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CLUSTER METHOD MULTIPLE SCATTERING CALCULATIONS OF DENSITY OF STATES OF LIQUID TRANSITION METALS, RARE EARTH METALS AND THEIR ALLOYS

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Résumé. — La méthode de diffusion multiple est utilisée pour étudier des amas d'atomes de Fe, Co, Ni, Cu, Sr, Ba, Ce, Cu-Ni et Ce-Co. Les amas ont une géométrie correspondant soit à l'état liquide, soit à l'état solide. Dans le « Cluster Method Approach », nous faisons un calcul exact des propriétés de diffusion des amas et une approximation des propriétés de diffusion du reste du système entourant l'amas.

Les résultats sont capables de décrire certaines propriétés expérimentales des systèmes réels. Nous présentons les densités d'états et les déphasages et discutons leur relation avec l'expérience.

Nous en concluons que la méthode des amas est applicable à l'étude de la matière condensée et spécialement aux solides amorphes, liquides et aux solides cristallins contenant un grand nombre d'atomes par cellule unité.

Abstract. — The cluster method approach to compute electronic properties of condensed matter has been applied to study the electronic density of states of solid and liquid Fe, Co, Ni, Cu, Sr, Ba, Ce and the Cu-Ni, Ce-Co alloys. The results are in excellent agreement with the observed properties of the liquid metals and alloys. The computed phase-shifts and density of states are presented and the correlation with observed properties discussed.

We conclude that our method is a practical and dependable approximation to study the electronic properties of condensed matter, especially suited for amorphous solids and liquids and for crystalline solids with a large number of atoms per unit cell.

With very few exceptions, the study of the electronic properties of liquid and amorphous metals has been based until now on models for the electronic wave functions and electronic density of states. Contrary to the development of the theory of crystalline materials where the Bloch-Brillouin theorem allowed the calculation of wave functions, band structures and density of states, the study of liquid materials has been based on a very crude set of models where general ideas can be discussed but numerical comparison with experiment is difficult. It is highly desirable to overcome these difficulties by realistic calculations where theoretical and computational improvements can be included systematically.

The solution of the one electron Schrödinger equation for a potential V_{CL} is to be found for a particular set of boundary conditions. In atomic and molecular calculations a very simple boundary conditions holds, either the wave function far from the nuclei must decay exponentially for large r if $E - V < 0$ or become free electron like if $E - V > 0$. For a crystal, periodic boundary conditions to the wave-function outside the potential V_{CL} are the exact solution. For an amorphous solid or a liquid only approximate boundary conditions are possible in practice.

In this paper a systematic approach to the calculation for the electronic properties of liquid metals is presented and results for some particular systems are reported.

1. **Calculation procedure.** — Our calculation procedure consists of the following steps :

a) Calculation of free atom charge densities for a given occupation of the atomic levels. The occupation of the levels is integer for all core levels but it is in general fractional for the valence levels. This fractional occupation of the valence levels is such that the amount of s, p, d and f charge agrees as much as possible with the character of the electrons in the condensed state filled energy bands. (A simplified Friedel sum rule analysis is used.)

These atomic calculation are performed with a modified version of the relativistic Liberman *et al.* (1965) statistical self consistent field method. The modifications include the use of the α - β statistical exchange (Herman *et al.*, 1969), and the possibility of minimizing the total energy as a function of the fractional occupation of the valence levels. Fractional occupation of levels is the equivalent to configuration interaction in Fock type exchange schemes.

The reason for the use of a relativistic free atom calculation is the generation of the best possible free atom charge densities for light or heavy atoms, including spin-orbit terms that will presumably give a reasonable position of d and f levels.

The α - β statistical scheme seems to be extremely good for predicting energy eigenvalues of atoms and molecules, it has the additional advantage of using two universal parameters $\alpha = \frac{2}{3}$ and $\beta = 0.003$ for any atom or combination of atoms, then it is particularly useful for the study of molecules and alloys.

