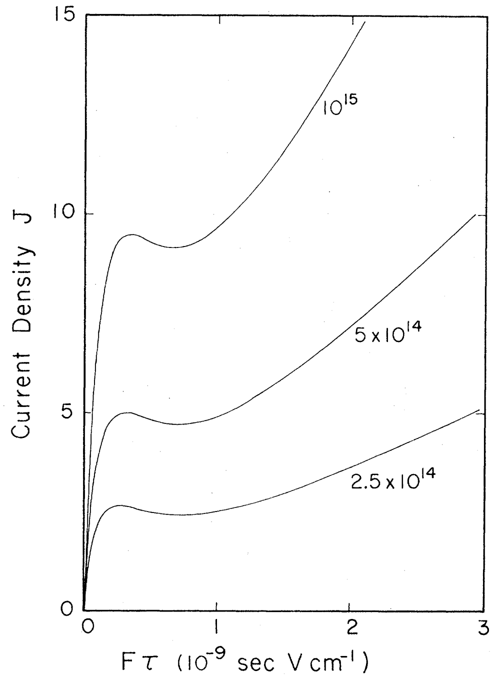

FIG. 3. Average current density J as a function of $F\tau$ for samples with different hole concentrations (in cm^{-3}). The current density is expressed in arbitrary units.

behavior. This is based on the consideration that for the conduction band, there is a region near the center of the B.Z. with a high density of states which is also anomalous. In other words, electrons excited to these states should also become negative-mass carriers, and contribute to current opposite to the electric field. Therefore, despite the oversimplified assumptions in our transport calculations, we think that the essential features of the I-V characteristics are elucidated by the present work. Thus the prediction by Liu[4] based on qualitative considerations that the NDR effect may be obtained in zero-gap semiconductors is confirmed. A detailed description of the present work and related investigations, such as the temperature effect on the I-V characteristics, will be presented in separate publications.

---

*Research supported by the U.S. Air Force Office of Scientific Research under Grant No. AFOSR 74-2731.

†Present address: Department of Physics, Imperial College of Science and Technology, London, England.

[1] B. J. Roman and A. W. Ewald, Phys. Rev. B 5, 3914 (1971).

[2] H. Busta and A. W. Ewald, in Proceedings of the International Conference on the Physics of Semimetals and Narrow Gap Semiconductors, Cardiff, United Kingdom, 12–14 September 1973 (to be published).

[3] There is, correspondingly, a region in which the electron effective mass becomes negative. However, since the valence-band structure is more suitable for obtaining the NDR effect, we shall confine ourselves to p-type samples in this paper.

[4] L. Liu, Phys. Lett. 45A, 285 (1973).

[5] W. Leung and L. Liu, to be published.

[6] G. E. Pikus and G. L. Bir, Fiz. Tverd. Tela 1, 154 (1959) [Sov. Phys. Solid State 1, 136 (1959)].

[7] W. Leung and L. Liu, Phys. Rev. B 7, 718 (1973).

O- and Na-Induced Surface States on Paramagnetic Ni

R. V. Kasowski
E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

(Received 13 June 1974)

The linear combination of muffin-tin orbitals technique has been used to calculate the effect of overlayers of O and Na on Ni(001) electronic-energy levels. We find that both Na and O induce surface states in the s-d gap with the density and energies depending on the overlayer separation d. The peak observed experimentally at -0.4 Ry and O on Ni is due to nonbonding oxygen states as originally interpreted by Hagstrum and Becker.

The linear combination of muffin-tin orbitals[1] (LCMTO) method has been used to calculate the electronic states of a paramagnetic Ni(001) thin film and the effect of a perfect $C(1\times1)$ overlayer of either O or Na on these electronic states for variable overlayer separation d. I find that the energy levels of a Ni thin film correspond closely to those of bulk Ni and that there are no surface states even though surface-charge regions are included. However, both O and Na overlayers induce surface states in the s-d gap, with the number and energy distribution depending critically on interlayer separation. It is believed that these are the first *ab initio* calculation of induced surface states.

