



HAL
open science

THE ELECTRONIC STRUCTURE OF RARE-EARTHS. Band structures of rare earth metals

B. Harmon

► **To cite this version:**

B. Harmon. THE ELECTRONIC STRUCTURE OF RARE-EARTHS. Band structures of rare earth metals. Journal de Physique Colloques, 1979, 40 (C5), pp.C5-65-C5-70. 10.1051/jphyscol:1979526 . jpa-00218943

HAL Id: jpa-00218943

<https://hal.science/jpa-00218943>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

THE ELECTRONIC STRUCTURE OF RARE-EARTHS. _____

Band structures of rare earth metals (*)

B. N. Harmon

Ames Laboratory-USDOE and Department of Physics, Iowa State University, Ames, Iowa 50011, U.S.A.

Résumé. — Des mesures récentes de propriétés magnétiques et optiques des métaux de terres rares ont fourni une information très détaillée concernant la structure électronique de ces métaux. Pour en rendre compte, il apparaît qu'il faut améliorer les modèles simples qu'on a employés jusqu'à présent pour interpréter les données expérimentales. Dans une théorie plus détaillée on doit incorporer un traitement relativiste de la polarisation des spins électroniques et aussi tenir compte de la localisation des électrons 4f au voisinage des atomes. On est guidé dans ces calculs par les résultats de mesures récentes des propriétés des métaux de terres rares et par des calculs de champ self-consistent des propriétés de métaux qui ne sont pas magnétiques mais possèdent une structure électronique semblable. Dans cet article je présente une revue critique des calculs de la structure électronique des métaux de terres rares et en particulier des calculs détaillés pour gadolinium.

Abstract. — Recent magnetic, optical and neutron scattering experiments made possible by the availability of high purity samples are providing increasingly detailed information about the electronic structure of the rare earth metals. The first calculations for the paramagnetic state of these fascinating metals have long served as a valuable heuristic model for understanding many earlier experimental results. It is expected that more accurate calculations for the magnetic ground state will be equally valuable in fostering the traditionally fruitful interaction between theory and experiment. Such calculations present a formidable challenge since they require a relativistic approach to spin polarization and a suitable treatment of the highly localized 4f-shell. The calculations can be guided by comparison with precise experimental results and by self-consistent calculations for non-magnetic metals with similar electronic structures. In this paper we review the present status of band structure calculations for the rare earth metals, and give details of a self-consistent, relativistic, ferromagnetic calculation for gadolinium.

It is of course not possible or necessary to present a comprehensive review of the electronic structure of rare earth metals. The reviews by Dimmock [1] and Freeman [2] are well known. In addition a new review by Liu [3] gives more recent results and emphasizes topics like optical and photoemission measurements which were not given detailed treatment in the earlier reviews. This paper will therefore focus on the directions taken by the most recent band theory calculations. In order to place these new calculations in proper perspective some brief historical remarks are first given. Then the fundamental problem of how to treat the 4f *bands* and their interactions with the conduction electrons is discussed. This problem was particularly evident in Professor Levy's talk and is also the central problem in understanding valence fluctuations. As will become evident in this paper it is also the major remaining problem in obtaining an accurate description of the electronic ground state for the rare earth metals.

In the beginning one of the most fruitful descriptions for the electronic structure of the rare earths was the free electron model. Without worrying about the complications of d electrons, theorists

quickly established many of the basic ideas which still govern our view of the interactions in these metals. RKKY theory, superzones, the temperature dependence of the ordering wavevector, and the excess conduction electron magnetic moment are all ideas which belong to this early era in which the limited number of precise experiments (mostly neutron diffraction) did not seriously challenge the over simplified model.

In 1964 Dimmock and Freeman [4] published the first bandstructure of a rare earth metal and demonstrated the transition metal character of the bands. This first calculation was non-self-consistent, non-relativistic, and non-spin-polarized. Nevertheless the general shape of the bands is surprisingly little affected by improved approximations. Typical of the early calculations the 4f levels were ignored as much as possible. A short time later Loucks developed the relativistic APW method and soon published the Keeton the relativistic bandstructure of a number of rare earths [5]. Two immediately noticeable effects caused by relativity are the net lowering of the s band relative to the d bands and the addition of spin-orbit coupling which removes most of the band crossings.

