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CALCULATION OF THE DENSITY OF STATES OF NbN_x BY THE RECURSION METHOD

Ana María Llois,* Norah V. Cohan and Mariana Weissmann*

Departmento de Física, Comisión Nacional de Energía Atómica, Avenida del Libertador 8250,
1429 Buenos Aires, Argentina

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The density of states, $n(E)$, of NbN_x has been calculated by means of the Recursion Method for $x \ll 1$. The results have been compared with experiment, obtaining that the most important trends of the density of states are reproduced fairly well, even if the variation of the density of states at the Fermi level, as a function of the concentration of N-impurities cannot be predicted.

1. INTRODUCTION

IT IS WELL KNOWN that superconductivity and structural properties of transition metals and their compounds change considerably with disorder [1–3]. Aeppli *et al.* [3] published recently the results of X-ray photoemission spectroscopy for a series of NbN_x films ($0 \leqslant x \leqslant 0.2$). One of the aims of their experiments was to observe how nitrogen impurities change the electronic states of the transition metal (Nb) host and to determine how the valence band density of states especially around the Fermi energy, E_F, is related to T_c and lattice constant behaviour. In the present work we calculate an approximation to the density of states, $n(E)$, of NbN_x for $x \ll 1$ and compare our results with the experimental ones.

In order to obtain the density of states of the system we have used the expansion of the resolvent in a continued fraction by means of the Recursion Method of Haydock [4]. Even with very few exact moments of the density of states we reproduce fairly well the behaviour of $n(E)$ as a function of the concentration of N.

2. CALCULATION OF THE DENSITY OF STATES OF NbN_x

As mentioned in the introduction, we treat the case of small concentrations of nitrogen ($x \leqslant 0.07$). In this range of concentrations the probability of finding clusters of more than one impurity is insignificant. Taking this into consideration we propose for the density of states of the system, $n(E)$, three different approximations:

$$n^{(0)}(E) = \frac{n^0(E)_{\mathrm{Nb}} + xn(E)_N}{1+x}. \tag{1}$$

In this expression $n^0(E)_{\mathrm{Nb}}$ denotes the local density of states of pure Nb and $n(E)_N$ is the local density of states on a N atom located on one of the octahedral sites of the b.c.c. Nb-lattice. Using expression (1) we are assuming that the presence of nitrogen does not perturb the surrounding Nb atoms. If one considers the perturbation on the first Nb-neighbours of the nitrogen impurity, the expression for the density of states of the system is the following:

$$n^{(1)}(E) = \frac{n^0(E)_{\mathrm{Nb}}(1-2x) + 2xn^1(E)_{\mathrm{Nb}} + xn(E)_N}{1+x} \tag{2}$$

In expression (2), $n^1(E)_{\mathrm{Nb}}$ is the density of states on the first neighbour of the impurity (there are two nearest Nb atoms). If we take into account the perturbation produced on the second Nb neighbours of the N, the density of states of the system has the following expression:

$$n^{(2)}(E) = \frac{n^0(E)_{\mathrm{Nb}}(1-6x) + 2xn^1(E)_{\mathrm{Nb}} + 4xn^2(E)_{\mathrm{Nb}} + xn(E)_N}{1+x}. \tag{3}$$

In equation (3), $n^2(E)_{\mathrm{Nb}}$ is the local density of states on a Nb atom, second neighbour of a N atom.

In the calculation we used a tight-binding Hamiltonian with interaction parameters taken from a LCAO-fitting made by Mattheiss for NbN on a band structure calculation by the same author [5]. The interaction parameters are different from zero only between nearest Nb–Nb and Nb–N neighbours. We consider the $2s$ and $2p$ bands of N and the $4d$ band of Nb as these bands seem to account for the most important features of the system [3].

It should be mentioned here that we are using in our

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* Consejo Nacional de Investigaciones Cientĺficas y Técnicas.

