

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: December 17, 1979

Project Title: *Correlation and Collective Modes in Narrow Band Materials: NiO and FeO*

Project No: *G-41-688*

Project Director: *Dr. Martin W. Ribarsky*

Sponsor: *U. S. Air Force Office of Scientific Research (AFOSR);
Bolling AFB, D.C. 20332*

Agreement Period: From 10/1/79 Until 9/30/80 (Grant Period)

Type Agreement: *Grant No. AFOSR-80-0023*

Amount: *\$23,990 AFOSR Funds (G-41-688)
5,280 GIT Contribution (G-41-330)
\$29,270 Total*

Reports Required: *Final Technical Report (Annual Technical, if grant extended beyond one year)*

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Defense Priority Rating: *None*

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Date: 5/1/81

Project Title: Correlation and Collective Modes in Narrow Band Materials
NiO and FeO

Project No: G-41-688

Project Director: Dr. Martin W. Ribarsky

Sponsor: U. S. Air Force, Office of Scientific Research

Effective Termination Date: 9/30/80

Clearance of Accounting Charges: 9/30/80

Grant/Contract Closeout Actions Remaining:

NONE

- Final Invoice and Closing Documents
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CONTINUED BY G-41-615



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5 June 1980

Air Force Office of Scientific Research
Bolling AFB, D.C. 20332

Attention: Dr. Thomas C. Collins
Program Manager
Directorate of Physics

Subject: Research Proposal Entitled, "Correlation and Collective
Modes in Narrow Band Materials: NiO and FeO"
(Continuation of Grant No. AFOSR-80-0023)

Gentlemen:

The GEORGIA TECH RESEARCH INSTITUTE desires to submit for your consideration the subject proposal prepared by Dr. M. W. Ribarsky, Research Scientist, School of Physics. This is for continuation of the work currently being conducted under AFOSR-80-0023.

We believe you will find the proposal complete; however, if anything additional is desired, please let us know. Any matters pertaining to the scientific program or personnel may be referred to Dr. Ribarsky at 404/ 894-5212. Administrative or contractual matters may be referred to the writer at 404/894-4814.

We appreciate the opportunity of submitting this proposal and look forward to the possibility of continuing work with you on this program.

Sincerely,

Phyllis R. Oliver
GEORGIA TECH RESEARCH INSTITUTE

cm

Addressee: Six (6) copies
Enclosure: Proposal - Six (6) copies

Proposal for Support of a Basic Research Grant

Submitted to

Air Force Office of Scientific Research

May 29, 1980

Grantee Institution: Georgia Institute of Technology
Atlanta, Georgia 30332

Principal Investigator: Dr. Martin W. Ribarsky, Research Scientist
School of Physics

Title: "Correlation and Collective Modes in Narrow Band Materials:
NiO and FeO".

Proposed Continuation Date: October 1, 1980

Proposed Duration: 2 years

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BIOGRAPHICAL SKETCH

Abstract

Narrow band materials present fundamental difficulties to the analysis of electronic structure using independent particle models and energy band theory. Correlations effects which depend on the configuration of electrons in a process and which reflect the local environment of the participating electrons strongly affect the properties and measurable quantities of these materials. Such narrow band materials as the 3d transition metal oxides have important electrical, optical and catalytic properties and knowledge of the oxide properties also provides insights about the corrosion of the metal. For these reasons it would be fruitful to provide a thorough investigation of correlation effects in these materials. We present a method based on first principles which uses our previously developed dielectric response model to place correlation in the interacting electron gas and electron interactions with the crystal potential on an equal footing. We will apply this method to calculations on NiO and FeO. We will investigate the effects of localized correlation on the band structure, how the excitation of localized electron-hole and hole-hole pairs affect the electron emission, the properties of collective modes such as plasmons in a strong crystal potential, and the loss processes an electron undergoes as it interacts with the material. These studies will naturally lead to an investigation of corrosion on an atomic scale. We will develop procedures to evaluate the important corrosion mechanisms, especially vacancy formation and how certain impurities may inhibit or promote corrosion.

I. Introduction

This proposal represents a continuation of research being conducted under Grant No. AFOSR-80-0023. We anticipate no major change in the direction of the research during the second year of the grant period and have outlined in this proposal only those additions and improvements in the methods necessary to accomplish this work. The reader should refer to the original proposal for further information on the quantities we investigate. We have made one addition to this work which we will explore further in the future and which is of vital interest to the Air Force. That is the nature of the corrosion process on the iron and nickel surfaces. This study is a natural addition to our investigation of the oxide structure. The microscopic theory of the corrosion process is quite incomplete, one reason being a lack of understanding of microscopic probes of systems with defect and vacancy structures. We will discuss how our work can be extended to these systems.

The great success of the one-electron theory in describing many of the electronic properties of materials make it and the concepts of energy band theory the starting point for most studies of materials. In this model the concept of correlation usually refers to effects beyond those due to the interaction of the electrons with their averaged self-consistent field. The averaged self-consistent field is most often described in the Restricted Hartree Fock (RHF) approximation.

Most of the approaches used to correlate the band structure¹ remain in the framework of the one-electron theory. Many times that theory is inadequate to describe some very interesting properties of systems. For example, in narrow band materials the final state energy of an optically excited electron depends on the initial state from which it was excited; this effect is ignored in the band theory limit. What one needs is a distinct determination of properties for

each many-electron state rather than an average as in the band theory limit. In addition the collective excitations of the system, such as plasmons, which are most often calculated in an electron gas model, could be strongly affected by the periodic lattice potential and could even form plasmon bands. The electron energy loss structure and valence band photoemission are likewise strongly affected by the localized nature of the holes created by these processes. What one needs for the solid-state system is a method which allows inclusion of the terms from each configuration which are most important for a given property at a given energy without requiring a separate SCF calculation or the mixing of a large number of configurations. The dielectric response theory, presented in the original proposal and discussed further in this one, is such a method which also has the advantage that it automatically chooses the most important electron states for a particular excitation from the set given it.

The narrow band materials we are studying are the transition metal oxides NiO and FeO. The transition metal oxide group displays a wide range of magnetic, electric, optical, and elastic properties. This range of properties allows great flexibility in the design of catalysts, optical and electrical devices, and in materials applications. The partially filled d-bands are the distinguishing feature of transition metal chemistry. These bands are relatively narrow, but they are overlapped by the next higher s-band causing a great deal of s-d hybridization. On the other hand in some transition metal compounds, such as many of the oxides, the bonds are mostly ionic and the highest metallic s-band is unoccupied. In this case the highest s-band moves away from the partially filled d-band. Then the s-d hybridization is much less and the d-band is quite narrow. In fact, the d states for these materials are sufficiently localized that configurations with d-electrons uniformly distributed at the ion centers have lower energies than those with excess d electrons at a given site

due to the extra intraatomic repulsion U in the latter case. These materials, which from the band structure ought to be metals or semi-metals, are in fact very good insulators called Mott insulators. This significant result cannot be obtained from the usual band theory.

The corrosion of narrow band materials appears to proceed by cation transport associated with the defect structure.^{2,3} The oxides are usually non-stoichiometric and cation deficient. The nature of the vacancy distribution and the location of possible impurities significantly affects the diffusion. Vacancy clusters which may migrate without dissociating are now thought to provide a great deal of the ion transport,³ but a microscopic theory has yet to be developed.

In the past most theories of corrosion have been phenomenological in nature. Experiments commonly deal with quantities such as diffusion rates, neutron diffraction, and the thermodynamic properties of the oxide, but there are few experiments dealing with the microscopic environment of the migrating cation. Recent "atomistic" theories of corrosion^{2,3} are now showing the phenomenological approach to be inadequate and have revealed the importance of vacancy clusters. Experiments such as optical or ultraviolet absorption, electron loss spectroscopy, photoemission, and Auger spectroscopy are needed to give important information about the local environment of the vacancies. But to understand these results detailed calculations of the excitation structure and correlated band structure would be needed. In Sec. VII, we will discuss how our methods for periodic systems will be extended to defect systems and how this information can be obtained.

In the following sections we will discuss an approach to simplify greatly the excitation structure and correlation calculations by converting our localized orbitals to Wannier functions. The procedure for fitting the Wannier

function with an appropriately chosen set of Gaussians is outlined in Sec. II. In Sec. V. We discuss how our fitting procedure can also be used to fit the charge density and exchange potential in the X- α model so that we can calculate the band structure in terms of Gaussians. We can then apply the very efficient techniques of quantum chemistry for calculating multi-center two electron integrals. The X- α procedure gives good results for band gaps, band widths, and densities of states for many systems. It will be a good starting point for our calculations which involve localized states and thus go beyond the one-electron picture.

II. An Alternative to Local Orbitals: Wannier Functions

Up to this point we have done calculations of the polarization response matrix $\underline{\Pi}(q, \omega)$ and other quantities describing the dynamical response or correlation of a system directly in our local orbitals basis set.¹ The matrices necessary to transform these quantities to the appropriate Bloch basis are rather complicated. More importantly, the partitioning of the basis into occupied and unoccupied sets of bands is not fulfilled for the local orbitals since they contribute more or less to all the bands so that, for example, the matrix equation for excitations between bands is much larger than if the states were partitioned. It would be quite useful for us to deal with orbitals which are labelled for particular bands, as the Bloch functions are, but which are localized. An easily derived set of such orbitals would be

$$a_n(\vec{r}) \equiv \frac{1}{\sqrt{N}} \sum_{\text{BZ}} \psi_{nk}(\vec{r}) \quad (2.1)$$

where N is the number of unit cells and n is the band index.

The orbitals of Eq. (1) are in fact Wannier functions⁴, and, if the Bloch functions are orthonormal, have the property

$$\langle a_n(\vec{r}-\vec{R}_n) | a_{n'}(\vec{r}-\vec{R}_{n'}) \rangle = \delta_{nn'} \delta_{\vec{R}_n \vec{R}_{n'}} \quad (2.2)$$

It can be shown that the Wannier functions are localized and in the case of simple bands decay exponentially at large r . Even though Wannier functions have been used extensively in the energy band theory of solids since their introduction in 1937,⁵ few quantitative calculations have been made using them. Two computational difficulties that arise are that the Wannier functions no longer decay exponentially for a hybridized band complex unless functions over the entire complex are mixed and that they are orthogonal on different sites so that their tails have complicated oscillations. In this

section we will show how these difficulties are overcome within the framework of a local orbitals basis set so that we can fit the Wannier functions in a straightforward manner using a representation of Gaussians.

The exponential decay for Wannier function of simple bands is related to the analyticity of the Bloch functions $\psi_{nk}^{\vec{r}}$ throughout the Brillouin zone.⁶ Since composite bands are multivalued with branch points or cuts, the Wannier functions of these bands no longer decay exponentially. However, the non-exponentially decaying part of these functions could be cut off at large distance and only Bloch waves and energies in small region of k-space near the band crossings would be much affected.^{4,7} Since the quantities of interest to us always involve sums in k-space, these inaccuracies would be smoothed over and not contribute much. In our case we can accomplish the wave function cutoff by merely choosing a set of predetermined expansion coefficients $C_{n\alpha}^{\vec{k}}$ for a given band which is single-valued and analytic. Then our $\psi_{nk}^{\vec{r}}$ must also be analytic, and its Wannier function decays exponentially.