b) Construction of a cellular potential. For the calculation of the potential that will be used in the subsequent steps, the clusters representing the system are divided into non-overlapping cells. Each cell is assumed to contain one atom. The cluster itself is constructed following the general procedures described, for example, in the paper concerning structural determinations in this volume. This potential in each cell is constructed by superposition of free atom charge densities, only the spherically symmetric part is kept, then the Poisson equation is solved for the Coulomb part of the potential and the exchange part is approximated in the α - β scheme. The constant potential between the cells V_{miz} is constructed by integration of the Coulomb part of the potential in a large volume containing some hundred cells, subtracting the integral of the Coulomb part of the potential inside the cells and normalizing the difference to unit interstitial volume. A similar calculation is made for the interstitial average charge density from which the exchange part is computed.

c) Calculation of the single site T -matrixes. The scattering properties of each cell are computed from the spherically symmetric part of the potential in the cell. The usual procedure of matching to a free incoming regular wave plus a free scattered irregular wave outside the range of the potential is followed. It should be noted that the cells are not necessarily spherical, a more general class of cells can be used provided that, if r_{ij} is the distance between the centers of cells i and j

$$|r_{ij}| \geq \max(|\underline{r} - \underline{r}_i|, |\underline{r}' - \underline{r}_j|)$$

all r in cell i and all r' in cell j , for atomic or empty cells or, if r_{i0} is the distance from cell i to the center r_0 of the exterior cell $|r_{i0}| \leq (r - r_0)$ for all points r of the outer cell.

These restrictions are given by the decomposition of the free space Green's function (See Keller 1973a for the explanation of terms)

$$G_L^0(r, r') = G_L^+(\underline{r} - \underline{r}_i) G_L^-(\underline{r}' - \underline{r}_j);$$

$$|\underline{r} - \underline{r}_i| > |\underline{r}' - \underline{r}_j|. \quad (1)$$

It should be noted that the usual formula for the calculation of the single site phase shifts

$$\tan \delta_L = \frac{[\{dj_1(Kr)/dr\} - \{j_1(Kr)/\varphi_L(r)\} \{d\varphi_L(r)/dr\}]}{[\{d\eta_1(Kr)/dr\} - \{\eta_1(Kr)/\varphi_L(r)\} \{d\varphi_L(r)/dr\}]} \Big|_{r=R} \quad (2)$$

contains already the conditions for the matching of the wave functions at the surface of the cells within our approximation

$$V(\underline{r}') \approx V(r) \approx V(r) \quad \begin{array}{l} \underline{r}' \text{ is a point inside the cell} \\ |\underline{r}'| = r \end{array} \quad (3)$$

of keeping only the spherically symmetric part $V(r)$ for the cellular potential. If the actual cellular potentials

$$V(\underline{r}) = \sum_{l,m} V_{lm}(r) Y_{lm}(\hat{r}) \quad (4)$$

were kept, then the matching at the surface of the cells would be exact.

d) The multiple scattering condition for the pseudo wave function

$$\psi(r) = \varphi^0(r) + \sum_i G^+(\underline{r} - \underline{r}_i) t(\underline{r}_i) \psi(\underline{r}_i) \quad (5)$$

(valid only for the interstitial space and the points \underline{r}_i) could be computed if required; in this paper we use the extension of the Friedel sum idea to a collection of scatterers as given by Lloyd (1967) for the differential density of states

$$N(E) = N_0(E) - \frac{2}{\pi\Omega} \times \times \text{Im} \ln \left\| \delta_{LL'} \delta_{ij} - \sum_{L''} G_{LL''}^+(\underline{r}_i - \underline{r}_j) R_{L''L}(r_j) \right\| \quad (6)$$

where $N_0(E)$ is the free electron density of states, to the case where the cluster is embedded in a medium of potential $V^b(r)$, intended to represent the influence of the rest of the material. For the original system

$$N(E) = N_0(E) - \frac{2}{\pi\Omega} \text{Im} \ln \| D \|$$

$$= N_0(E) - \frac{2}{\pi\Omega} \text{Im} (\ln \| A \| + \ln \| B \|) \quad (7)$$

$$(D) = (A) \cdot (A^{-1}D) = (A) \cdot (B).$$

If A is a block diagonal matrix where each block represents a cluster

$$N(E) = N_0(E) - \frac{2}{\pi\Omega} \sum_{\text{cluster}} N_{\text{cluster}}(E) + N_{\text{intercluster}}(E). \quad (8)$$

The idea of the cluster method (Keller 1971, 1973) is to write the previous equation in the form

$$N(E) = \sum_{\text{clusters}} \frac{\Omega_c}{\Omega} \{ N_0^c(E, V^b) + N_c(E, V^b) \} \quad (9)$$

where Ω_c is the volume of the cluster and V^b is considered by the substitution of the previous equation of $G^+(\underline{r} - \underline{r}')$ by the renormalized propagator

$$G^+(\underline{r} - \underline{r}', V^b) = G^+(\underline{r} - \underline{r}') + G^+(\underline{r} - \underline{r}_0) T(V^b) G^+(\underline{r}_0 - \underline{r}'). \quad (10)$$

$T(V^b)$ is the scattering matrix of the potential $V^b(\underline{r} - \underline{r}_0)$.