(*) The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-7405-eng-82. Accordingly, the U.S. Government retains a nonexclusive, royaltyfree license to publish or reproduce the published form of this contribution, or allow others to do so for U.S. Government purposes.

These early calculations did show that as one went across the rare earth series the d bands rise in energy relative to the s-p band. Recently Duthie and Pettifor were able to be more quantitative and showed that the number of d-like electrons decreases from about 2.5 in La to 1.9 in Lu [6]. They managed to correlate the dhcp \rightarrow Sm \rightarrow hcp structural change along the series with this change in d band occupancy. This trend is discussed by Delley *et al.* in this conference and in a recent publication dealing with the electrical resistivity of liquid rare earth metals [7].

We had to wait 10 years after these initial calculations for precise experiments like the de Haas-van Alphen measurements of Young [8] to challenge the theory. Before this there were several experiments which did not require the high purity electrotransported samples and which did substantiate the general features of the theoretical calculations.

One of the first of these less precise type experiments was the measurement of the position annihilation spectrum by Williams and Mackintosh [9]. In comparing theory with these experiments Loucks was one of the first investigators to use good electron and positron wavefunctions to compute the necessary matrix elements [10]. This study gave convincing evidence that the free electron model was inadequate and that the APW calculations were correct in showing the importance of the d bands. Another experiment of this less precise type which was performed just recently involved the measurement of the induced magnetic form factor of Lu metal using neutron diffraction [11]. The application of a strong magnetic field splits the bands slightly and the Fourier transform of the uncompensated spin up density for states near the Fermi level can be measured. The RAPW calculations performed in corroboration with the experiment were very dramatic in showing the anisotropic and spread out character of the d like conduction electrons compared with the more tightly bound 5d electrons from an atomic calculation. The agreement between experiment and the spin only theoretical form factor was in fact too good, and the authors questioned the quality of the band wavefunctions from their non-self-consistent calculation. They are presently making the calculation self-consistent to see if presence of an expected orbital contribution can be ascertained.

Before discussing the results of the dHvA measurements on gadolinium let us turn to the problem of treating the 4f levels in a self-consistent manner. An example of the kinds of problems one encounters is demonstrated in Yb where the complications of a magnetic ground state are not present. Using the traditional Slater $\rho^{1/3}$ approximation for exchange and correlation Johansen and Mackintosh [12] calculated the non-self-consistent band structure of fcc Yb. The spin-orbit split 4f bands were found 0.2 and 0.3 Ry below the Fermi level and therefore had little influence on the states near E_F . However rather

than finding fcc Yb to be a semimetal they found a small gap. The situation is quite different for the self-consistent calculation performed by Koelling [13] which is shown in figure 1. Koelling used the form of the approximate exchange correlation potential given by Hedin and Lundquist [4] since it involves no adjustable parameters and has been found to work well in self-consistent calculation for various transition metals [15]. One sees immediately that the 4f levels have moved close to the Fermi level and that with the addition of spin-orbit coupling (which Koelling dropped in these preliminary calculations) the 4f bands will have some direct influence on the conduction bands states near E_F . One also sees that the band structure now exhibits a semimetal character (the electron pocket needed to compensate the hole pocket shown in located on an off symmetry position of the zone). Questions naturally arise as to the accuracy of these calculations and the actual extent to which the 4f states influence the conduction bands at E_F . The answers to these questions await the completion of dHvA measurements on fcc samples.