Des Cloiseaux⁷ has shown how to deal with the problem of orthogonality of Wannier functions. One may construct them from a set of localized, non-orthogonal orbitals f_n with the same point group symmetry as a_n by writing,

$$a_n^{\vec{r}} = \sum_{n',a} f_{n'}(\vec{r}-\vec{R}_a) d_{n'n}(\vec{R}_a) \quad (2.3)$$

where

$$d_{n'n}(\vec{R}_a) = \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_a} G_{n'n}^{-\frac{1}{2}}(\vec{k})$$

$$G_{n'n}(\vec{k}) \equiv \sum_{R_a} \langle f_{n'}(\vec{r}), f_n(\vec{r}-\vec{R}_a) \rangle e^{i\vec{k}\cdot\vec{R}_a}$$

For an exponentially decaying a_n , the f_n would be a smooth, localized function. Of course we already have a set of local orbital ϕ_α which fulfill the role of the f 's since

$$a_n^L(\vec{r}) = \sum_{k, \alpha, R_a} e^{i\vec{k} \cdot \vec{R}_a} C_{n\alpha}^{\vec{k}} \phi_\alpha(\vec{r} - \vec{R}_a), \quad (2.4)$$

where $C_{n\alpha}^{\vec{k}}$ is a Bloch expansion coefficient. The index α , however, runs over the whole set of local orbitals. We really only need an expansion in f_n , which runs over the band complex of interest (for the example of TiO considered in Sec. VI, we need only 10 orbitals instead of the 40 local orbitals which span the entire band structure). Since we could not generate all the two-electron integrals necessary for the full local orbital basis set, we would have to truncate that set anyway. We can think of the restricted number of f_n 's as an optimally truncated basis set.

We may construct the f_n 's in the following way. We assume

$$f_n(\vec{r} - \vec{R}_a) = \sum_i T_{ni} \phi_i(\vec{r} - \vec{R}_a). \quad (2.5)$$

In general the expansion in Eq. (2.5) must be over sites as well, but we assume there is sufficient variability in the set ϕ_i to restrict it to site \vec{R}_a . The coefficients T_{ni} are variational parameters which may be found by minimizing

$$I = \int \left[a_n^F(\vec{r}) - a_n^L(\vec{r}) \right]^2 d\vec{r} \quad (2.6a)$$

We can get the most localized functions possible by also requiring

$$\int f_n^2(\vec{r}) r^2 d\vec{r} = \text{minimum}. \quad (2.6b)$$

which can be introduced into the variational equation by using Lagrange multipliers. From Eqs.(2.3) and (2.5) we see that the coefficients T_{ni} appear in f_n and $d_{n'n}$. The dependence in $G_{n'n}^{-\frac{1}{2}}$ is complicated, but for our

localized functions f_n we may use the Löwdin expansion⁸

$$d_{\nu',\nu} = \delta_{\nu',\nu} - \frac{1}{2} S_{\nu',\nu} + \frac{3}{8} S_{\nu',\nu''} S_{\nu''\nu} + \dots \quad (2.7)$$

$$\nu \equiv (n, R_a) \quad f_{\nu}(\vec{r}) \equiv f_n(\vec{r} - \vec{R}_a)$$

with the overlap integrals

$$S_{\nu',\nu} = \langle f_{\nu'}, f_{\nu} \rangle (1 - \delta_{\nu',\nu})$$

which exclude onsite overlap. Then we have

$$\frac{\delta d_{\nu',\nu}}{\delta T_{ni}} = -\frac{1}{2} O_{i',i} T_{n',i'} (1 - \delta_{\nu',\nu}) + \dots \quad (2.8)$$

$$\frac{\delta f_{\nu}}{\delta T_{ni}} = \phi_i(\vec{r} - \vec{R}_a)$$

where

$$O_{i',i} = \langle \phi_{i'}(\vec{r} - \vec{R}_a), \phi_i(\vec{r} - \vec{R}_a) \rangle.$$

The minimization procedure yields a set of simultaneous equations for the T_{ni} which can be solved analytically. Owing to the dependence in $d_{\nu',\nu}$, the equations are non-linear and must be iterated to convergence. The procedure of minimizing Eqs. (2.6) to find the best fit with a set of Gaussians has been developed by Sambe and Felton⁹ and improved by Dunlap *et. al.*,¹⁰ We shall discuss the introduction of the Wannier functions and their optimally localized f 's into our models for the dielectric response and correlation in the following sections.

III. The Polarization Response Matrix in the Wannier Representation.

Now that we have shown in the last section how we may calculate our Wannier functions a_n and their orbitals f_n , we may proceed to reveal how the a_n 's simplify the construction of the polarization matrix. We recall that under certain approximations the equation for the polarization response function reduces to a Dyson-like equation.¹¹

$$\underline{\Pi}(\vec{q}, \omega)^{-1} \vec{C}(\vec{q}, \omega) = \Lambda(\vec{q}, \omega) \vec{C}(\vec{q}, \omega) \quad (3.1)$$

with

$$\underline{\Pi}(\vec{q}, \omega)^{-1} = \underline{\Pi}^0(\vec{q}, \omega)^{-1} - \underline{K}(\vec{q}, \omega). \quad (3.2)$$

We look for the excitation energies of the system, which are solutions for which $\Lambda(\omega) = 0$. The matrix \underline{K} contains Coulomb matrix elements describing electron-hole interactions, and in a single particle model for the band structure the matrix $\underline{\Pi}^0(\omega)$ is just the familiar polarization response function of Ehrenreich and Cohen.¹² In the Wannier representation

$$\Pi_{\omega\omega'}^0(\vec{q}, \omega)^{-1} = \frac{1}{N^2} \sum_{\vec{k}} e^{i(\vec{k}+\vec{q}) \cdot \vec{R}_a} \delta_{n_1 n_1'} \delta_{n_2 n_2'} X^0(n, k, n_2 k+q; \omega)^{-1} e^{-i(\vec{k}+\vec{q}) \cdot \vec{R}_a'} \quad (3.3)$$

$$\omega = \{n_1 n_2, R_a\}$$

where

$$X^0(n_1 \vec{k}, n_2 \vec{k}+q; \omega)^{-1} = f_{n_1 \vec{k}} (1-f_{n_2 \vec{k}+q}) \{\omega - E_{n_2 \vec{k}+q} + E_{n_1 \vec{k}}\} \\ - f_{n_2 \vec{k}+q} (1-f_{n_1 \vec{k}}) \{\omega - E_{n_2 \vec{k}+q} + E_{n_1 \vec{k}}\}, \quad (3.4)$$

and $E_{n\vec{k}}$ and $f_{n\vec{k}}$ are the energy and occupation number for Bloch state $n\vec{k}$.

We may contrast Eqs. (3.3-4) with the result in the local orbitals basis

$$\Pi_{ss'}^0(\vec{q}, \omega)^{-1} = \sum_{n_1 n_2 k} T_s^*(n_1 \vec{k}, n_2 \vec{k}+q) X^0(n_1 \vec{k}, n_2 \vec{k}+q; \omega)^{-1} T_s(n_1 \vec{k}, n_2 \vec{k}+q) \quad (3.5)$$

$$T_s(n_1 \vec{k}, n_2 \vec{k} + \vec{q}) = \frac{1}{N} \sum_{\ell \ell'} e_{\ell}(n_2 \vec{k} + \vec{q})^* e_{\ell'}(n_1 \vec{k})$$

$$e^{-i(\vec{k} + \vec{q}) \cdot \vec{R}_b} \sum_{cd} S_{0 \ell, cj} e^{i(\vec{k} + \vec{q}) \cdot \vec{R}_c} S_{0 i, dl'} e^{i\vec{k} \cdot \vec{R}_d} \quad (3.6)$$

$$s = \{j i i b 0\}$$

The construction of Π^0 is greatly simplified in the Wannier representation, but that is not all. Π^{0-1} contains a term $\omega \underline{M}$ where \underline{M} is an hermitian matrix. In order to cast Eq. (3.1) as an eigenvalue problem, we must multiply Eq. (3.1) by \underline{M}^{-1} . Inverting such a large matrix (e.g., for TiO valence band excitation including next nearest neighbor interactions, \underline{M} has a dimension over 650.) is quite time-consuming. Our studies show that \underline{M} does not block readily either, so that techniques which find a solution in a main block and then consider the effects of sub-blocks as perturbations¹³ do not converge very fast. However, in the Wannier representation \underline{M} is block diagonal in the band indices $n_1 n_2$ and the blocks only range over the lattice vector \vec{R}_a . In this case we must only invert blocks of dimension 19 if we include just the next nearest neighbor shells.

The two-electron integrals in \underline{K} are now in terms of Wannier functions a_n . Since we will expand the local f 's in Gaussians for which multicenter two-electron integrals can be computed analytically and quite economically, we will first calculate the matrix \underline{K} in terms of the f 's and then transform it to the Wannier basis. In either representation, because of the method of Sec. II, the number of basis functions needed is the same as the number of bands in the complex. Since the a_n 's are as localized as possible by construction, we will not need many neighbors in the interaction calculation and matrices like \underline{K} should be reducible to sub-blocks.

IV. Collective Modes and Correlation.

Now that we have a better procedure for calculating Π , we will see that it also makes the calculation of collective effects simpler. The collective excitation energies as well as the electron-hole excitation energies are given by the poles of

$$\epsilon^{-1}(\vec{q}, \vec{q}; \omega) = V(\vec{q}) \Pi(\vec{q}, \vec{q}; \omega) \quad (4.1)$$

where

$$\begin{aligned} \Pi(\vec{q}, \vec{q}; \omega) &= B_{ij}(\vec{q}) \Pi_{ij,kl}(\vec{q}, \omega) B_{kl}(\vec{q}), \\ B_{ij}(\vec{q}) &= \langle \phi_i | e^{-\vec{q} \cdot \vec{r}} | \phi_j \rangle. \end{aligned} \quad (4.2)$$

As \vec{q} approaches zero, the electron-hole excitations disappear, but the collective modes remain as well-defined structures called plasmons. Now for a periodic solid, plasmon bands may form.¹⁴ Also, if the plasmon energy lies in the region of inter-band transition energies, excitations via umklapp processes will damp the plasmons. There might even be quite different plasmon dispersions and damping in the same material if, for example, one has both narrow and wide valence bands. No detailed calculation has ever been done which includes band structure effects, though calculations have been done which treat the lattice potential as a perturbation.^{14,15}

The \vec{q} -dependence appears in both \underline{K} and $\underline{\Pi}^{0-1}$ (see Eq. 3.1), but the dependence of $\underline{\Pi}^{0-1}$ is more complicated, at least in the local orbitals basis; as indicated by Eqs. (3.5-7). The quantities $\underline{\Pi}^{0-1}$ and \underline{K} must be constructed and the excitation spectrum found at each \vec{q} . By contrast the optical absorption need only be calculated at $\vec{q}=0$. We see from Eq. (3.3), however, that in our Wannier representation the construction of $\underline{\Pi}^0(\vec{q}, \omega)^{-1}$ is much simpler, and in particular, the matrix inversion we must do at each \vec{q} to set up the eigenvalue

problem is easier.

For correlation the use of Wannier functions causes a similar reduction in effort. A useful example is the second order correction to the Hartree Fock (HF) band structure. This correction has also been found to give reasonable estimates of correlation for atomic systems,^{16,17} and we will suggest further uses for it in Sec. VIII. The second order self-energy is (neglecting the exchange or "ladder diagram" contribution¹⁶)

$$\begin{aligned} \Sigma_{n,n_2}^2(\vec{k}, \omega) = & \sum_{\substack{m', m \\ \ell, \vec{k}', q}} V_{n_1 \vec{k} m' \vec{k}+q, \ell \vec{k}' +q} \vec{k} \vec{m} \vec{k}' \\ & \times \frac{V_{m \vec{k}' \ell \vec{k}' +q, m' \vec{k}+q} n_2 \vec{k}}{\omega + E_{\ell \vec{k}' +q} - E_{m \vec{k}'} - E_{m' \vec{k}+q}} \quad (4.3) \\ & + \sum_{\substack{m' \rightarrow \ell' \\ \ell, k, q}} (m' \rightarrow \ell') \frac{1}{\omega + E_{m \vec{k}'} - E_{\ell \vec{k}' +q} - E_{\ell' \vec{k}+q}} \end{aligned}$$

where $(m' \rightarrow \ell')$ signifies that the second set of V 's is the same as the first except that m' is replaced by ℓ' . The matrix elements of the Coulomb interaction $V(\vec{r}-\vec{r}')$ are over HF Bloch states, and m always refers to particle states ($E_m > E_F$) while ℓ always refers to hole states ($E_\ell \leq E_F$).