Several choices of V^b are practical approximations to the potential representing the boundary of the cluster under study, some examples

$V^b(r) = \bar{V}$ the average potential outside the cluster.

$V^b(r) = V(r)$ the spherically averaged potential outside the cluster.

$V^b(r) = \Sigma$ the self energy of a wave propagating in a complex medium, the lowest order approximation to Σ is the average density of t -matrix

$$\Sigma \approx \sum_i c_i t_i \quad (11)$$

c_i = particles of type i per unit volume.

In other calculations, for example the first study of a transition metal (Keller and Jones, 1971)

$$V^b = V_{\text{miz}}$$

where the backward scattering from the rest of the system is ignored.

e) Once the single site phase shifts, transition matrices and the cluster density of states have been computed, the Fermi level is obtained by direct integration of the density of states histogram. The calculated Fermi level E_f , the density of states at $E = E_f$ and its energy derivatives are used together with the previous results to compute quantities as resistivity, Hall effect, unenhanced Pauli susceptibility and related properties using the simple, but practical and adequate formulas available at the present time.

The electric resistivity in the Born's approximation to the multiple scattering (Evans *et al.*, 1972)

$$\rho = \frac{3 \pi \Omega}{4 e^2 \hbar V_f^2 K_f^4} \int_0^{2K_f} a(q) q^3 |t(q)|^2 dq. \quad (12)$$

There is no precise definition of the Fermi momentum K_f except for the NFE case, also the structure factors $a(k)$ are known for only a few liquid metals, the result depend strongly on these quantities.

The Hall effect main contribution from electron-like quasiparticles is the generalization of the nearly free-electron formula (Künzi, 1973)

$$R_H = \frac{3 \pi^2}{e K_f^3} \left\{ 2 - \frac{K_f^3}{\pi^2 N(E)^2} \frac{\partial N(E)}{\partial E} \right\}_{E=E_f} \quad (13)$$

(see also Szabo, 1973).

Spin orbit contributions to the Hall effect can be estimated with the Ten-Bosch (1973) formalism.

Our present extensions of the method and programs to include self consistent field calculations and total energy subroutines can also handle spin-polarized potentials from which more information about physical properties of crystalline, amorphous, defective and molecular-like clusters is expected to be obtained.

2. Preliminary study of some actual systems. —

2.1 IRON. — There is a large amount of theoretical and experimental work available on solid and liquid iron. For this reason and the fact that iron presents a large number of complications for the study of its unfilled and uncompletely localized d-bands, iron has been one of our main examples to test the reliability of the computational procedures.

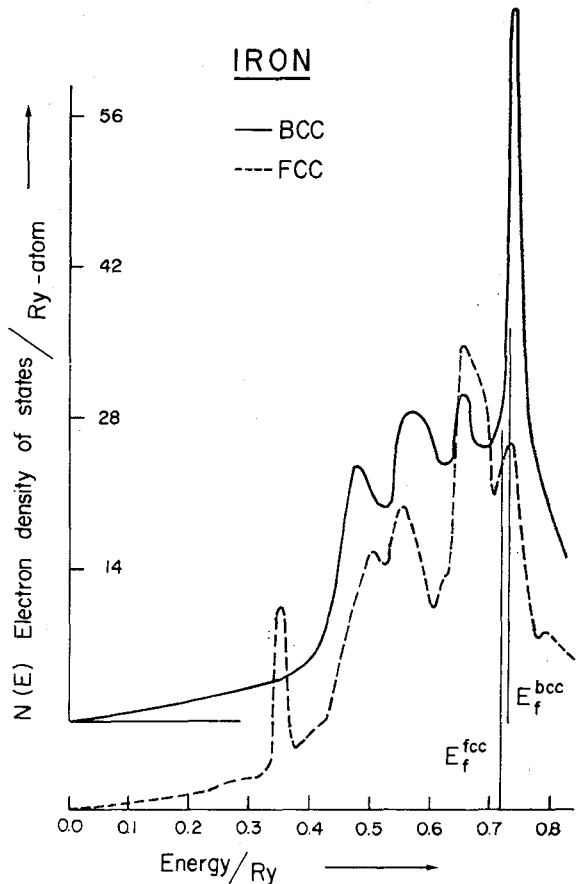


FIG. 1. — Electronic density of states of solid iron. BCC and FCC.