Hamiltonian only interactions among first nearest neighbours and in $n^{(1)}(E)$ we are taking into account only perturbations on the first neighbours of a nitrogen impurity, that is on the two Nb atoms, which have direct interaction with the impurity. On the other hand in $n^{(2)}(E)$ we are considering perturbations on the first and second nearest neighbours of a N atom, without considering interactions among second nearest neighbours. Therefore, this last approximation might be better from one point of view but worst from the other.

Each local density was calculated using:

$$n^i(E) = -(1/\pi)\,\mathrm{Im}\,G^i_{00}(E+i\epsilon), \tag{4}$$

$$G^i_{00}(E) = \cfrac{1}{E - a^i_1 - \cfrac{b^i_1}{E - a^i_2 - \cfrac{b^i_2}{\begin{array}{c}\cdot\\ \cdot\\ \cdot\\ E - a^i_N - \cfrac{b^i_N}{E - a^i_\infty - b_\infty g^i(E)}\end{array}}}}\,. \tag{5}$$

In expression (5), $g^i(E)$ is defined by the condition:

$$g^i(E) = \frac{1}{E - a^i_\infty - b^i_\infty g^i(E)}\,. \tag{6}$$

The coefficients a^i_j, b^i_j were calculated by means of the Recursion Method of Haydock [4]. a^i_∞ corresponds to the middle of the band and b^i_∞ is equal to $W_i^2/16$, being W_i the bandwidth of subband i.

For each of the subbands of the Nb d-band (bulk) we obtained b^i_∞ as the smallest value such that each subband integrates to 2, with an absolute error of less than 10^{-4}. Each of the local densities of states of the nitrogen subbands has a continuous spectrum due to mixing with the Nb d-band and a δ-peak localized near to the self-energy of the subband. Nearly the whole weight of these subbands lies on the δ-peak. For the continuous part of the nigrogen spectra a^i_∞ and b^i_∞ were taken equal to those of the broadest of the d-subbands of the bulk.

3. RESULTS AND DISCUSSION

The densities of states per atom and per eV for $x = 0.0$, 0.03 and 0.07 were calculated using $N = 6$ [see expression (5)] for the three different approximations, $n^{(0)}(E)$, $n^{(1)}(E)$, and $n^{(2)}(E)$ introduced in the preceding section. Figure 1 shows the results for $n^{(2)}(E)$, the other two approximations are quite similar. There is also a discrete spectrum not shown in Fig. 1. Comparing our curves with the background corrected valence band spectra obtained by Aeppli *et al.* [3], we see that peaks A and B are in nearly the same positions with respect to the Fermi level as in the experiments. In our calculations peaks A and B lie at -0.5 and -1.2 eV while the experimental ones are at -0.5 and -1.13 eV [3] and the calculations of Mattheiss give -0.5 and -1.4 eV [7]. In our curves the height of peak B appears too depressed with respect to the heigh of peak A, we attribute this to the fact that we have not taken into account in our calculations the 5s Nb-band. Also, as a consequence of not having taken into account the 5s Nb-band, peak C does not appear, since this feature is mainly derived from that band [6]. Aeppli's valence band spectra show a relative decrease in the heights of peaks A and B with increasing concentrations of nitrogen, this decrease being much larger than the percentage of N impurities. In Table 1 we present the relative decreases of the average heights of peaks A and B for $x = 0.03$ and 0.07. We also obtain for $n^{(1)}(E)$ and $n^{(2)}(E)$ relative decreases that are larger than the concentration of N. $n^{(2)}(E)$ gives, in this case, the results that are nearer to the experimental ones. We can also reproduce in our calculations, for $n^{(2)}(E)$, the fact that with increasing N-concentration, instead of two peaks only one is left (see Fig. 1).