I will show that the surface state at -0.4 Ry observed in photoemission[2] and ion-neutralization-spectroscopy (INS)[3] data is due to a nonbonding O p state and thus confirm a previous interpretation by Hagstrum and Becker. The surface states in the s-d gap and the bonding O p state contribute to the width of the peak at -0.4 Ry. Finally, the position of the O p surface state is sensitive to the separation d of the overlayer, thus allowing me to predict $d = 1.13$ Å which corresponds to the NiO bond length. This bond length is in much closer agreement with the low-energy electron diffraction (LEED) results of Demuth, Jepsen, and Marcus[4] ($d = 0.90$ Å) than that of Andersson *et al.*[5] ($d = 1.50$ Å). However, I will present evidence that the Ni atoms at the surface should be relaxed as already suggested by Hagstrum and Becker.

There appears to be no photoemission or INS data for Na on Ni to allow an independent investigation of d. However, these results provide new insight into the photoemission peaks observed by Callcott and McRae[6] for Cs overlayers on Ni(111). I propose that these peaks are associated with Cs-induced surface states instead of surface plasmons as proposed by Callcott and McRae.[6]

Application of LCMTO to thin films proceeds exactly as in solids except that the layer structure constants of Kambe[7] are used in place of the bulk structure constant of Ham and Segall.[8] The method of constructing wave functions and potentials has already been described in an application[9] to Cu.

The Ni(001) thin-film model consists of a total of seven layers, with the inner five layers containing Ni atoms and the outermost two layers representing surface charge. The overlayer model consisted of 5 Ni layers and one layer of adatoms in fourfold sites above the hollows as previously determined by LEED.[4,10] The oxygen surface structure I choose, however, is $C(1\times1)$ instead of LEED-determined $C(2\times2)$. It was necessary to work with the (1×1) structure because the (2×2) structure involves twelve atoms per unit cell instead of six. However, I will show that my results are applicable to the (2×2) structure because the O-O overlap is weak and that it is the underlying Ni electronic states that determine the overlayer structure. We note that the weak O-O overlap could be expected beforehand because the Ni-O and O-O distances here are the same as a NiO crystal. Electronic energy models[11,12] for NiO indicate that O-O overlap is relatively unimportant relative to Ni-O overlap.

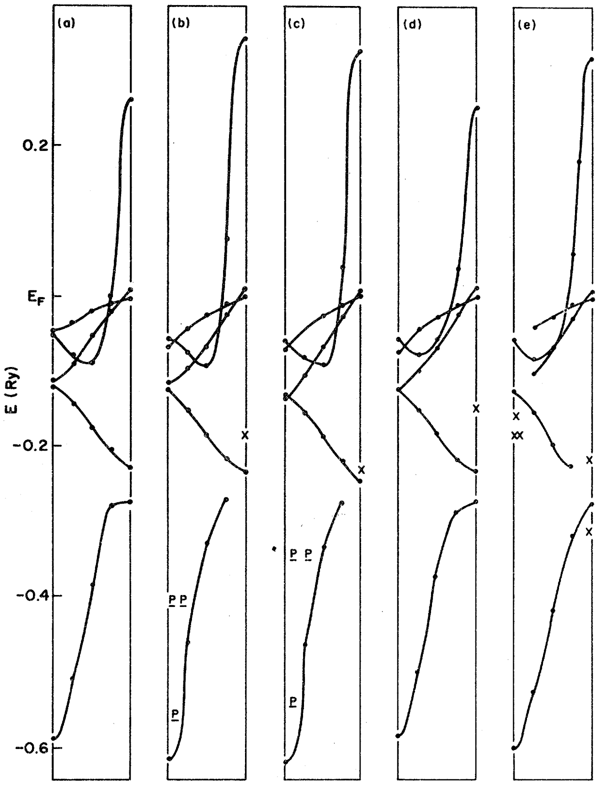

FIG. 1. The energy states of (a) five-layer Ni (001) thin film and the effect on these thin film states of (b) O overlayer at $d=0.90$ Å, (c) O overlayer at $d=1.50$ Å, (d) Na overlayer at $d=2.87$ Å, and (e) Na overlayer at $d=1.76$ Å. O $2p$ states are represented by a p while induced surface states are represented by an X.

Overlayer potentials were constructed for O-Ni separations of $d = 1.13$ (from NiO bond length) and 1.50 Å and for Ni-Na separations of $d = 1.76$ and 2.87 Å (from Andersson and Pendry[10]).