In figure 1 we present the computed density of states of crystalline-like clusters of iron atoms in the fcc and bcc structures. In both cases only the three shells of atoms were considered (19 and 15 atoms respectively). We observe that the calculation reproduces the d-bands in width and position of the main peaks, the Fermi level and its relation with the last

peak in the d-band density of states is also similar to the band structure calculation results. It is clear that a finite number of atoms in the cluster cannot reproduce effects due to long range order, for example singularities or sharp depressions in the density of states; it can however give sharp maxima or minima corresponding to these singular points. The increasing computing capability of machines and optimization of the codes may increase by an order of magnitude the number of atoms that could be included in future calculations, then the method will be useful even in those applications where finer details will be needed.

Suppose now we want to argue that liquid iron being the melt of a bcc structure will have a local structure intermediate between fcc-and-bcc-like clusters, we see from figure 1 that we may expect the Fermi level to be in almost the same place and that some of the features of both calculations in figure 1 will be present when a cluster of 15 atoms where the central atom has almost 10 nearest neighbours is made. The result of this calculation is actually shown in figure 2.

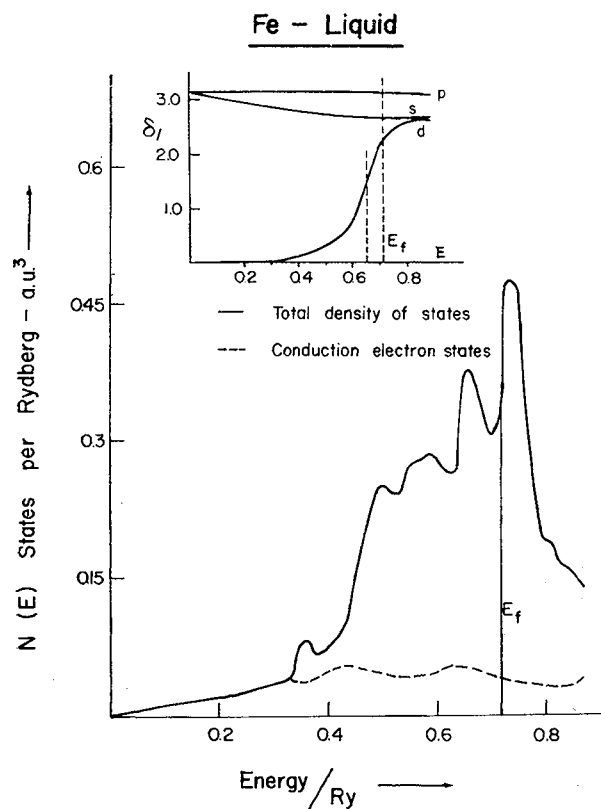


FIG. 2. — Electronic density of states and scattering phase shifts of liquid iron.

The main feature for some practical considerations is that we have the Fermi level to the right of a shallow valley in the density of states histogram. This produces a positive Hall effect according to the formula (13). A large magnetic susceptibility with localized d-like

character is also expected (Curie-Weiss law behaviour), and an increase of its value per atom of iron in an alloy with a normal metal if the Fermi level rises on alloying, if the enhanced spin susceptibility formula (see Levin *et al.* (1972), and Bush *et al.* (this number)) is used as a basis for a theoretical analysis of an alloy with a concentration $C_T = 1 - C_N$ of the transition metal

$$X_{\text{Alloy}} = C_T \frac{N_L B^2 N_d(E_f) F(T)}{1 - V_{\text{eff}} N_d(E) F(T)} + C_N X_N.$$