In Fig. 2 we show the local density of states on a N atom, $n(E)_N$, and in Fig. 3 the local density of states

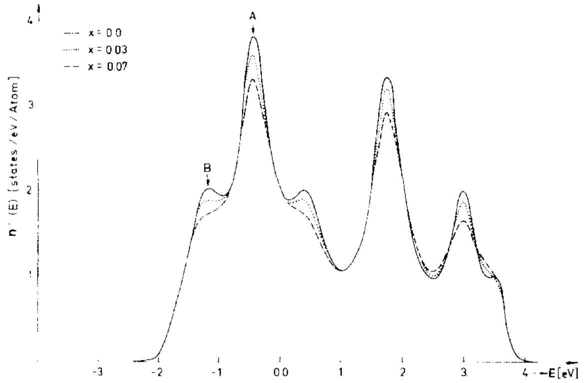

Fig. 1. Density of states of NbN$_x$ (continuous part) calculated using expression (3) for $x = 0$ (full line), $x = 0.03$ (dotted line) and $x = 0.07$ (broken line). The zero of energies falls on the Fermi level for $x = 0.0$.

Table 1. Relative decrease of the average of the heights of peaks A *and* B *calculated using the three different approximations proposed in this work with* N = 7 *[see equations* (1), (2) *and* (5)] *and values obtained from the experimental results of Aeppli* et al. [3]

x	$n^{(0)}(E)$	$n^{(1)}(E)$	$n^{(2)}(E)$	Aeppli *et al.*
0.03	−0.028	−0.038	−0.056	−0.137
0.07	−0.064	−0.099	−0.140	−0.260

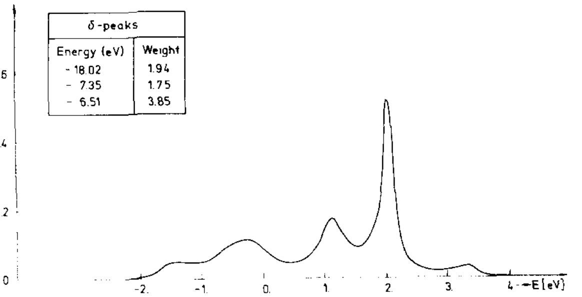

Fig. 2. Local density of states on one of the nitrogen impurities $n(E)_N$. The zero of energies falls on the Fermi level of NbN_x for $x = 0.0$.

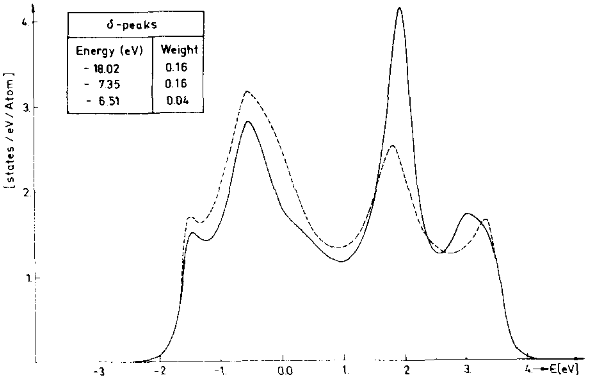

Fig. 3. Local density of states on the first Nb neighbour of a N impurity $n^1_{Nb}(E)$ (full line) and on the second Nb neighbour $n^2_{Nb}(E)$ (dotted line). The inset corresponds to $n^1_{Nb}(E)$. The weights of the δ-peaks for $n^2_{Nb}(E)$ are negligible.