The transformation of Eq. (4.3) to the Wannier representation requires removal of the factors like $e^{i\vec{k} \cdot \vec{R}_1}$ from the sum and the formation of the sum

$$\frac{1}{N} \sum_{\vec{k}' q} \frac{e^{-i(\vec{k}' + q) \cdot (\vec{R}_a - \vec{R}_a')} \cdot e^{i\vec{q} \cdot (\vec{R}_b - \vec{R}_b')}}{\omega + E_{\ell \vec{k}' +q} - E_{m \vec{k}'} + E_{m' \vec{k}+q}}$$

Then the V 's are matrix elements over the Wannier states. We see that the sums over band index in Eq. (4.3) are limited to states above or below the Fermi level, and this restriction will reduce computational effort. More importantly our Wannier functions are restricted to the band complex which

contributes most strongly to correlation in a given energy region of the band structure. We will see that this group of bands can be much smaller than the total number of bands.

V. Band Structure Calculations.

Our method for investigating excitation structure and correlation effects requires a good SCF calculation to obtain a starting band structure and set of Bloch states. The Bloch states must be expanded in a well-localized set of basis functions (not necessarily local orbitals), and these basis functions must describe the states in the energy range of interest, even if that energy range goes beyond the occupied orbitals. It is difficult to find calculation which fulfill these last two criteria. The SCF band structure need not be HF; local exchange methods which include correlation can also be used since we can modify the self-energy expression to correct for the difference from HF.¹ In fact recent calculations show the X- α local exchange method gives good results for TiO bulk and surface states, and we can use the methods outlined in Sec. II to make the local exchange calculations economical. We are therefore preparing to generate our own SCF band structures.

In the SCF-X α model, the charge density contributes to two potential terms,¹⁹

$$V_c(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}', \quad (5.1)$$

$$V_{x\alpha}(\vec{r}) = -3\alpha \left[\frac{3}{8} \Pi \right]^{\frac{1}{3}} \int \frac{\rho(\vec{r}')^{\frac{1}{3}}}{|\vec{r}' - \vec{r}|} d\vec{r}'. \quad (5.2)$$

If the coulomb term is constructed in the usual manner with the charge density constructed from orbitals expanded in atom-centered Gaussians, the matrix elements of V_c can be done analytically but contain four-center integrals. The X- α potential, however, cannot be expanded analytically at all because of the $\rho^{\frac{1}{3}}$.

Sambe and Felton⁹ suggest the substitution

$$\rho(r) = \sum_i a_i h_i(r), \quad (5.3)$$

$$-3\alpha \left[\frac{3}{8} \Pi \rho(r) \right]^{\frac{1}{3}} = \sum_j b_j g_j(r). \quad (5.4)$$

The h_i and g_j denote separate sets of Gaussians called auxiliary functions which are chosen to describe the different ranges of ρ and $\rho^{\frac{1}{3}}$. The wave functions are expanded in another set of Gaussians, and the resulting energy expressions involve no more than three-center integrals.

The expansion coefficients a_i and b_j are found by fitting the charge density using a technique like the one in Sec. II. However, since the $\rho^{\frac{1}{3}}$ cannot be determined analytically, a mesh of sample points must be used for the fitting so the following expression is minimized,

$$\sum_I \int_{V_I} \left[c \rho_I(r)^{\frac{1}{3}} - \sum_j b_j g_j(r) \right]^2 d\vec{r} + \sum_{\mu} W(\vec{r}_{\mu}) \left[c \rho(\vec{r}_{\mu})^{\frac{1}{3}} - \sum_j b_j g_j(\vec{r}_{\mu}) \right]^2 \quad (5.5)$$

where $c \equiv -3\alpha(3/8\pi)^{\frac{1}{3}}$, V_I is the spherical core volume around nucleus I , $\rho_I^{\frac{1}{3}}$ is the spherically averaged $\rho^{\frac{1}{3}}$ in V_I , and $W(\vec{r})$ is a weight function.

Sambe and Felton⁹ obtain a good fit to ρ and $\rho^{\frac{1}{3}}$ in their molecular calculations using sets of atom-centered $1s$ Gaussians. An additional set of centers not at lattice points was used in the TiO surface slab calculation.¹⁸ The choice of sampling points \vec{r}_{μ} must be made carefully. Dunlap¹⁰ et. al., have come up with a systematic way to sample which gives stable results as atomic spacings are varied. One distinct advantage of the above method over scattered-wave $X-\alpha$ methods²¹ is that in the latter methods spherically averaged solutions around each atom are joined to plane wave solutions in the interstitial region. This muffin tin approximation leads to inaccuracies in the band structure which do not occur in the present method.

With our approach we will be able to generate self-consistent bulk band structures and Bloch states with basis sets of our own choosing. These results will be interesting in their own right and will be the basis for our excitation structure and correlation calculations. In addition we can do

calculations to be used in our analysis of vacancy and surface defect structures. These calculations will provide the background environment in which we will embed our cluster describing the vacancy or defect.

VI . Summary of Progress.

During the first seven months of this research our main concern has been twofold. We have wanted to formulate a simplified method to calculate the excitation structure and electronic response in an optimized basis, and we have wanted to set up our own self-consistent band structure calculations to be used as a starting point for our correlation and excitation calculations.

We have settled on a set of Wannier functions as the best basis because of their localized nature and their dependence on the band index. As we showed in Sec. II, the Wannier functions may be expanded in a set of local functions which are chosen to be optimally smooth and localized. We are now studying the properties and localization of the transformed quantities which enter into the construction of the Wannier functions a_n . For example, Eq. (2.4) shows that the quantity

$$g_{n\alpha}(\vec{R}_a) = \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_a} C_{n\alpha}^{\vec{k}} \quad (6.1)$$

enters the Wannier function calculation. The rate at which $g_{n\alpha}$ falls off at large \vec{R}_a determines the decay rate of a_n and the number of sites that should be included in the excitation and correlation calculations. We have developed methods to solve Eq. (6.1) using fast Fourier transforms and are studying the properties of $g_{n\alpha}(\vec{R}_a)$ for the TiO band structure.

We are now adding the second-order correlation correction described in Sec. IV to the HF energy bands of TiO calculated by Jennison and Kunz. These bands turn out to give a density of states quite different from the most recent photoemission spectra. With our calculation we hope to settle the question of whether or not the difference between the HF result and experiment is due to correlation effects. If the difference is a correlation effect, it will be the first time such an ab-initio calculation has been made for a solid state system

and the first time correlation has been shown to cause such a large change.

We may indicate the elements of the calculation in the Wannier basis by outlining the TiO calculation. There are 9 bands in the valence-conduction band cluster, according to the calculation of Ern and Switendick. Three bands are fully occupied, three are partly occupied, and three are unoccupied (if we neglect a very small dip below the Fermi energy for one band). Thus we have an immediate partitioning and need consider only 6 bands for the occupied states and 6 bands for the unoccupied states. We are including up to next nearest neighbors in the calculation which means 19 atom sites including the origin. This means, for example, that we must invert 36 (19x19) matrices in the excitation calculation (see Sec. III) instead of one huge (684x684) matrix. The partitioning of bands and the number of lattice sites used is the same for both the excitation and correlation calculations.

To relieve our second concern, we are now investigating the LCAO-X α band structure formulation. We are applying the fitting procedure of Dunlap, for which we have computer codes, to the ρ and $\rho^{\frac{1}{3}}$ terms entering the SCF equations. We are also receiving from Dunlap computer codes which can be used to treat surface electronic structure. Our first calculations will be the unpolarized bulk band structures for NiO and FeO. To these results we shall add up through the second order spin-dependent self-energy corrections. In general the spin-dependence may break the periodic symmetry of the system and the correlated states will exhibit local behavior. In this case our Wannier representation will be quite useful in describing the Hubbard bands which may form.

VII. Proposed Research

In the next year we will continue our study of correlation and collective modes and their effects on several experimentally measurable properties of NiO and FeO. We will use our LCAO-X α procedure developed as outlined in Sec. V to obtain bulk ground state properties of NiO and FeO. Then with the experience gained from our TiO calculations, we will find optimally localized sets of functions describing the Wannier states of the valence and conduction bands. In these calculations we will use the variational fitting method of Sec II.

We will calculate the excitations from the ground state in the Wannier basis. This representation will lead to a simpler structure for the optical absorption equations. We will also calculate the second-order self-energy corrections for NiO and FeO, as we did for TiO. These calculations, however, will be spin-dependent so that we can explore the formation of Hubbard bands. We also hope to look at the rich satellite structure which appears in the photoemission of these materials.

With the polarization response matrix obtained in the optical absorption calculation, we will first look at the formation of plasmons, what their dispersion is, and whether they form bands. This will entail calculating Π at several values of \vec{q} but with the simpler expressions for Π in the Wannier representation, these calculations are feasible. We will use $\Pi(\vec{q}, \omega)$ to calculate the full screened exchange as well.¹ This calculation will allow us to explore the effect of plasmons and multi-pair excitations on the correlated band structure. Finally, using Π we will want to develop a rigorous treatment of the Electron Energy Loss Spectra (EELS). We will start with an investigation of electron-hole interactions, which are quite important for NiO and FeO and for which a full interpretation is necessary to understand the EELS.

A final area we will begin exploring is the microscopic theory of corrosion. Here the defect nature of the solid is important, and we will need ideas we have been developing on the embedding of localized clusters of atoms in a periodic medium. The cluster will be useful for defects we believe to be localized, and the LCAO orbitals used will be compatible with our bulk basis sets.

Quite briefly, our approach divides the defective solid into a cluster including the defect and the rest of the solid except for the atoms in the cluster. The central assumption is that the effect of the defect is localized in the cluster so that the coefficients of the basis function on the sites outside the cluster are fixed at their bulk values. Thus we may write the density matrix for the system,

$$\underline{P} = \begin{pmatrix} \underline{P}^C & 0 \\ 0 & \underline{P}^F \end{pmatrix} \quad (7.1)$$

where \underline{P}^F is fixed at its bulk value and

$$P_{rs}^C = \sum_j a_{rj}^\dagger a_{sj} \theta(\epsilon_F^f - \epsilon_j) \quad (7.2)$$

the a 's are the expansion coefficients in the cluster basis and ϵ_F^f is taken to be the bulk Fermi energy.²⁰ The expression for the ground state energy of the system is

$$E_0 = \sum_i h_i P_{ii} + \frac{1}{2} \sum_{ij} W_{ij} P_{ij} \quad (7.3)$$

The W_{ij} contains the Coulomb and exchange matrix elements in the HF approximation or the coulomb and local exchange-correlation matrix elements in the X- α approach. The variation of E_0 with respect to the a 's, with the orthogonality condition imposed, yields

$$F^c \vec{a} = \epsilon \underline{S} \vec{a} \quad (7.4)$$

where \underline{S} is the overlap matrix and

$$\underline{F}^c = \underline{F}_o^c + \underline{F}_o^f - \underline{\Delta}^f . \quad (7.5)$$

The dimensionality of \underline{F}^c is now just the cluster dimension. \underline{F}_o^c is the Fock matrix for the cluster but depends on the a 's obtained in Eq. (7.4), \underline{F}_o^f is the Fock matrix of the bulk but in the cluster basis, and $\underline{\Delta}^f$ consists of those terms which must be removed from \underline{F}_o^f because they are already included in \underline{F}_o^c . An additional assumption made to obtain Eq. (7.5) is that interactions between the defect states in the cluster and the bulk states in the rest of the solid can be neglected.