2.2 COPPER, NICKEL AND COPPER-NICKEL ALLOYS. —

In the study of a metallic alloy a few new problems are present. The universal α - β statistical exchange is now more important because it is almost impossible to give the correct position of the s, p, d and f bands for two or more components with the only adjustment of the value of α even if the space can be partitioned in proper regions. We have assumed that the range of the cells for the component atoms are in the ratio of the nearest neighbour distances in the pure crystal before melting. In the lack of enough structural information we have assumed until now that the nearest neighbours distance for atoms of a given kind is the same as in the pure crystal before melting and that this distances for two atoms of different types A-B is given by the average of A-A and B-B. The interstitial potential V_{mtz} is more difficult to evaluate and it is assumed that it changes linearly with concentration. A new calculation of the phase shifts is made at each concentration.

In the particular example of the copper-nickel alloy it is found that the relative distance of the d-bands for copper and nickel are almost the same as for the solid alloys. In our calculation this relative distance is not fixed *a priori*. In absolute energies the d-bands of copper and nickel in the pure liquids are almost at the same place but on alloying the V_{mtz} is changed to lower values with increasing concentration of nickel, this shifts the copper d-band to lower energies. Conversely the nickel d-band moves up with increasing copper concentration. This effect gives the relative distances of the d-bands in the alloy. At the same time the character itself of the bands change, the d-band of copper becomes less localized in the high nickel side and the nickel d-band becomes more localized, but also more hybridized with the s-band (mainly in the Fermi energy region!), in the copper rich concentration. This features should be relevant to the understanding of both, the liquid and the solid alloys.

2.3 STRONTIUM. —

The calculation for strontium was made on the assumption that the coordination number $n \approx 10$, the volume per atom being the only known quantity. It shows a large Fermi level. The density of electronic states at the Fermi level, also $dN(E)/dE$ is large at E_f . Strontium is thus quite different from a nearly free electron metal, it is more

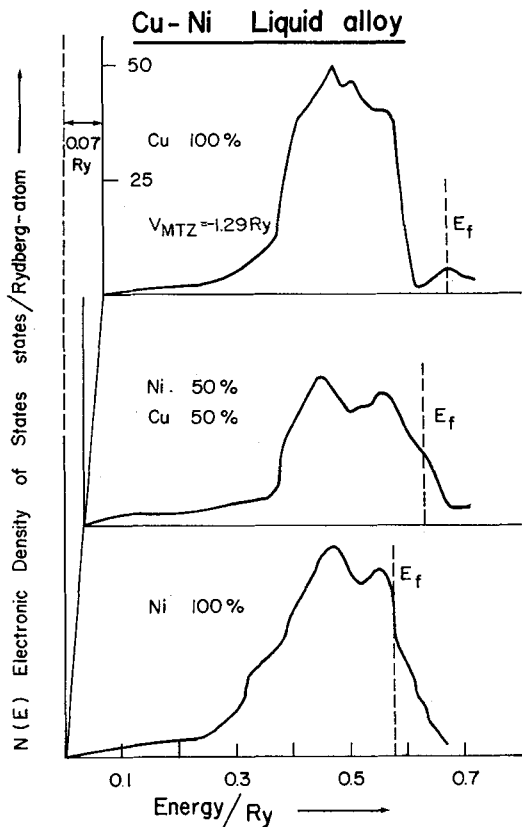


FIG. 3. — Electronic density of states of liquid copper-nickel alloys.

to be considered as a p-electron metal. These conclusions are consistent with the particular behaviour of its resistivity and Hall effect constant. No d-electron character was found at the Fermi level.

2.4 BARIUM. — Before attempting a calculation for barium, atomic calculations for the first half of the 6th row of the periodic table were made and satisfactory agreement with other calculations and some experimental values were found. The liquid barium was again supposed to have a local structure with coordination number $n \approx 10$. It is found that it is not a nearly free electron metal with a superimposed d-band, rather it is highly depressed from NFE like behaviour with almost 0.3 d-like electrons before the E_f . A f-band is 1.5 eV after the E_f . The density of states at the Fermi level is like the value it would have if the metal were NFE with two electrons per atom, but E_f is more than 1.5 eV above the NFE value.

The scattering phase shifts are very large at the E_f , it means that high electrical resistivity will be encountered from large s and p-scattering, but the structure factor $a(k)$ plays a dominant role in the resistivity of the alkaline-earth metals. The explanation of the high resistivity of these materials is to be given in terms of both: high single site scattering and high structural scattering, this suggest that Ba is also to be considered a p-electron metal.

