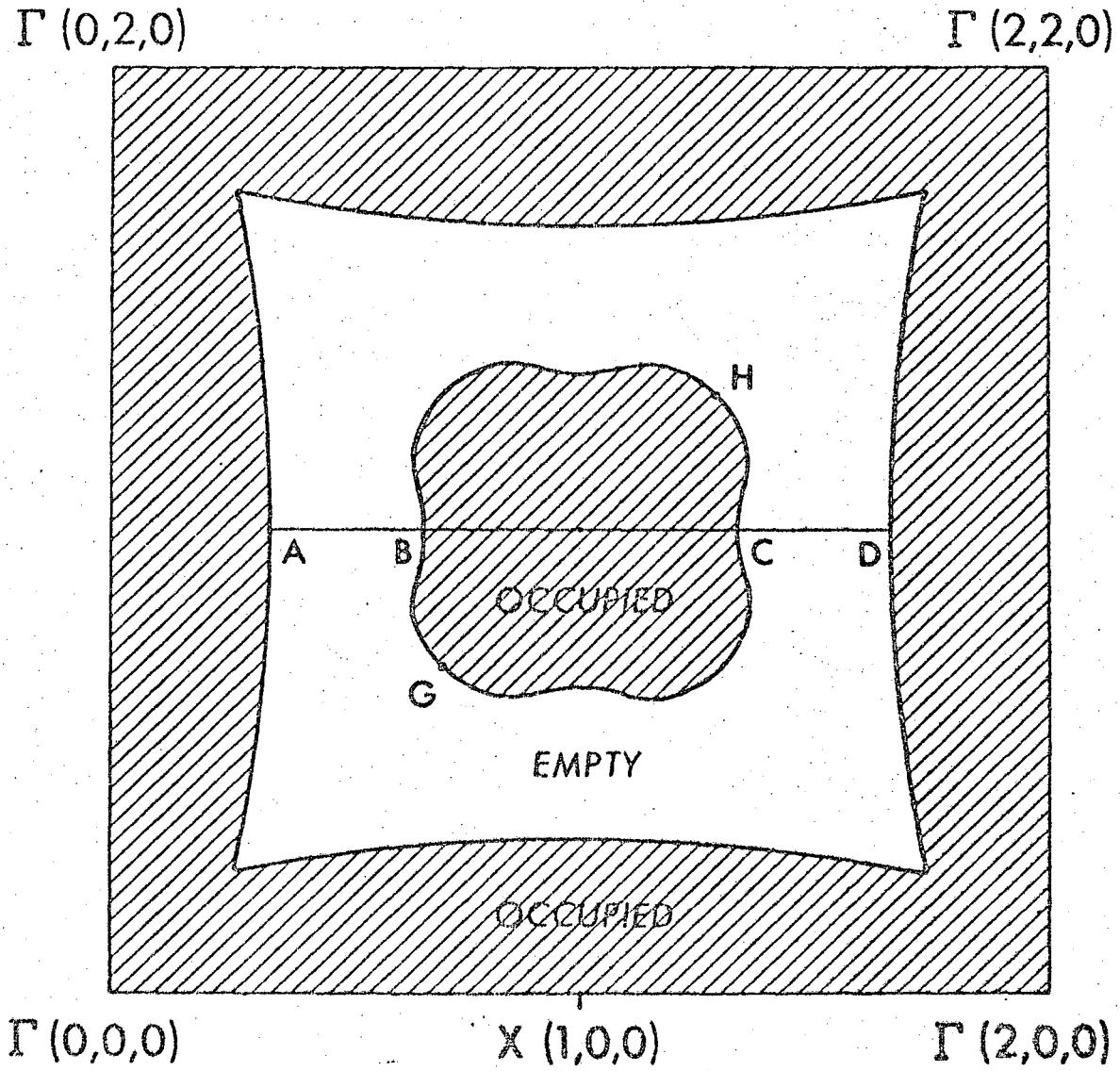
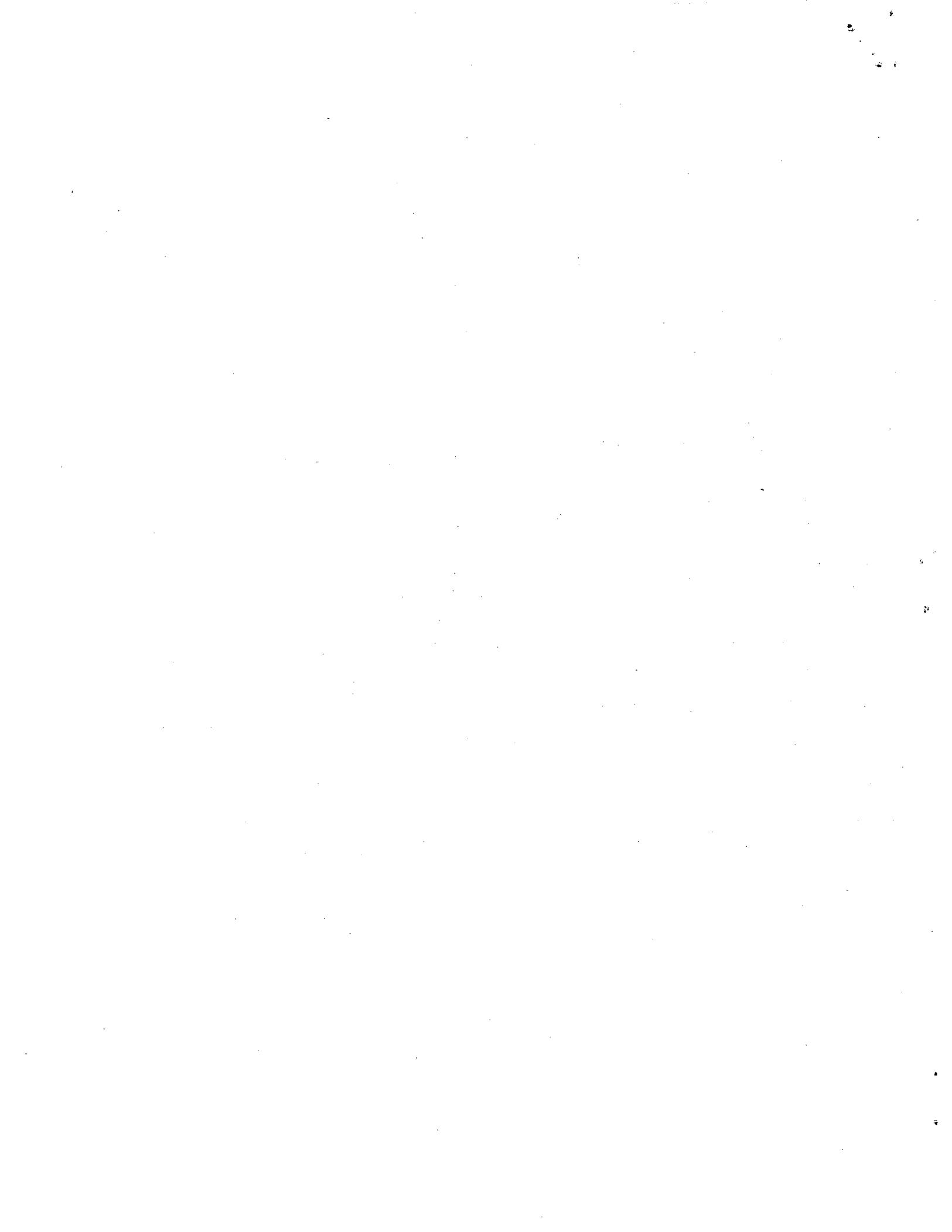


Figure 14





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