Pisani²¹ has shown that Eqs. (7.4-5) result also from a partitioning of the Green's function into a space over the basis of the cluster and a space over the rest of the solid, if the same assumptions about the cluster-bulk interaction are made that we have made. However, we have shown that in addition the solutions of our equations variationally minimize the ground state energy.

In the future we will use our embedding procedure to study the formation and structure of defects and especially vacancies in our systems. The variational character of our method will be especially important for locating the most stable vacancy structures. We will study the effects of these structures on the optical absorption and photoemission spectra. Up to now, precise, microscopic probes such as these have not been used much in studies of the mechanism of corrosion, but they must be used in the future if we are to gain a microscopic view of the process.

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IX. Work Statement

The one significant addition to the work schedule outlined in the original proposal is the development of our own band structure codes using methods described in Sec. V. By the end of the present research period, we will be able to calculate bulk band structures for the transition metal oxides and convert the Bloch functions to a Wannier basis. In the future we will extend our method to surface calculations.

The tasks we have set for the second year are:

- Calculation of second-order correlation corrections to the NiO and FeO band structure.
- Investigation of the formation of Hubbard bands in the spin polarized band structure of these materials.
- Study of the effect of the strong crystal potential on the plasmon bands.
- Development of methods for investigating the electron energy loss structure.
- Ongoing study of cluster embedding procedures for applications to defects in NiO and FeO.

X. Interactions

During the period of this research we have had several interactions with people at other laboratories or universities which will continue to be fruitful in the ensuing year. We have continued our consultations with Dr. Frank Tobin at Johns Hopkins University on the problem of cluster calculations of transition metal oxides. We have incorporated several new features into the computer codes originally written by him. He is now also using these new features and in addition has helped us understand the powerful package for computing and sorting multicenter Gaussian integrals contained in the code which we will convert to our correlation calculations.

We have established and are maintaining contact with Professor Ronald Felton and Dr. Hideo Sambe of the School of Chemistry at Georgia Tech and with Dr. Brett Dunlap at the National Bureau of Standards regarding the LCAO X- α formalism. We are implementing Dunlap's improved fitting procedure on the Georgia Tech computer and will make the improved code available to Professor Felton's group. Felton, Sambe, and Dunlap are also providing advice on the use of the Gaussian fitting procedure for the charge density and exchange correlation terms in our bulk calculations; and our results for NiO and FeO will be of use to Dr. Dunlap, who is doing similar calculations on transition metal systems.

We are continuing our interaction with Dr. Dwight Jennison and have established contact with Dr. Peter Feibelman, both at Sandia Laboratories. Dr. Jennison is providing advice on the general problem of energy band calculations, and we are converting a band code developed by himself and Barry Kunz at the University of Illinois. Dr. Feibelman has given us insight into the Gaussian fitting procedure he used in calculating TiO bulk and surface band structures.

G-41-688

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

OFFICE OF
THE
COMPTROLLER

January 13, 1981

Ricky Bailey, 2 Lt., USAF,
Contract Negotiator
AFOSR
Bolling Air Force Base, D.C. 20332

Dear Lt. Bailey:
Enclosed is the Interim Financial Status Report (Form SF-269)
for Grant #AFOSR-80-0023 covering the period 10/1/79 - 9/30/80.

If you have questions or require additional information, please
let us know.

Sincerely,

David V. Welch, Manager
Grants and Contracts Accounting

DVW/BITS/jb
Enclosure
cc: Dr. M. W. Ribarsky
Dr. C. H. Braden
Mr. J. W. Dees
Mr. O. H. Rodgers ✓
Ms. Faith Costello
File G-41-688



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FINANCIAL STATUS REPORT

(Follow instructions on the back)

Air Force Office of Scientific Research

FEDERAL GRANT NUMBER
AFOSR-80-00

3. RECIPIENT ORGANIZATION (Name and complete address, including ZIP code)

Georgia Tech Research Institute
Atlanta, Georgia 30332

4. EMPLOYER IDENTIFICATION NUMBER

58-0603146

5. RECIPIENT ACCOUNT NUMBER OR IDENTIFYING NUMBER

G-41-688

8. PROJECT/GRANT PERIOD (See instructions)

FROM (Month, day, year)

10/1/79

TO (Month, day, year)

9/30/81

9. FROM (Month, day, year)

10/1/79

10.

STATUS OF FUNDS

PROGRAMS/FUNCTIONS/ACTIVITIES ▶	(a)	(b)	(c)	(d)	(e) Total Direct Costs
a. Net outlays previously reported	\$	\$	\$	\$	-0-
b. Total outlays this report period					17,017.28
c. Less: Program income credits					
d. Net outlays this report period (Line b minus line c)					17,017.28
e. Net outlays to date (Line a plus line d)					17,017.28
f. Less: Non-Federal share of outlays					3,000.00
g. Total Federal share of outlays (Line e minus line f)					14,017.28
h. Total unliquidated obligations					-0-
i. Less: Non-Federal share of unliquidated obligations shown on line h					
j. Federal share of unliquidated obligations					-
k. Total Federal share of outlays and unliquidated obligations					14,017.28
l. Total cumulative amount of Federal funds authorized					15,486.00
m. Unobligated balance of Federal funds					1,468.72

11. INDIRECT EXPENSE

b. TYPE OF RATE (Place "X" in appropriate box) PROVISIONAL PREDETERMINED FINAL FIXED

c. RATE 10/1/79-6/30/80 76% BASE S&W as of 7/1/80 73%

d. TOTAL AMOUNT 10,642.89

e. FEDERAL SHARE 8,362.89

13. CERTIFICATION

I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.

SIGNATURE OF AWARD OFFICIAL

David V. Welton

TYPED OR PRINTED NAME
David V. Welton
Grants & Contracts

12. REMARKS: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.

Dr. M. W. Ribarsky

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "Correlation and Collective Modes in Narrow Band Materials: NiO and FeO".		5. TYPE OF REPORT & PERIOD COVERED Interim Oct 1, 1979 to Sept. 30, 1980
7. AUTHOR(s) Martin W. Ribarsky		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Georgia Institute of Technology School of Physics, Atlanta, Ga. 30332		8. CONTRACT OR GRANT NUMBER(s) AFOSR-80-0023
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research Bolling AFB, Bldg. 410 Washington, D.C. 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE Feb. 1, 1981
		13. NUMBER OF PAGES 28
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; Distribution unlimited.		
17. DISTRIBUTION STATEMENT (of this abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Transition metal oxides, correlation, plasmons, interband excitations, energy loss spectra, superconductivity, band structure.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A procedure has been developed for studying the effects of electronic correlation on the band structures of narrow band materials. This procedure is being applied to TiO, FeO and NiO. The procedure will also be useful for studying the plasmon structure in the presence of a strong lattice potential and the response of electrons in the material to an optical or electronic probe. The experimental electronic loss structures for bulk and oxidized transition metals is analyzed in terms of this model. The effects on		

superconductivity of the dynamical response of electrons and especially coupling via plasmons or excitons is being studied for Cu_2O . It is shown that there may be a connection between experiments on copper oxides which show nearly complete shielding of electric fields and experiments which show excitons in the oxide may obey Bose-Einstein statistics. More careful calculations for this and other transition metal oxides are discussed.

I. Introduction

The background for most of the work described in this report has been given previously and no attempt is made to repeat it here. The reader who wants further details should refer to the original or continuation proposals entitled "Correlation and Collective Modes in Narrow Band Materials: NiO and FeO," under Grant No. AFOSR-80-0023. The progress in this research during the past year is described in Section III. An important new component of our studies of electronic excitations and collective modes is work on the effect of plasmons and excitons on superconductivity in transition metal oxides which is described in Section III-C.

II. Research Objectives

The overall objective of this research is to study the effects of electronic excitations, especially plasmons and interband excitations, on the properties of materials for which these effects are significant. The materials we have chosen are narrow band systems, such as the transition metal oxides. For these materials, it is necessary to emphasize their localized properties and, especially, strong electron-lattice interactions in constructing the correlation and response functions. In the first year of this work, we have set up this description of the electronic structure in terms of a local orbitals approach and have begun some calculations.

Our studies of electronic correlation and its effect on the band structure have begun with TiO. We will continue with investigations of systems where the effects of electronic excitations are even stronger, such as FeO and NiO. For these systems interband excitations become quite prominent and complicate the optical or electron energy loss spectra. We will also continue our studies of collective modes for these systems, such as plasmons, in the presence of strong lattice interactions.

We are investigating the contributions of electronic excitations to quantities which can be measured experimentally. Presently we are analyzing the electronic loss structure of TiO and FeO. In the future we will extend this analysis to NiO and other narrow band systems. We will want to know how the loss structures due to plasmon and interband excitations behave in these materials, and we will want to develop methods for explaining the significant changes that occur in some cases when the surface is contaminated or the material is implanted with impurities. From these studies we hope to develop an important tool for explaining the effects of surface or bulk contamination on these systems.

We are investigating plasmon and exciton coupling in the establishment of superconductivity for narrow band systems. We will want to know how electrons coupled by these mechanisms shield external fields, and what effect the strong coupling has on the superconducting properties. We have begun studies on Cu_2O for which some interesting experimental evidence exists. In the future we will move to other transition metal oxides.

III. Progress

A. Correlation in Narrow Band Materials.

The effect of correlation on the band structure of a material is contained in the self-energy matrix $\underline{\Sigma}$. To find the correlated energy bands and wave functions, one solves the energy dependent matrix equation

$$\left[\underline{H}_0 + \underline{\Sigma}(\omega) \right] \vec{A}(\omega) = E(\omega) \vec{A}(\omega) \quad (3.1)$$

where \underline{H}_0 is, for example, a one-electron Hamiltonian such as Hartree Fock (HF) and ω is the frequency. Now in general we must diagonalize Eq. (1) to find the energy bands $E(\omega)$. However, if the diagonal terms in $\underline{H}_0 + \underline{\Sigma}$ are dominant, the correlated energy bands are just

$$E_{\vec{k}} = E_{\vec{k}}^{\text{HF}} + \underline{\Sigma}^D(\vec{k}, E_{\vec{k}}), \quad (3.2)$$

assuming that \underline{H}_0 is the HF Hamiltonian. The self-energy to second order in the coulomb interaction between Bloch states is

$$\begin{aligned} \sum_{n_1 n_2}^2 (\vec{k}, \omega) &= \sum_{\substack{m, m' \\ \ell, \vec{k}', \vec{q}}} V_{n_1 \vec{k} m' \vec{k}+\vec{q}, \ell \vec{k}'+\vec{q} m \vec{k}} \\ &\times \frac{V_{m \vec{k} \ell \vec{k}'+\vec{q}, m' \vec{k}+\vec{q} n_2 \vec{k}}}{\omega + E_{\ell \vec{k}'+\vec{q}} - E_{m \vec{k}} - E_{m' \vec{k}+\vec{q}}} \\ &+ \sum_{\substack{\ell, m \\ \ell, \vec{k}, \vec{q}}} (m' \rightarrow \ell') \frac{1}{\omega + E_{m \vec{k}} - E_{\ell \vec{k}'+\vec{q}} - E_{\ell' \vec{k}+\vec{q}}} \end{aligned} \quad (3.3)$$

where $(m' \rightarrow \ell')$ signifies that the second set of V's is the same as the first except that m' is replaced by ℓ' . Here V refers to the coulomb interaction,

and m always refers to particle Bloch states ($E_m > E_F$) while l always refers to hole states ($E_l < E_F$).