In Fig. 1(a) are shown the energy states for the five-layer plus surface charge Ni film at the Γ point of the two-dimensional Brillouin zone. The states are arranged at 1/5 intervals to emphasize their similarity with the bulk energy bands since differences of less than 0.015 Ry exist with bulk energy-band results for $\vec{k} = (0,0,0), (0,0,0.25), (0,0,0.5), (0,0,0.75), (0,0,1)$. A further justification for arranging the thin-film states to correspond to bulk counterparts is that the wave functions obey approximate Bloch symmetry. The coefficients of the muffin-tin orbitals alternate as $\exp(i\vec{k}\cdot\vec{R}_n)$ although the magnitudes of the coefficients from layer to layer are not equal as required for Bloch symmetry. Furthermore, investigation of the muffin-tin orbital (MTO) coefficients reveals that the charge densities of all the states extend over all the layers, thus ruling out the possibility of surface states.

We note that the d bandwidth $(X_1 - X_5)$ here is 0.29 Ry whereas most theoretical calculations[13] obtain a bandwidth of 0.30 to 0.34 Ry. A more accurate Ni potential would not change the present results.

In Figs. 1(b) and 1(c) is shown the effect of O on the Ni electronic states for $d = 1.13$ and 1.50 Å. The O $2p$ states are labeled p while an X is used to label band states that have now become surface states. Comparison of Figs. 1(a), 1(b), and 1(c) indicates that only the top of the bottom Δ_1 band has been converted into a surface state whereas the other band states are relatively unaffected by the overlayer. The surface states were identified by investigating the coefficients of the MTO's to see whether the charge density is localized to the Ni layer next to the overlayer. The top of the bottom band is primarily of d_{z^2} symmetry, and these coefficients are tabulated in Table I to show how a band state is localized by the overlayer. The coefficients indicate that the top of the bottom band $(E = -0.262)$ is spread nearly equally over the five layers in Fig. 1(a), while in Fig. 1(b) this state $(E = -0.173$ Ry) is about 70% localized to the first Ni layer. In Fig. 1(c) the top of the bottom band $(E = -0.217)$ has appreciable amplitude on the second layer, and one could argue that $d = 1.50$ Å does not localize a surface state.

The O p states are also surface states. The doubly degenerate p state at -0.4 Ry is localized in the O overlayer because its interaction with the underlying Ni states is very weak. The singly degenerate state at about -0.55 Ry is responsible for the induced-band surface state in the s-d gap because of strong hybridization with the Ni states.

Photoemission[2] $(h\nu = 21.2$ eV) and INS[3] data identify a surface state at -0.4 Ry below E_F that extends from -0.53 to about -0.24 Ry. The peak maximum coincides exactly with the nonbonding O p state in Fig. 1(b) at -0.4 Ry. Hagstrum and Becker also identified this as a p state since it moves higher in energy for S and Se on Ni. Photoemission with $h\nu < 11$ eV will only sample the induced surface state. It would appear that the O p state in Fig. 1(c) at -0.34 Ry is inconsistent with the large peak at -0.4 Ry found experimentally, and thus I feel that $d = 0.90$ Å (from Demuth, Jepson, and Marcus[4]) is more in accord with my results than $d = 1.50$ Å (from Andersson *et al.*[5]).

Calculations were repeated at the M and X points but the overlayer of O did not induce any surface states. At the M point, the lowest band was bent upwards by 0.04 Ry thus reducing its separation from the higher-level d bands. At the X point, the O layer did not even bend the bands. Furthermore, I find only a small dispersion in the O p states, thus confirming the assumption that the O atoms do not overlap significantly and that results for a $C(1\times1)$ structure are applicable to the $C(2\times2)$ structure.

Since the O atoms are too far apart to interact strongly with each other, the existence or nonexistence of surface states is related to the underlying Ni electronic states. The most significant difference between the Γ, M, and X points is the position of the Ni $4s$ band, which is lowest at Γ and highest at the X point. A most important observation is that a surface state does not form at Γ when the $4s$ state is not included in the wave function. Thus the energy of the induced surface state depends directly on the energy of the $4s$ band which in turn is very sensitive to $\vec{k}$ because of its large spatial extent.

The $C(2\times2)$ structure has a lattice constant of a whereas the $C(1\times1)$ structure has a lattice constant of $a/\sqrt{2}$. Figure 2 shows the Brillouin zone for the $C(1\times1)$ structure and indicates how this structure folds into the $C(2\times2)$ Brillouin zone.

The results for the $C(1\times1)$ structure enable me

TABLE I. Complex coefficients for the d_{z^2} part of the eigenfunction with (a), (b), and (c) corresponding to top of bottom band in Figures 1(a), 1(b), and 1(c), respectively. The overlayer of O is next to layer No. 1.