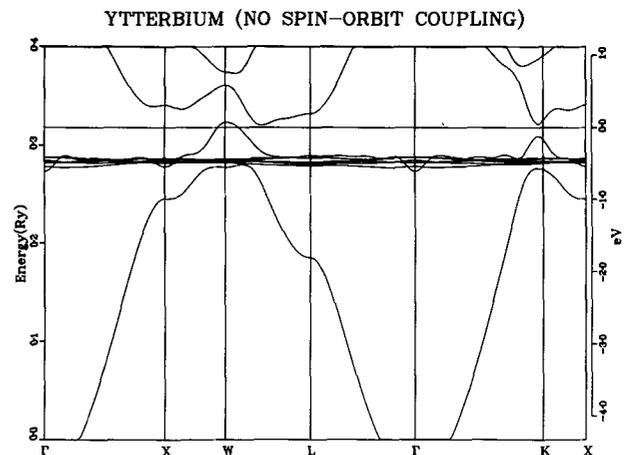


Fig. 1. — The self-consistent bands of Yb (ref. [13]).

The importance of 4f levels in self-consistent calculations was also clearly demonstrated for La and Ce by the work of Glötzel reported at this conference and in a recent publication [16]. An interesting aspect of this study was the apparent Mott like behavior of the 4f band in Ce as a function of lattice spacing. Glötzel also found the 4f bands made a substantial contribution to the cohesive energy. However this contribution was overestimated, which probably indicates the inadequacy of the local density approximation for exchange and correlation. It would be helpful in understanding this work if more details of the bandstructure were published.

In calculating the bandstructure for the magnetic rare earths the effects of self-consistency can be important. Figure 2 shows the results of a non-

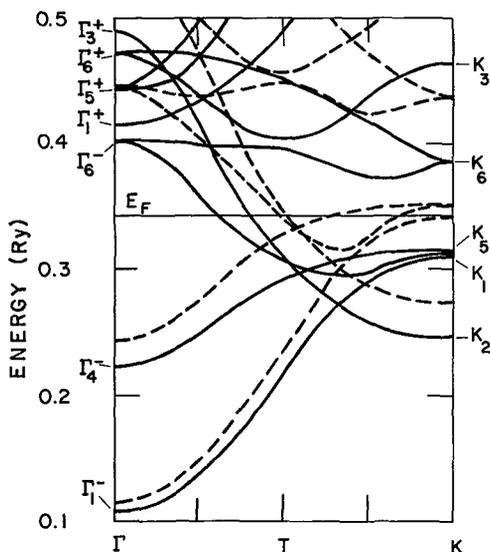


Fig. 2. — The non-self-consistent bands of Gd (ref. [17]).

self-consistent calculation for Gd [17]. The solid curves are the spin up bands. The important point to note is the s-band splitting is much smaller than the d-band splitting. We can understand this from figure 3 where it is obvious that the d-4f overlap and hence exchange interaction is much larger than the s-4f overlap. However in a self-consistent calculation one finds the s-band splitting is increased. This is because the d-states which have a net polarization from the 4f's act in turn on the s-states and cause a substantial s-polarization. One should also note that the occupied d states in the rare earths are at the bottom of the d bands and are therefore quite spread out spatially compared to the 3d states in Fe, Co or Ni.

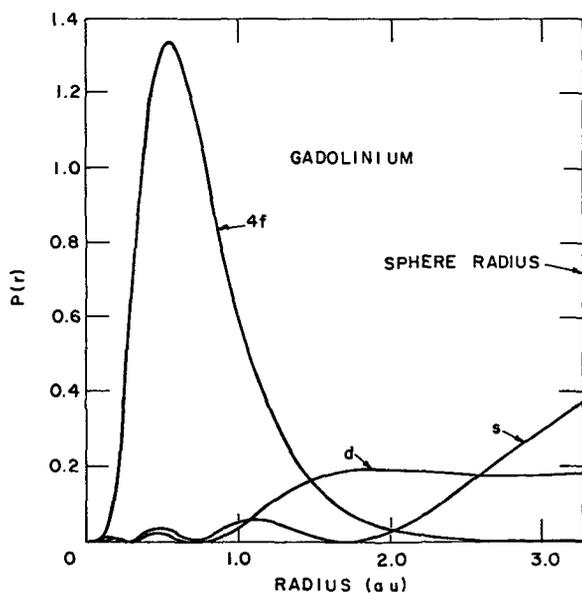


Fig. 3. — Radial densities in Gd for typical Bloch states.