There is a great savings in computational effort to be had by converting Eq. (3.3) into a sum over Wannier states (for details see proposal for continuation of AFOSR-80-0023). This savings makes the solutions of Eqs. (3.1-3.2) possible. The transformation of Eq. (3.3) to the Wannier representation requires use of the relation

$$a_n(\vec{r}-\vec{R}_1) = \frac{1}{\sqrt{N}} \sum_{\text{BZ}} \psi_{n\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{R}_1} \quad (3.4)$$

between the Wannier and Bloch states where N is the number of unit cells and n is the band index. Thus we must remove factors like $e^{i\vec{k}\cdot\vec{R}_1}$ from the coulomb matrix elements in Eq. (3.3) so that we have the sum

$$\frac{1}{N} \sum_{\vec{k}'\vec{q}} \frac{e^{-i(\vec{k}'+\vec{q})\cdot(\vec{R}_1-\vec{R}_1')} e^{i\vec{q}\cdot(\vec{R}_2-\vec{R}_2')}}{\omega + E_{l\vec{k}'+\vec{q}} - E_{m\vec{k}'} + E_{m'\vec{k}+\vec{q}}} \quad (3.4')$$

Then the V 's are matrix elements over the Wannier states. We see that the sums over band index in Eq. (3.3) are limited to states above or below the Fermi level, and this restriction will reduce computational effort. More importantly our Wannier functions are restricted to the band, complex which contributes most strongly to correlation in a given energy region of the band structure. We will see that this group of bands can be much smaller than the total number of bands.

The effect of correlation on the valence bands of NiO and FeO is still not fully explained. Especially for NiO, the detailed structure and width of the d-band region is uncertain. We are planning on doing calculations of correlation corrections for these two materials, but first we have undertaken a calculation of \sum^2 in Eq. (3.3) for TiO. This material was the subject of some controversy a few years ago. An ab-initio Hartree Fock calculation by Jennison and Kunz¹

showed hybridized oxygen 2p and titanium 3d bands with no energy gap between them. These results differed sharply from local exchange calculations² which show a band gap of at least 2eV between the oxygen 2p and titanium 3d bands. Experimental X-ray photoemission results [by Ichikawa et al.³] for what was evidently TiO seemed to support the Jennison and Kunz calculation. However, later experiments⁴ showed that the Ichikawa samples must have oxidized to become TiO₂ and thus the d band structure in the XPS spectrum was missing. The correct TiO spectra⁴ had a band gap and were in agreement with the local density calculations. Subsequently, Kunz⁵ argued that the gap was due to correlation corrections neglected in the Hartree Fock calculation and asserted that relaxation would raise the d bands with respect to the p bands. Our calculation should test Kunz' assertion and will also provide an assessment of correlation effects.

We have included 9 bands in the TiO self-energy calculation which arise from the titanium 4s and 3d states and the oxygen 2p states. The other bands are well out of the valence - conduction band region, and we consider them to not contribute much to the self-energy near the Fermi surface. Except for a small region around the Γ point in the uncorrelated band structure where all the bands are above the Fermi level, three bands are occupied, three are unoccupied, and three are partly occupied. Thus by working in the Wannier representation, we have an immediate partitioning and need only consider 6 bands for the occupied states and 6 bands for the unoccupied states.

The self-energy calculation still requires a major computational effort in spite of the partitioning. We must evaluate the self-energy matrix at k-points throughout the Brillouin zone and at frequencies ω which cover the valence band energies for each k-point. In the TiO calculation we have chosen 10 frequency points at each k to evaluate $\Sigma(k, \omega)$ and must interpolate between the solutions of Eq. (3.1) to find $E_n = E(E_n)$ for a given band n. We have used every possible

symmetry to make the calculation manageable. The computation of the Wannier coefficients

$$C_{n\alpha}(\vec{R}_1) \equiv \sum_{\vec{k}} C_{n\alpha}^{\vec{k}} e^{i\vec{k}\cdot\vec{R}_1} \quad (3.5)$$

is greatly reduced by the fact that all rotations of the lattice set are equivalent and thus we need calculate only one $C_{n\alpha}(\vec{R}_1)$ for each shell of atoms. Furthermore, since our system has inversion symmetry, we can choose $C_{n\alpha}^{-\vec{k}} = C_{n\alpha}^{\vec{k}*}$ and thus Eq. (3.5) becomes

$$C_{n\alpha}(\vec{R}_1) = \sum_{\vec{k}} \text{Re} \left\{ C_{n\alpha}^{\vec{k}} e^{i\vec{k}\cdot\vec{R}_1} \right\} \quad (3.6)$$

The index α normally runs over all the basis functions in the basis set (e.g., 40 functions for TiO). This number of functions can be reduced to 9, the number of bands in our complex, by variationally choosing optimized basis functions.¹ However, since in this case we are using local orbitals which are in a sense already optimized for each band, we may simply choose the 9 local orbitals contributing most to the Bloch functions in our band complex. Once calculated, the $C_{n\alpha}(\vec{R}_1)$ is used to construct the coulomb matrix elements $V_{n_1R_1, n_2R_2; n_3R_3, n_4R_4}$ which appear with expression (3.4') in the construction of $\sum_{\vec{k}}^2 (\vec{k}, \omega)$. If we suppress the band indices n and basis functions indices α , we may write the coulomb matrix element as

$$V_{\vec{R}_1, \vec{R}_2; \vec{R}_3, 0} = \sum_{R_1 R_2 R_3 R_4} C(\vec{R}_1 - \vec{R}_1) C(\vec{R}_2 - \vec{R}_2) C(\vec{R}_3 - \vec{R}_3) \quad (3.7)$$

$$\times C(\vec{R}_4 - \vec{R}_4) V_{\vec{R}_1 - R_4, \vec{R}_2 - \vec{R}_4; \vec{R}_3 - \vec{R}_4, 0}$$

showing that we need only consider interactions which include the origin in our sum. Since the sum in Eq. (3.3) involves only certain combinations of occupied and unoccupied bands, not all matrix elements V' need be evaluated.

The final term appearing in \sum^2 is the expression appearing in (3.4'). This expression is similar in structure to the free electron polarization and thus we call it $\underline{\chi}(\vec{k}; \vec{R}_1, \vec{R}_2)$. We may write (3.4') as

$$\chi(\vec{k}; \vec{R}_1, \vec{R}_2) \equiv \sum_{\vec{k}', \vec{q}'} \chi(\vec{k}, \vec{k}', \vec{q}'; \vec{R}_1, \vec{R}_2) \quad (3.8)$$

again suppressing all band indices. To calculate every element in Eq. (3.8) would require a large amount of time and a massive amount of storage. Fortunately, not every element need be calculated since many are related by symmetry. The basic relation is

$$\chi(R\vec{k}, R\vec{k}', R\vec{q} ; \vec{R}_1, \vec{R}_2) = \chi(\vec{k}, \vec{k}', \vec{q} ; R^{-1}\vec{R}_1 R^{-1}\vec{R}_2) \quad (3.9)$$

where R is a rotation belonging to the rotation group of the crystal. In particular Eq. (3.9) indicates that we need calculate χ for only those \vec{k} values in an irreducible wedge of the Brillouin zone if we include all rotations of the other variables. Furthermore all rotation of the type $R'\vec{k} = R\vec{k}$ where $R\vec{k}$ has already been calculated need not be redone.

We have written computer codes to handle the above three elements which go into the \sum^2 calculation. These codes employ all the symmetry relations we have discussed. The calculation of the matrix elements V in Eq. (3.7) requires a major effort. We have used very efficient quantum-chemistry computer codes for calculating two-electron integrals over Gaussians.⁶ By fitting each local orbital to contracted sets of Gaussians, we are able to write the matrix elements V in terms of the Gaussian integrals.

The transformation in Eq. (3.7) is then carried out using quantum chemistry integral transformation programs for configuration interaction calculations.

We use only up to next nearest neighbors in the sum over \vec{R}_1, \vec{R}_2 in Eq. (3.3) for our TiO calculation since we find adding more shells of atoms do not affect the major results of the correlation calculation. We have only gotten results for TiO at $\vec{k}=0$ so far, but these indicate that the $\Gamma_{12}(d)$ $\Gamma_{15}(p)$ points move away from one another as Kunz expected. We will need to calculate other points in the zone, however, before we can make out the positions of the correlated bands. Our results indicate that the diagonal elements of $\sum_{\omega}^2(\vec{k}, \vec{\omega})$ give a qualitative picture of the correlation effects even without diagonalizing Eq. (3.1).

After we complete the TiO studies, we will use the procedures we have developed to study correlation in NiO and FeO. For these studies we will need self-consistent energy bands and wave functions in a Gaussian basis. We have implemented bands structure codes here due to Wang and Calloway⁷ and have modified them to accept two atoms per unit cell for these calculations.

B. Electron Energy Loss Structure of Clean and Oxidized Transition Metals.

The characteristic energy loss structure of a material provides a direct measure of the contributions from interband transitions and collective modes such as plasmons to the electronic excitation spectrum. The loss structure is altered by changes in bulk properties and also by surface modification or adsorption, particularly certain features which are quite sensitive to adsorption. In addition, since the loss structure provides a direct measure of plasmon energies and intensities, one can use it to test the basic understanding of these modes. These tests are especially important for systems with strong crystal potentials, such as the transition metals, where the plasmon behavior is not expected to follow the simple free-electron result.

Unfortunately there is qualitative disagreement between the experimental results themselves, and in addition the results have been given different interpretations so that very different energies for plasmons and interband transitions have been reported. To clean up the confusion, we have undertaken a careful reexamination of the loss structure for certain transition metals⁸ by analyzing a new series of measurements made by Keith Legg in our department. These measurements are for clean and oxidized polycrystalline iron samples and also clean and oxidized polycrystalline titanium samples for comparison. This analysis fits into the objectives of this program since it has allowed us to clearly identify plasmon structures and has provided data for comparison with the more basic theoretical calculations we have undertaken.

The characteristic loss structure measurements fall into two classes: measurements of losses suffered by electrons with energies of many kilovolts as they are transmitted through thin films and measurements of losses suffered by electrons with energies around 100eV as they are reflected from the material. The former experiments are dominated by electrons which do not undergo elastic scattering while the latter are more highly resolved but contain electrons which have been elastically scattered at least once. The two types of spectra for evidently clean Ti surfaces are shown in Fig. 1^{9,10}. There are large qualitative differences between the spectra at energy losses below 20eV, especially between the lower reflection spectrum and the transmission spectrum. The data from our measurement for clean Ti, which is a reflection measurement, is shown in Fig. 2a. It is more highly resolved than the reflection data in Fig. 1a, but it is qualitatively in agreement with it.