	E (Ry)	1	2	3	4	5
(a)	-0.262	$(-0.3, -0.11)$	$(0.36, 0.13)$	$(-0.28, -0.11)$	$(0.36, 0.13)$	$(-0.3, -0.11)$
(b)	-0.273	$(0.36, -0.29)$	$(-0.09, +0.07)$	$(-0.05, 0.04)$	$(0.04, -0.03)$	$(-0.002, 0.002)$
(c)	-0.217	$(0.38, 0.01)$	$(-0.24, -0.07)$	$(0.026, 0.00)$	$(0.054, 0.001)$	$(-0.043, -0.001)$

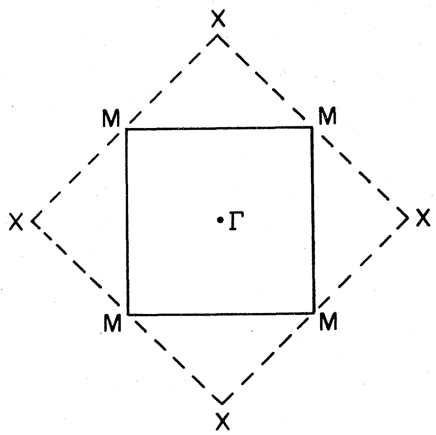

FIG. 2. Two-dimensional Brillouin zone for $C(1\times1)$ structure (dashed line) and how $C(2\times2)$ structure (solid line) results from $C(1\times1)$.

to propose the following for $C(2\times2)$. The Ni atoms must relax or reconstruct about the O atoms so that surface states can now form at M in the badly bent bottom band. The induced surface-state energy will no longer go continuously to zero as it would for an unreconstructed surface. There is now a threshold through which O atoms must tunnel to leave the surface and thus the $C(2\times2)$ structure is stabilized. I add that the number of surface states would be one per O atom in this proposed configuration. My hypothesis is consistent with experiment in that NiO forms on the surface as more oxygen is added to $C(2\times2)$. Hagstrum and Becker[3] have already postulated some possible reconstructions.

The position of the 4s states on the surface atoms will be sensitive to how the crystal face is cut. The position of the 4s states directly affects the number and energy of surface states which in turn will determine the surface properties such as structure and catalytic activity.

The 4s band may also have an important effect on the magnetic properties. We observe in Fig. 1(a) that the 4s band width is 0.032 Ry less than that for bulk Ni whereas the 3d band width for a thin film is virtually the same as that in the bulk (~ 0.002 Ry difference). This is to be expected since the 4s states have a much larger spatial extent than do d states. As a result of this band bending, the wave function of the electrons (which extends throughout the crystal) will have a greater admixture of s character in the vicinity of the surface than within the bulk. This increased s-d hybridization is allowed only near the surface where the Bloch condition on the wave function is relaxed and the symmetry is no longer cubic. The band bending would of course be less dramatic for a thick film but the trend in s-d mixing would remain and thus could contribute to the layer at the surface being magnetically dead.[14] Adsorption of O on the surface would decrease the s content of the wave function near the surface.

Finally, we briefly discuss the Na on Ni results for $d = 2.87$ and 1.76 Å where again I choose the hollow positions and a $C(1\times1)$ structure instead of $C(2\times2)$. In Figs. 1(d) and 1(e) for $d = 2.87$ and 1.76 Å, respectively, we see that surface states are induced at the bottom of the bands. Overlayer separation of $d = 2.87$ Å produces only one surface state whereas $d = 1.76$ Å produces five surface states (one for each d band). No surface states are found at X and M. There is no INS or photoemission determination of the surface-state energy so that we could try to make an independent determination of d to compare with a LEED calculation[10] ($d = 2.87$ Å).

However, we can use the Na-Ni theoretical results to give a new interpretation of the photoemission data of Cs on Ni by Callcott and MacRae.[6] They find their spectra to depend on the amount of Cs deposited on the Ni(111) surface. I suggest that the peak at − 4.5 eV for what they refer to as clean Ni is actually due to small amounts of contaminant such as O or Cs. For coverages of more than a monolayer of Cs, peaks occur at − 4.0 and − 5.4 eV, which are much stronger than the peak at − 4.5 eV. The results in Fig. 1(e) show that several surface states can be induced while leaving the remainder of the bands unperturbed. The rest of the bands must remain unperturbed to get the characteristic emission of clean Ni.