The importance of accurately describing the 4f-conduction electron coupling is nicely illustrated in the experiment of Legvold *et al.* [18] shown in figure 4. This shows the reduction of the superconducting transition temperature of La by the addition of dilute amounts of Gd and Eu. Now both Gd and Eu have seven unpaired 4f electrons and hence the same magnetic moment. However the 5d-4f exchange integral for Eu is only 0.7 times that for Gd [18], and since this integral is squared to get the suppression of T_c , the factor of two difference in slopes is accounted for.

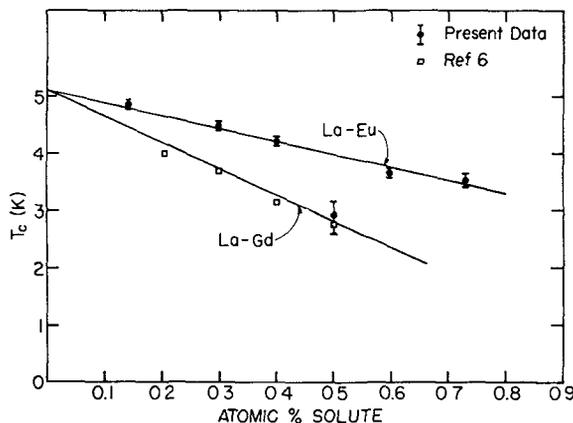


Fig. 4. — Superconducting T_c of La versus impurity concentration.

In the remaining part of this paper the problem of calculating the magnetic ground state for gadolinium will be treated in detail [19]. Gadolinium is a natural choice because of the simplifications resulting from a spherical 4f shell and the amount of precise experimental data available. The first difficulty one encounters is the necessity of including relativistic effects and the incompatible desire to keep spin as a good quantum number for describing the Russell-Saunders-like 4f shell and the exchange polarization of the conduction electrons. For systems like Gd where the exchange interaction is much larger than the spin-orbit coupling we have developed a technique for performing relativistic spin polarized calculations which treats the spin-orbit interaction as a perturbation on the self-consistent exchange split bands [20]. This technique together with the local spin-density approximation for exchange and correlation [21, 22] gives an *atomic* 4f spin form factor in excellent agreement with experiment [23] and with mixed configuration Dirac-Fock calculations [24]. The situation when this technique is applied to the solid is quite different.

The spin up bandstructure is quite straight forward. The conduction bands look similar to the original bands of Dimmock and Freeman and the 4f's form 14 bands within the narrow shaded region shown in figure 5 (there are 14-4f bands because there are two

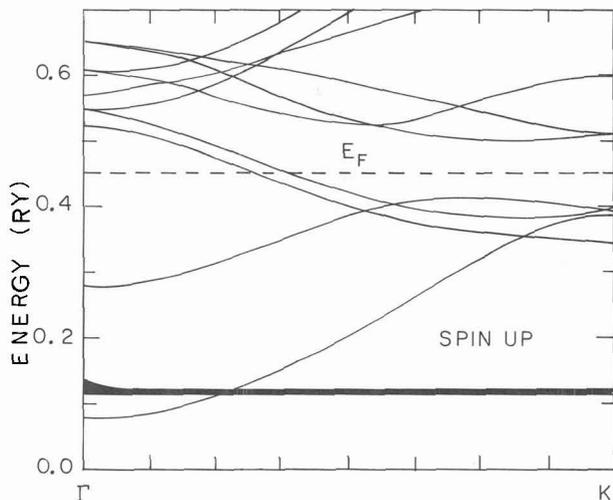


Fig. 5. — Self-consistent spin up bands of Gd.