Our analysis of the clean Ti data is as follows. The peak around 5eV is undoubtedly a surface peak since it is quite sensitive to surface contamination and since it is less pronounced for higher primary electron energies as shown in Fig. 1a. The latter behavior is consistent with a surface excitation since

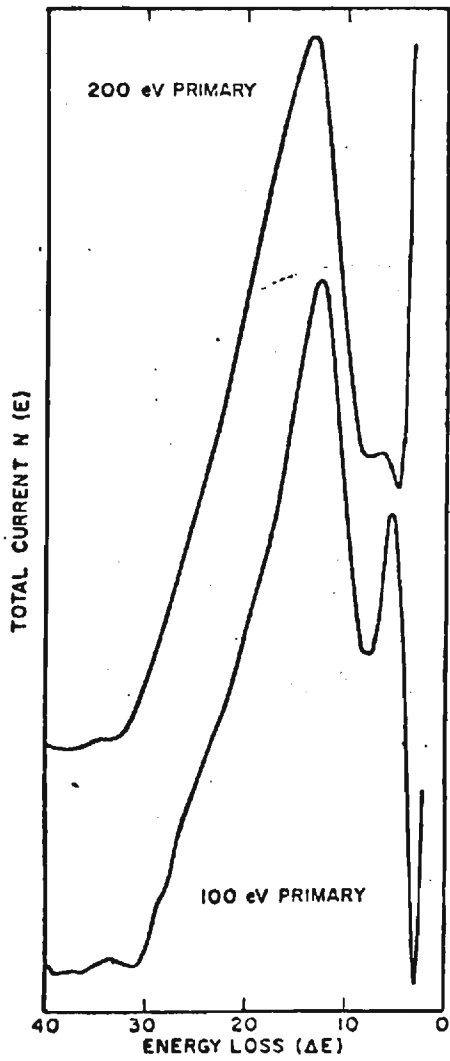


Fig. 1a Energy loss spectrum of clean titanium.

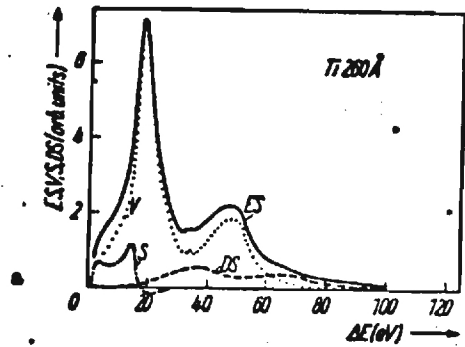


Fig. 1b Transmission energy loss spectrum (full curve) for a titanium film.

the mean free paths of the primary electrons are greater at higher energies which means the bulk signal would be enhanced with respect to the surface. We have identified this peak tentatively as a surface plasmon in agreement with Simmons and Scheibner⁹ (SS) since collective modes should be more prominent at this energy relative to interband excitations. However we need to confirm this identification with further measurements and analysis of how the intensity of this peak changes as the scattered electrons deviate from the specular direction. An intensity maximum at an angle away from the specular direction would indicate that the peak is a surface plasmon.¹¹ The prominent peak at about 10eV is the volume plasmon. The structure extending below this peak for about 20eV probably contains the second volume and surface-volume contributions postulated by SS, though our higher resolution data shows this structure to be less prominent than theirs. However, we also find a double peaks at about 35eV which also appears in the appropriate place in the iron data, and we identify this as the split ($\frac{1}{2}, \frac{3}{2}$) Ti 3p interband excitation.

The loss spectrum changes greatly upon adsorption of only a monolayer of oxygen. Most significantly, the surface peak disappears completely and new losses appear around 20eV and 45eV. The sensitivity of the spectrum to oxygen points out one of the causes for differences between the measurements of others workers. Only carefully cleaned Ti specimens in a vacuum of 10^{-8} Torr or less exhibited the true clean surface loss spectrum. We identify enhancement in loss structure at about 20eV as due to the O 2s interband excitation. A similar structure appears in the same place in oxidized iron. The peak at about 45eV is more mysterious. Transmission measurements for Ti (presumably partly oxidized)¹⁰ and TiO¹² show this structure quite prominently in both the loss spectrum and the imaginary part of the dielectric function ϵ_2 derived from a Kramers-Kronig analysis. Its appearance in ϵ_2 means it is not a collective mode

and must be an interband transition. A similar peak does not appear in the oxidized iron spectrum (see Fig. 3b), and there are no interband losses expected in this region. No strong explanation has ever been offered for this peak, though it could be a double interband excitation or an excitation to a higher conduction band. It seems possible that the structure is connected to the metal 3p peak since it appears about 9eV above this peak for both titanium and vanadium.¹³ It could be a double excitation involving the metal 3p and O 2p electrons, but it would be surprising that such a process would be stronger than the 3p excitation alone. We certainly need further theoretical analysis here and have undertaken an investigation of the calculated loss spectrum in this region.

But what about the differences between the transmission spectrum for Ti in Fig. 1b and our reflection spectra in Fig. 2? Fig. 1b most resembles Fig. 2b because the transmission sample undoubtedly had an oxide layer. However this does not explain the difference in energy between the volume plasmon peaks in the two experiments, and this difference is important in an analysis of collective modes in transition metals since the transmission spectrum places the plasmon near its free electron value while the reflection spectrum does not. Fig. 1a and also reflection experiments on vanadium done at several primary electron energies¹³ indicate that the plasmon peak moves to higher energy as the primary energy increases. These results imply that the differences between the plasmon peaks in the two spectra may be due to the great difference in primary energies used. A primary energy increase would lessen the lateral spread of the electron beam due to multiple scattering for a given target thickness. However, in the reflection experiment as the primary energy increases, the depth of the target probed increases also. We can do a crude calculation based on the plural scattering theory which should give us an estimate of the lateral spread for electrons transmitted through a 300 Å film at 35 keV and for reflected

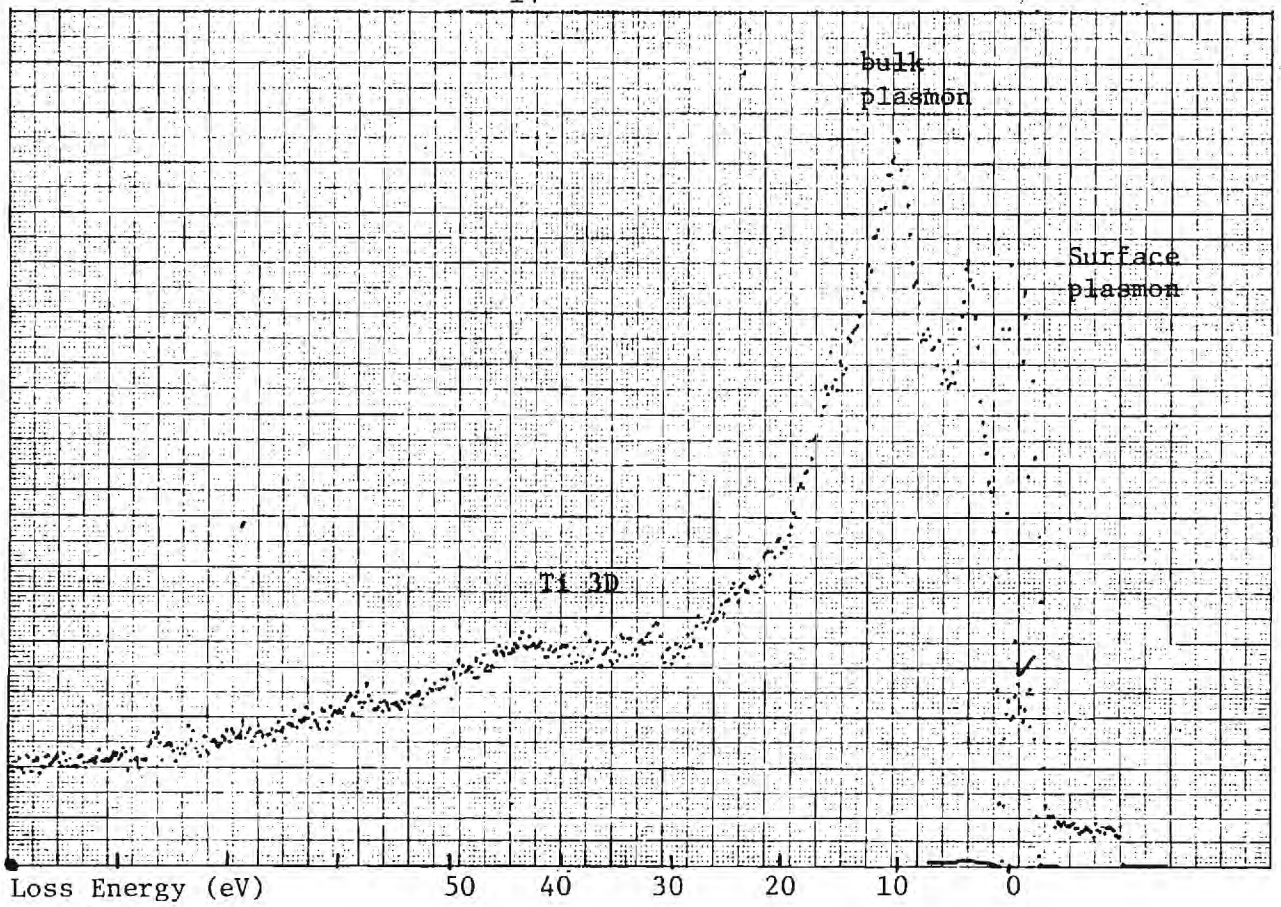
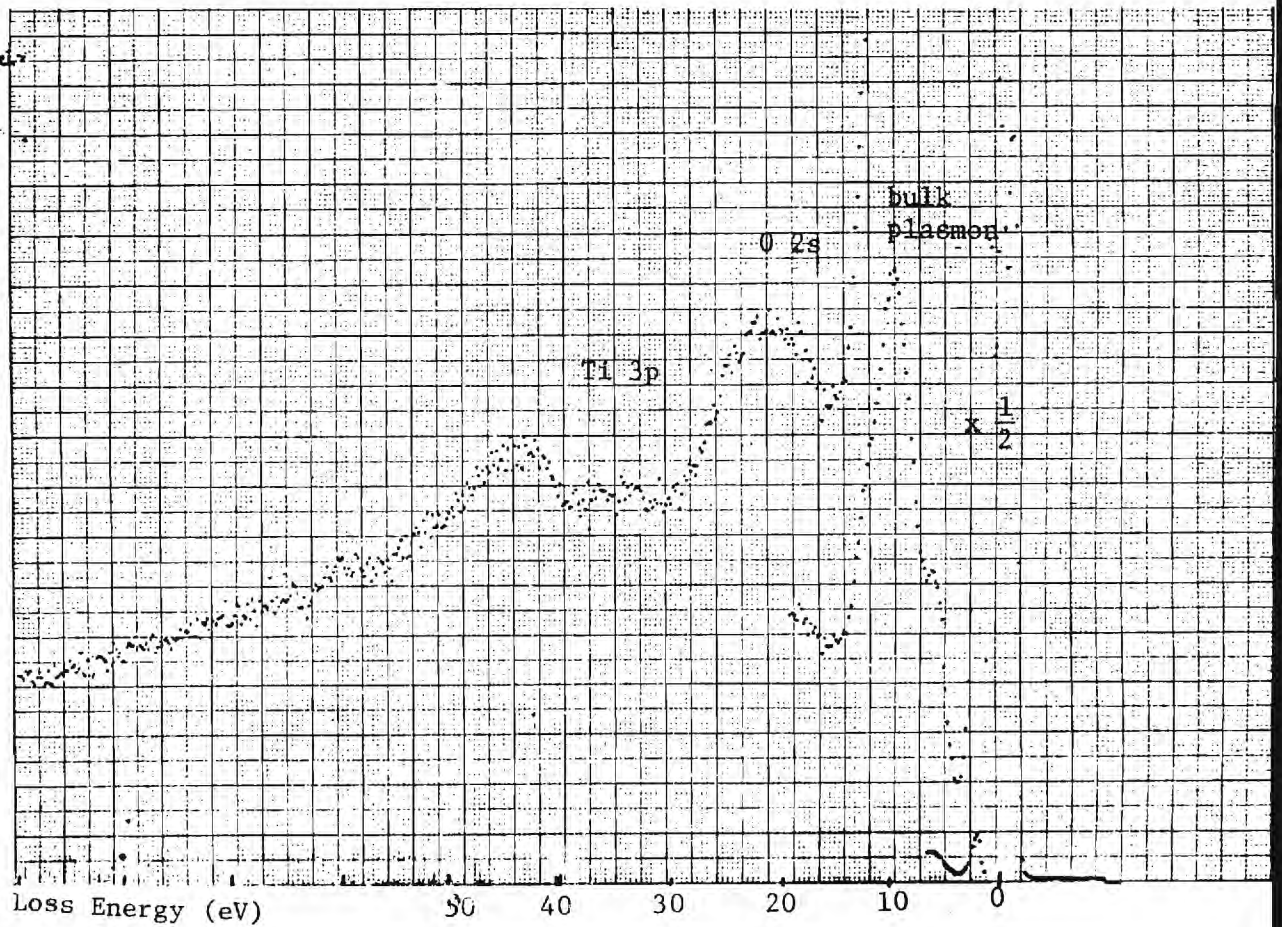