In conclusion, we see that donor atoms (Na) and acceptor atoms (O) both produce surface states in the s-d gap. This makes it difficult to identify contaminants in an experiment.

I feel that study of thin film models with overlayers holds much promise. It would be useful to calculate the dielectric dispersion $\epsilon_2(\omega)$ and the photoemission probability to see how close the agreement with bulk is. However, the calculations require a minimum of five atoms per unit cell and would require a sizable amount of computation time.

---

[1] O. K. Andersen and R. V. Kasowski, Phys. Rev.

B 4, 1063 (1971); R. V. Kasowski and O. K. Andersen, Solid State Commun. 11, 799 (1972).

[2] D. E. Eastman, Phys. Rev. B 3, 1769 (1971).

[3] H. D. Hagstrum and G. E. Becker, Phys. Rev. Lett. 22, 1054 (1969).

[4] J. E. Demuth, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. 31, 540 (1973).

[5] S. Andersson, B. Kasemo, J. B. Pendry, and M. A. Van Hove, Phys. Rev. Lett. 31, 595 (1973).

[6] T. A. Callcott and A. U. MacRae, Phys. Rev. 178, 966 (1969).

[7] K. Kambe, Z. Naturforsch. 22a, 322 (1967).

[8] F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961).

[9] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J. 1963).

[10] S. Andersson and J. B. Pendry, J. Phys. C: Proc. Phys. Soc., London 5, 141 (1972).

[11] L. F. Mattheiss, Phys. Rev. B 5, 290 (1972).

[12] D. Adler, Solid State Phys. 21, 1 (1968).

[13] J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973).

[14] L. M. Liebermann, D. R. Fredkin, and H. B. Shore, Phys. Rev. Lett. 22, 539 (1969).

Theory of Gor'kov Model for *A*15 Compounds

J. Noolandi
Bell Telephone Laboratories, Holmdel, New Jersey 07733

(Received 15 July 1974)

The Gor'kov model for the *A*15 compounds predicts the appearance of a gap in the d-electron spectrum between the superconducting transition temperature, T_c, and the martensitic-phase-transition temperature, T_m. A mean-field calculation of the gap parameter is carried out for Nb_3Sn and V_3Si, using the measurements of the soft mode in the cubic phase. It is suggested that the theory be verified by optical or tunneling measurements.

In spite of considerable effort over the past fifteen years, there is still little basic theoretical understanding of the properties of the *A*15 compounds.[1] The temperature dependences of the magnetic susceptibility, Knight shift, and shear modulus, as well as the large linear heat capacity, are all supposed to originate from the closeness of the Fermi level to a peak in the density of states,[2] which in turn is thought to originate from the one-dimensional behavior of the d electrons.[3] However the band-structure calculations of Mattheiss[4] do not show any one-dimensional effects in any simple sense, and the calculations are not accurate enough to resolve the postulated fine structure of a few millivolts in the density of states. Theories of the martensitic phase transition predict the frequency of the Γ_{12} optical phonon mode for Nb_3Sn,[5] and the magnetic field dependence of the transition temperature for V_3Si,[6] but do not provide a direct check on the assumptions underlying the calculations. Recently another theory of the *A*15 compounds has been put forward by Gor'kov.[7] It is the purpose of this Letter to calculate the gap in the electronic spectrum above T_c and below T_m predicted by this theory, and to suggest that either optical or tunneling measurements be carried out to check the theory.[8]

In the Gor'kov model the Fermi level is assumed to lie near the X point in the reciprocal lattice, as compared to the Γ point in the Weger-Labbé-Friedel model. From the symmetry of the space group it can be shown that all the representations at X are doubly degenerate in the cubic phase, and the energy bands have linear dispersion in the vicinity of X. As the crystal goes through the martensitic transition to the low-temperature phase, the degeneracy at the X point is lifted[9] and a peak appears in the density of states. The model may also be viewed as a modified version of the Peierls transition in a half-filled band. In the Gor'kov theory it is possible to develop a correlation between the martensitic and superconducting transitions,[7] and the calculated quantities vary as $\ln T$, which agrees well with experiment.[10]

I have carried out a mean-field calculation of the gap parameter, assuming that the d-electron bands are one-dimensional[11] and that the martensitic transition is second order,[12] and neglecting the Coulomb interaction.[13] I obtain values of the gap parameter above T_c for both Nb_3Sn and V_3Si, using the measurements[10] of the shear modulus in the cubic phase for both crystals. The calcu-