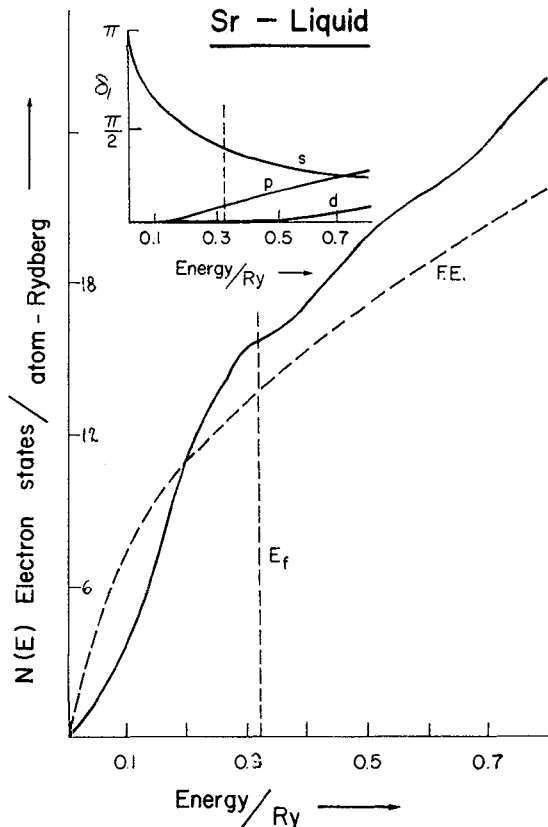


FIG. 4. — Electronic density of states and scattering phase shifts of liquid strontium. F. E. = free electron.

2.5 CERIUM AND CERIUM-COBALT ALLOYS. — A calculation of the rare-earth metals is now being made to correlate the properties of the row Ba-La-Ce...-Lu. From the calculations made until now it is found that the f-band is not at the Fermi level for any of the liquid metals. It is above for Ba and La and below from Ce on. It is not easy to do a calculation with f-bands for various-practical reasons, but the main is a consistency condition: if a f-band is assumed with occupation n_f in the atomic calculation it should have the same occupation, to a very small fraction of an electron, in the condensed state. Now, the position of the band changes one to several eV if the occupation is changed to $n_f + 1$ or $n_f - 1$. We will discuss this problem on the basis of Ce and Ce-Co, but our results are derived from the study of several systems (including recently uranium).

As said before the f-band is found not at the Fermi level of liquid cerium, different from the study of high-pressure γ -cerium where it is found just at the Fermi level. The calculation is made in the following consistency scheme: 1) An occupation n_f of the free atom is assumed; 2) the potential is constructed by superposition of free atom charge densities and the density of states is evaluated; 3) The Fermi level is found by direct integration of the density of states histogram *but only n_f electrons are contributed from the f-band*; 4) If the Fermi level is found below an

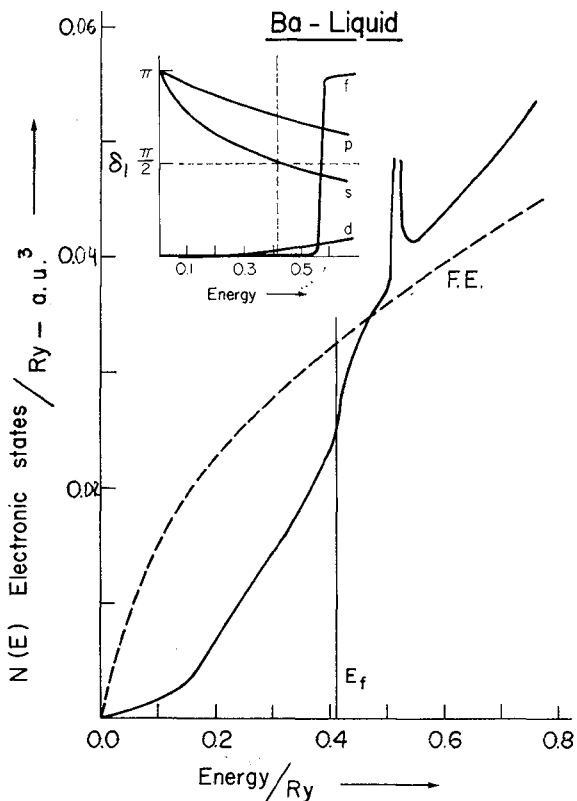


FIG. 5. — Electronic density of states and scattering phase shifts of liquid barium.

occupied f-band it is assumed from considerations of total energy that the result is inconsistent and a new calculation is made with original assumed occupation $n_f = 1$ of the f-band.