Fig. 2a Loss spectrum for clean titanium 200 eV primary.



electrons at 100eV which go through about 20 \AA . The calculation shows that the transmitted electrons have a spread in momentum transfer of several times k_f . Thus even though the spectrum in Fig. 1b had an analyzer acceptance angle for scattered electrons of only about 5 mrad.¹⁰ which corresponds to a momentum transfer of less than $.3 q_f$ for Ti, there must be a great deal of scattering of electrons with larger momentum transfers back into this region. The dispersion of the plasmon is

$$\omega_1(q) = \omega_p + \alpha(\hbar/m)q^2 \quad (3.10)$$

in an RPA-like theory. Since α is positive, dispersion increases the plasmon energy and would result in the effect noted for the transmission experiment as well as significant peak broadening. For Al the dispersion is as much as 13eV,¹⁴ so it is possible to have an average peak shift of several eV. We thus conclude that the peak shift in the transmission experiment is due to dispersion and that, in this case, the reflection experiment peak is closer to the true volume plasmon energy.

Our loss spectra for clean and oxidized polycrystalline iron, shown in Fig. 3, have some similarities with the titanium spectra. The volume plasmon peak at 15eV is well below the free electron value of about 30eV, and the spin-orbit split Fe(3p) transition is clearly visible in the appropriate place at about 55eV. However, in contrast to titanium, the interband excitations are much stronger in the iron spectra. The region below 10eV is dominated by interband excitations from the iron d-bands which completely cover the effect of the surface plasmon. As the oxide grows a pronounced O 2s peak appears at about 19eV and grows larger than the volume plasmon. The structure below 10eV is also changed due to the growth of the O 2p peak and some charge transfer from the surface d bands. The peak at about 45-50eV does not appear in the

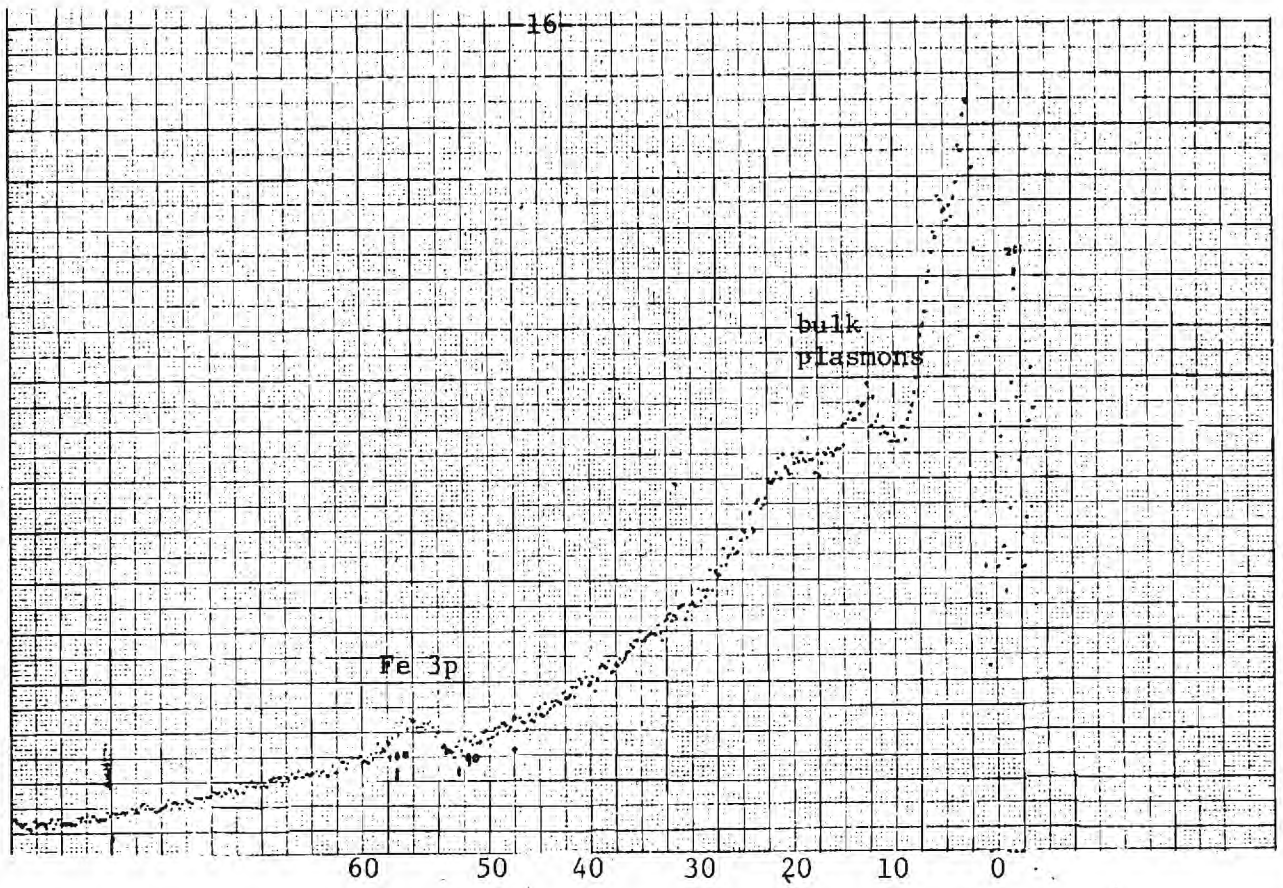


Fig. 3a Loss spectrum for clean iron 200 eV primary energy.

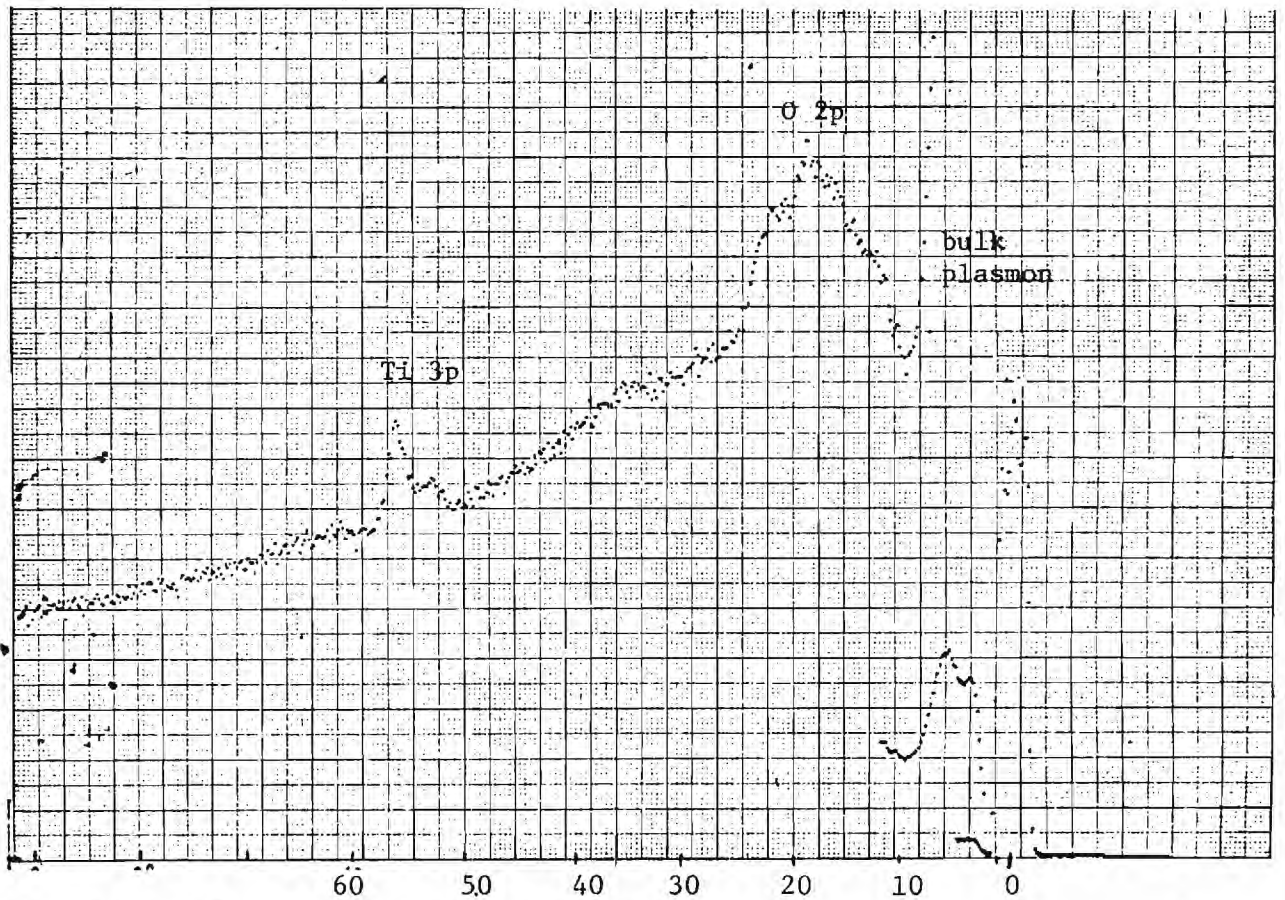


Fig. 3b Loss spectrum for iron + oxygen.

oxidized loss spectrum as it does for Ti and V which is consistent with the idea that it is connected with the metal 3p band. However, it does not appear beyond the Fe 3p peak either in Fig. 3b. The inelastic electron transmission loss data for iron¹⁰ differs from the reflection data in a similar manner to that from titanium. Here again we believe the multiple scattering caused as the electrons traverse the sample mixes in plasmons from a large range of momentum transfers and results in a shift of the plasmon peak to higher energy. We are presently calculating the band structures for both iron and iron oxide with the intent of making a comparative study of how band structure and transition probabilities affect the loss processes.

C. Effects of the Dynamically Screened Coulomb Interaction on Bose Condensation and Superconductivity.

We have recently extended our investigation of the dynamical response of electron in transition metals to the conditions of Bose condensation and superconductivity. The usual BCS theory of superconductivity¹⁵ approximates the term involving the coulomb interaction as a constant, but the inclusion of the dynamical interaction allows the study of a rich variety of effects caused by plasmons and excitons. Up to recently ideas about the existence of strong effects of this type were merely speculative, but some experimental evidence now suggests that the effects may exist for some systems.^{16,17} Also, calculations indicate that these effects should be enhanced in two dimensional systems such as surfaces or interfaces.^{18,19} All this work improves the prospects of finding condensates with unusual properties or high critical temperatures.

We have been exploring ways to add more accurately the band structure effects to the calculations of the properties of these Bose Einstein systems. Local field effects are assumed to significantly affect the critical temperatures of certain excitonic systems, although there is disagreement about whether the

temperature is enhanced²⁰ or depressed.²¹ These arguments are based on a qualitative analysis and a more quantitative analysis for specific two-dimensional and three-dimensional systems, such as we have undertaken, would be quite useful.