Table 2. Charge transfer on the nitrogen impurity, the first Nb-*neighbour* (Nb^1) *of an impurity and the second* Nb-*neighbour* (Nb^2) *of an impurity, calculated using* $n^{(2)}(E)$ [*see equation* (3)] *and* N = 6 [*see expression* (5)]

x	N	Nb^1	Nb^2
0.01	−2.663	0.442	0.023
0.03	−2.661	0.469	0.061
0.05	−2.660	0.495	0.098

on the first Nb-neighbour of a N-impurity, $n^1(E)_{Nb}$, and the local density of states on the second Nb-neighbour of an impurity, $n^2(E)_{Nb}$. The spectrum of the first Nb-neighbour of the impurity still shows the δ-peaks of the N-subbands, that is not the case for the second Nb-neighbour, even if the peaks of $n^2(E)_{Nb}$ are still broader than in $n^0(E)_{Nb}$. In Table 2 we show the charge transfer on the different kinds of atoms considered in the calculation for $n^2(E)$ and $N = 6$. As a consequence of the lack of self-consistency in the calculations the charge transfer that comes out is too large, but, as expected, the most perturbed Nb atoms are the first nearest neighbours of the impurity.

We have calculated the weight of the so-called feature D [3], that is the ratio $Q(x)$ of the valence band spectrum's intensity integrated over the − 10.5 to − 3.9 eV energy range, to its area between − 10.5 and 1.0 eV (all these energies are measured from the Fermi level). We obtain that $Q^*(x) = Q(x) - Q(0)$ increases with increasing x, our results being nearly one half of those obtained by Aeppli. We obtain $Q^*(0.03) = 0.044$ and $Q^*(0.07) = 0.101$ while Aeppli's values are 0.08 and 0.2 respectively. This can be explained by the fact that we have used interaction parameters different from zero only between first-nearest neighbours, while it is reasonable to assume that the second Nb neighbours of the impurity also interact directly with it, being then the mixing among N and Nb subbands larger than the one obtained by us.

$n(EF)_{x=0.0}$, the value of the density of states for pure Nb at the Fermi level was evaluated for $N = 4$, 5, and 6 [see expression (5)], giving respectively, 2.42, 2.24 and 1.99. The successive approximations converge rapidly towards the value calculated by Mattheiss of 1.75 [7]. Taking into account that we have used tight-binding parameters that correspond to NbN, which

Table 3. Value of the density of states of NbN_x *at the Fermi level for different concentrations,* x, *of nitrogen, calculated using the three different approximations proposed in this work* [*see equations* (1), (2) *and* (3)] *and in each case for* N = 4, 5 *and* 6 [*see expression* (5)]

	$N = 4$			$N = 5$			$N = 6$		
x	$n^{(0)}(EF)$	$n^{(1)}(EF)$	$n^{(2)}(EF)$	$n^{(0)}(EF)$	$n^{(1)}(EF)$	$n^{(2)}(EF)$	$n^{(0)}(EF)$	$n^{(1)}(EF)$	$n^{(2)}(EF)$
0.0	2.419	2.419	2.149	2.238	2.238	2.238	1.994	1.994	1.994
0.03	2.342	2.313	2.329	2.301	2.225	2.028	2.013	1.969	2.030
0.05	2.292	2.247	2.326	2.342	2.216	1.897	2.034	1.956	2.053
0.07	2.244	2.187	2.371	2.381	2.206	1.772	2.060	1.946	2.074

means that our bandwidth must be smaller than the one corresponding to b.c.c. Nb, we expect our value for $n(EF)$ to be larger than $n(EF)_{\text{Mattheiss}}$. It is seen, then, that $N = 6$ is already a good approximation. However, if one intends to calculate the change of $n(EF)$ with concentration x, the trend is not so clear. It depends both on the level N and the approximation used for calculating the density of states [$n^{(0)}(E)$, $n^{(1)}(E)$ or $n^{(2)}(E)$]. As shown in Table 3 the approximation $n^{(1)}(E)$ is the only one that gives consistently a decrease in $n^{(1)}(EF)$ for increasing x, in agreement with the experimental result [3].

In conclusion, in the case of small concentrations of N impurities in Nb, the use of the Recursion Method with very few exact moments ($N = 6$ corresponds to 13 exact moments) and perturbation only on the nearest neighbours of the impurities reproduces fairly well the most important trends of the density of states, even if the variation of $n(EF)_x$ with x depends on the approximation used.

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