In figure 6 we show the results of a calculation for cerium, the f-band was assumed to contain only one electron, if assumed to contain two electrons it would be two electron volts above the Fermi level. But if assumed to be empty then it will be 5 eV below the Fermi level. Then we have two possibilities : to

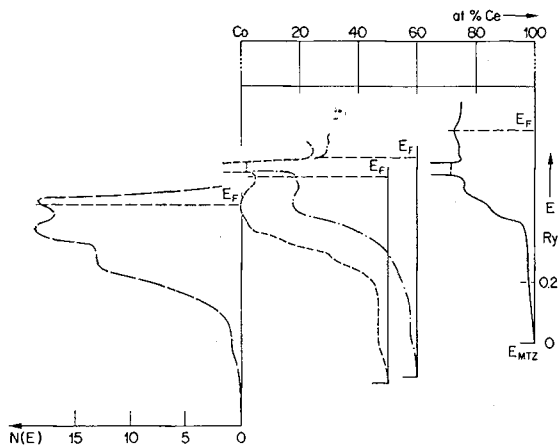


FIG. 6. — Electronic density of states of liquid cerium-cobalt alloys.

have an empty f-band 5 eV below the Fermi level or to have a partially occupied $n_f \approx 1$ f-band below but nearer the Fermi level. From the atomic calculation we know that the minimum of total energy is found with the f-band partially occupied ($n_f \approx 1-2$) then we assumed that the most probable configuration is the one shown in figure 6 in the absence of external influences. Our present study of the α - γ cerium transition shows that it takes a much smaller volume per atom than that of the liquid cerium to have the f-band with one electron unstable (it is above the Fermi level), in this case, α -cerium, it would be empty but below the Fermi level. We emphasize again that all calculations are made with the statistical exchange approximation, then similar to the Hartree-Fock method a transition from a highly localized state m (in the sense that the largest part of the f-charge density is « trapped » in the f-atomic well) to another state n, requires an energy which is not the difference of the eigenvalues in the initial state ; it may be given by the difference of total energies or approximated by

$$E_{final} - E_{initial} \approx ((\epsilon_n - \epsilon_m)_{initial} + (\epsilon_n - \epsilon_m)_{final})/2.$$

When alloying Ce and Co the interstitial potential decreases at almost the same rate as the Fermi level, but f-bands are little affected by small changes in V_{mtz} in the rare-earth alloys, then the Fermi energy is eventually below the f-level at a concentration 50%-55% Ce — 50%-45% Co, then it will be emptied. Alloying with cobalt has a similar effect in the stability of the f-band as pressure and low temperature in the solid cerium.

At this concentration the resistivity may have a sharp maximum from the fact that a) for some atoms the Fermi energy is at a f-resonance (increased single site scattering) and b) the cerium atoms with an empty f-level will have smaller atomic volume and the structure constant will have the first peak closer to $2 K_f$ in the integral of formula (12), then a larger intersite scattering contribution.

On the other hand, at this concentration the Fermi energy is in a valley of the density of states histogram, then from formula (13) the Hall coefficient will have a sharp minimum with a (negative) NFE value.

On the high cobalt side the properties should change almost linearly with concentration from this high resistivity, no-magnetic moment, NFE Hall effect behaviour at 50 % Ce-50 % Co alloy.

An application of the method to amorphous semi-conductors is presented elsewhere (Keller and Fritz, 1973).

In conclusion we find that the cluster method is a dependable approach to the study of the electronic properties of condensed materials, it has the further advantage that it can be improved systematically in any of the points, a, b, c, d and e described above.

We would like to thank the group working in liquid

metals in the E. T. H. Zürich for many discussions and for their hospitality, for a discussion of the properties of the actual systems we refer to their many accounts, see for example Bush *et al.*, this issue, specially to Dr. Hans Güntherodt for his continuous interest and encouragement.

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