We are exploring the properties of systems with the Hamiltonian,

$$H = \sum_{\substack{n,k, \\ \sigma}} E_n^k C_{n\sigma}^{\dagger k} C_{n\sigma}^k + \frac{1}{2} \sum_{p,k} \sum_{\sigma\tau} V^{\sigma} C_{p\sigma}^{\dagger} C_{q\tau}^{\dagger} C_{k-q\tau} C_{p+q\sigma} \quad (3.10)$$

where $p=n_p, p; q = n_q, q; \text{etc...}$ and we have suppressed the indices of the Coulomb matrix element $V_{n_p p, n_q q}^{\sigma}$. The index n refers to band n , E_n^k is a band energy, and all matrix elements are over Bloch states. The anomalous Green's function in the Gor'kov ladder approximation would then be at $T=T_c$ ¹⁸

$$F_n(p, i\omega_p) = \frac{1}{(i\omega_p)^2 - \epsilon_p^2} T \sum_{\Omega_q} \sum_q V_{nn}(q, i\Omega_q) \quad (3.11)$$

$$\times F_n(p+q, i\omega_p + i\Omega_q).$$

where $\omega_p = \pi T(2p+1)$ and $\omega_q = 2\pi T q$, with p and q integers. The quantity $V_{nn}(q, i\Omega_q)$ is the effective interactions between electrons in the n 'th band, and we have assumed that intraband interactions dominate interband interactions. The effective interaction may be written

$$V_{nn}(q; i\Omega_q) = (\underline{V}_0 \underline{\epsilon}^{-1}(q, i\Omega_q))_{nn} \quad (3.12)$$

where the parentheses $(\dots)_{nn}$ indicates the diagonal matrix element of the product of \underline{V}_0 and $\underline{\epsilon}^{-1}$. If we were to neglect local field effects, then

$$\epsilon_{nn}^{-1}(q, i\Omega_q) \rightarrow \frac{1}{\epsilon_{nn}(q, i\Omega_q)}$$

and we could use the usual dielectric function in the analysis of Eq. (3.11). This analysis has been done for the case of weak - coupling superconductors with a very simple plasmon pole approximation for general surface and bulk systems¹⁸ and a more complicated screening function for a Si(111)-SiO₂ interface system.¹⁹ We plan to study the influence of local field effects on the critical temperature in the weak-coupling case for some transition metal oxides. Since the plasmon or exciton mediated coupling may not be small at all, we will also look at the strong-coupling case for these systems using the theory of Eliashberg.²²

Measurements by Witteborn and Fairbank¹⁶ have established the existence of an anomalously weak electric field outside the surface of copper at low temperatures. Analyses have shown that one should expect a combined electric field due to gravitationally induced strain fields and patch fields of the order 10^{-6} V/m,²³ but, in fact, the electric field is only about 10^{-11} V/M below 4.5°K. Above 4.5°K a phase transition seems to occur,¹⁶ and the electric field outside the copper surface is in the expected range. Many analyses which suggest mechanical or electronic explanations of this phenomenon have been put forth, but perhaps the most likely and most intriguing explanation is that the surface electrons couple and obey Bose-Einstein statistics at low temperatures.²³ They then form a Bose condensate below 4.5°K. The coupling mechanism would be something other than phonons, perhaps excitons or plasmons. The possibility of superconductivity below the transition temperature is also being explored. Since the copper surface in the experiments is covered with an oxide of some 20 Å,¹⁶ this shielding effect must take place in or near the oxide. Now very recent experiments on Cu₂O¹⁷ indicate that an exciton gas formed in this material by laser excitation obeys Bose-Einstein statistics. This may be the mechanism we need to explain the

anomalous shielding effect seen by Witteborn and Fairbank since their copper oxide was most likely reduced and could have been Cu_2O .

Madey and Hanni have made an estimate of the density of surface bosons needed to provide the observed shielding of the ambient electric field above 4.5°K . Their result is about 10^{11} bosons/cm² which is in the low density region where exciton or plasmon coupled superconductivity is expected to be enhanced.^{18,19}

However, if, for example, one assumes the excitons in Cu_2O behave like an ideal Bose gas, the volume condensation temperature is¹⁷

$$T_{c\infty} = \frac{m_0}{m} \left(\frac{n}{g6.2 \times 10^{15}} \right)^{2/3} \quad (3.13)$$

where m_0 is the free-electron mass, m is the particle mass, g is the degeneracy factor, and n is in units of cm⁻³. For Cu_2O , $m/m_0 \sim 3$ and, since the most likely exciton state to obey Bose-Einstein statistics is the triplet,¹⁷ $g=3$. Assuming a volume density of $n=(10^{11})^{3/2}$, the result from Eq. (3.13) is $T_{c\infty} = .329^\circ\text{K}$. However, we are dealing with an essentially two-dimensional system for which Ginzburg and Kirshnits²⁴ estimate the transition temperature for an ideal Bose gas should be

$$T_c = \left\{ dn^{1/3} / \ln(Adn) \right\} T_{c\infty} \quad (3.14)$$

where d is the film thickness and A is the film area. With $d=20 \text{ \AA}$ and $A \sim 100 \text{ cm}^2$, $T_c = 2.32 \times 10^{-3} T_{c\infty} = .76 \times 10^{-3} \text{ }^\circ\text{K}$. This temperature is considerably below the observed transition temperature. As Ginzburg and Kirshnits observe,²⁴ Eq. (3.14) may underestimate the transition temperature since superconducting films of thickness $d \sim 30 \text{ \AA}$ and $T_c \approx T_{c\infty}$ exist.

Unfortunately the ideal gas result, Eq. (3.13), is probably an upper limit to $T_{c\infty}$. For finite exciton coupling constant λ the critical temperature would be lower and still well below the transition temperature observed. This discrepancy is a serious defect in explanations of the anomalously weak electric field in terms of screening by a Bose condensate.

A review of the screening calculations of Madey and Hanni²³ indicates that assuming an ideal Bose gas composed of coupled free electrons may overestimate the screening. The electric field in the surface region due to the system of substrate and surface electrons and ions is²³

$$\epsilon = -\frac{1}{e} \frac{\partial \mu}{\partial z} - \frac{ma}{e} \quad (3.14)$$

where μ is the chemical potential of the electrons and a is the acceleration due to gravity. Now since μ varies mainly through the change in the surface density n_s ,

$$\begin{aligned} \frac{\partial \mu}{\partial z} &= \frac{\partial \mu}{\partial n_s} \frac{\partial n_s}{\partial z} \\ &\approx \frac{1}{4\pi e^2 d} \frac{\partial \mu}{\partial n_s} \epsilon_z \end{aligned} \quad (3.15)$$

The last expression involves an estimate of the variation of n_s due to the substrate electric field ϵ_z which involves both patch fields and gravitationally-induced lattice compression fields. The quantity $\frac{1}{4\pi e^2 d} \left(\frac{\partial \mu}{\partial n_s} \right)$ is then the shielding factor. Now, for an uncondensed ideal Bose gas in two-dimensions, μ is defined by the expression

$$n_s = \frac{2}{2\pi} \int d^2 k \left(e^{\beta(E_0 + \hbar^2 k^2 / 2m_0 - \mu)} - 1 \right)^{-1} \quad (3.16)$$

where $\beta = 1/k_B T$ and E_0 is the ground state energy. The integral in Eq. (3.16)

is analytic in the two-dimensional case and the result is

$$\mu = \beta^{-1} \ln \left[1 - \exp(-2\pi\hbar^2 n_s \beta / m_0) \right] + E_0 \quad (3.17)$$

the electric field at the surface state is then

$$-\frac{1}{e} \frac{\partial \mu}{\partial z} \approx \frac{\hbar^2 \epsilon_z}{2e^2 d m} \left[\exp\left(\frac{2\pi\hbar^2 n_s \beta}{m_0}\right) - 1 \right]^{-1} - \frac{m_0 a}{e}. \quad (3.18)$$

It is Eq. (3.18) that Madey and Hanni use to fit the experimental data of Witteborn and Fairbank with an $\epsilon_z \sim 10^{-6}$ V/m and $n_s \sim 10^{11} \text{ cm}^{-2}$.

We can include the band structure effects on the excitonic gas in Cu_2O as before, with an effective mass replacing the electron mass in Eq. (3.16). The degeneracy factor g should also multiply the integral in Eq. (3.16), and the result for μ would be

$$\mu = \beta^{-1} \ln \left[1 - \exp(-2\pi\hbar^2 n_s \beta / gm) \right] + E_0 \quad (3.16')$$

Since $g=3$ and $m \sim 3m_0$ for the excitons in Cu_2O , we can now fit the experimental data with $n_s \sim 10^{12} \text{ cm}^{-2}$. This value of n_s gives $T_{c_\infty} \approx 3.3^\circ\text{K}$. The value $\epsilon_z \approx 10^{-6}$ V/m for the substrate fields may also be low due to a larger patch field.

It is obvious from these estimates that we must make a more careful examination of the shielding due to the exciton gas in Cu_2O by including in our calculations band structure effects, exciton interactions, and the effects of electron-hole coupling. The condensation temperature for an interacting gas of excitons should also be studied. We will also explore the possibility that the condensed phase is superconducting. Finally, the excitonic gas in Cu_2O was obtained by laser excitation in the experiments; we must study the possibility that a surface layer of excess electrons can also form the gas.

IV. Publications and Presentations.

The following papers are being prepared for publication:

1. "The Effects of Correlation on the Band Structure of TiO ".
2. "Analysis of Energy Loss Spectra of Clean and Oxidized Titanium and Iron," with K. O. Legg.

The following paper is scheduled for presentation:

1. "Characteristic Energy Loss Spectra of Clean and Oxidized Titanium Surfaces," with K. O. Legg; March Meeting of the APS, Phoenix, Az. (1981). An abstract for this paper is attached to this section.

Abstract Submitted
for the March Meeting of the
American Physical Society

16 March 1981

Physics and Astronomy
Classification Scheme
Number 73

Suggested title of
session in which paper
should be placed:
Energy Loss Spectroscopy

Characteristic Energy Loss Spectra of Clean and Oxidized Titanium Surfaces, M.W. Ribarsky and K.O. Legg, Georgia Institute of Technology.*--We present recently taken energy loss spectra for clean and oxidized titanium and analyze the loss structures. The use of different primary electron energies and electron exit angles and comparisons with optical absorption data help identify surface and bulk plasmons and interband transitions. Our interpretation of the spectra, especially for the oxide, differs from earlier interpretations, and we discuss the implications of this for our view of characteristic losses in titanium oxide and for other processes occurring at the surface. We also analyze the plasmon structure in the light of various theoretical models.

V. Personnel

The following personnel have been partially compensated by funds provided in this grant for conducting the research during the period October 1, 1979 to September 30, 1980.

Dr. Martin W. Ribarsky - Research Scientist and Principal Investigator.

Mr. David Luedtke - Ph.D candidate.

VI. Interactions

We had the following interactions relative to this research during the period October 1, 1979 to September 30, 1980:

1. With Professor Joseph Callaway and his group at Louisiana State University about our modification and use of LCAO self-consistent band structure codes developed by his group.
2. With Peter Feibelman and Dwight Jennison at Sandia Laboratories about calculations on transition metal oxides to be used as a basis for calculating electronic excitation structure and plasmon structure.
3. With Dr. Brett Dunlap of N.R.L. about developing and using LCAO- $X\alpha$ cluster codes for the calculation of the electronic structure of surface oxides.

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and d functions. The s,p codes were developed by R. Euwema and F. Tobin
of Battelle Memorial Institute while the d codes were written by H. King
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