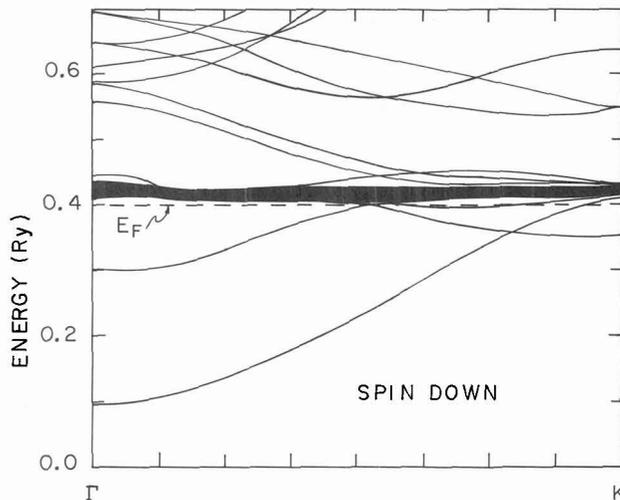


Fig. 7. — Self-consistent spin down bands of Gd.

atoms per unit cell and 7 electrons per atom). The corresponding density of states is shown in figure 6. The Fermi level is drawn at the position resulting from the self-consistent calculation, but as we shall see, E_F needs to be shifted upward by about 7 mRy to get agreement with the dHvA measurements and the electronic specific heat measurement. The spin down bands shown in figure 7 are where the interesting problems arise. There are 14 bands in the shaded region just above E_F . Because of hybridization this results in approximately 0.03 4f spin down electrons per site and an extremely large density of states at the Fermi level. Both results are unphysical and indicate the atomic-like correlation within the 4f shell is not being handled properly by the local spin density formalism.

$0.61 \mu_B$ /atom which is close to the experimental value of $0.63 \mu_B$ /atom [25]. The density of states at E_F is also lowered to about 11 states/Ry-atom instead of the ~ 28 states/Ry-atom typical of paramagnetic calculations. This agrees with the low value measured for the electronic specific heat [26].

A key experiment which indicates the 4f spin up bands have been prevented from moving low enough in energy is the measurement of the neutron magnetic form factor [23]. Figure 8 shows the theoretical form factor (the points) falls below the experimental curve (the solid line). (Note that the solid line is an essentially exact fit to the data except for the few points marked by x at low scattering angles.) This indicates the calculated 4f density is too spread out. Lowering the 4f up bands by ~ 0.1 Ry would

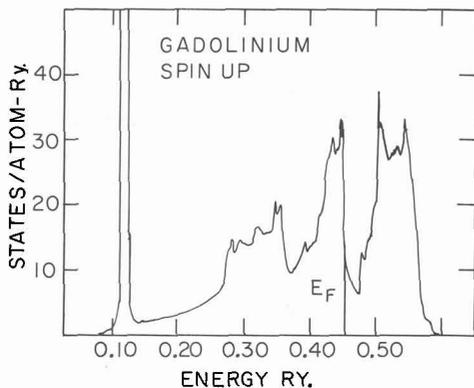


Fig. 6. — Spin up density of states.

The self-consistent calculation gives the net conduction electron moment as $0.52 \mu_B$ /atom, whereas by shifting the 4f spin down bands upward by 0.4 Ry the net moment becomes $0.78 \mu_B$ /atom. If the spin up Fermi level is moved to agree with the dHvA and the 4f down band shifted the net moment is

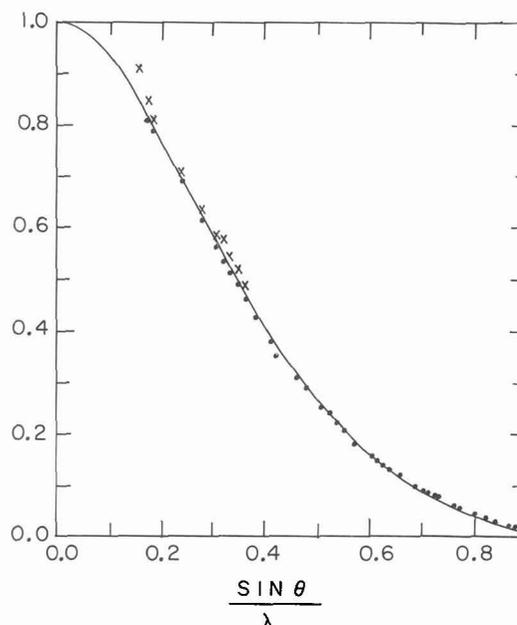


Fig. 8. — Neutron Magnetic form factor (solid curve is experiment).

correct this. Both this lowering and the removal of the 4f spin down states from the region of the Fermi level could be accomplished by increasing the exchange correlation potential. However the dHvA experiments suggest a slight decrease in the exchange correlation potential is needed to get the correct relative sp and d band positions. We turn to this problem next.

The long awaited first dHvA measurements for a rare earth metal were made on Gd in 1974 [8] and later extended [27, 28]. A large number of smaller orbits were seen and most can roughly be accounted for as occurring along Γ to K in the spin down bands. Because of the present position of the 4f down bands we have not yet added spin orbit coupling so it is premature to attempt positive assignments of the small orbits. The larger orbits can be assigned accurately and agree with Young's original interpretation. In figure 9 we show only the belly and neck orbits for the band 3 spin up surface. The solid curves show the experiment [28] and the dashed curve the orbits from the self-consistent calculation. Shifting the spin up Fermi level upward by 7 mRy gives the dotted curves. The wavefunction character on this surface changes from 30% d character inside the muffin-tin spheres in the Γ KM plane to 70% d character in the AHL plane. This means the detailed shape of the belly frequencies and the neck orbit could be brought into agreement by a slight upward shift of the d bands relative to the s-p band. This could be accomplished by a small decrease in the exchange correlation potential which would hurt the 4f situation. We are thus in a quandary when using traditional band methods. It seems a hybrid technique which will treat the 4f correlation in a suitable manner is needed next. Certainly some sort of l -dependent potential will improve the agreement with the key experiments.

Summary. — Two of the major themes of this conference are the nature of the 4f states and the coupling mechanisms between the 4f states and the

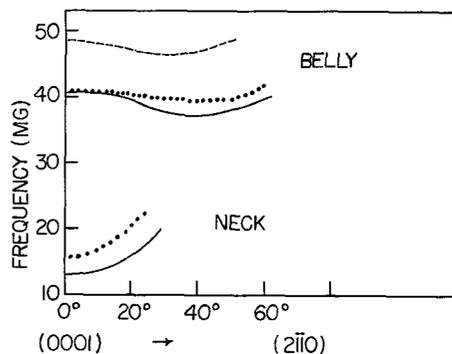


Fig. 9. — dHvA frequencies for Gd.

conduction electrons which give rise to anisotropic interactions. In trying to sort out the myriad of fascinating experimental results concerning these problems it would be valuable to have accurate calculations of the electronic ground state for some of the interesting systems. Such calculations are not yet available, however recent band structure work on rare earth metallic systems is finally addressing the problem of how to properly treat the 4f bands and their interactions with the conduction electrons. The wavefunctions from such calculations are probably accurate enough at the present time to make reliable estimates of the various 4f-conduction electron interactions which lead to the different transport anisotropies reported at this conference. The ground state for systems exhibiting valence fluctuations is a more difficult problem from the traditional band structure approach which does not treat the atomic like correlation of the localized 4f shells properly. Future work will undoubtedly attempt to correct this deficiency. Any new models or techniques will be greatly aided by the careful experiments now becoming available on pure rare earth samples.

Acknowledgments. — This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.

References

- [1] DIMMOCK, J. O., *Solid State Phys.* (Ehrenreich, H., Seitz, F. and Turnbull, D. Eds.) **26** (1971) 104.
- [2] FREEMAN, A. J., *Magnetic Properties of Rare Earth Metals*, Elliott, R. J. Ed. (Plenum Press, London) 1972, p. 245.
- [3] LIU, S. H., To be published as chapter 3 in *Handbook on the Physics and Chemistry of Rare Earths*, edited by Gschneidner, K. A. and Eyring, L. (North-Holland) 1978.
- [4] DIMMOCK, J. O. and FREEMAN, A. J., *Phys. Rev. Lett.* **13** (1964) 750.
- [5] KEETON, S. C. and LOUCKS, T. L., *Phys. Rev.* **146** (1966) 429.
- [6] DUTHIE, J. C. and PETTIFOR, D. G., *Phys. Rev. Lett.* **38** (1977) 564.
- [7] DELLEY, B., BECK, H., KÜNZI, H. and GÜNTHERRODT, H. J., *Phys. Rev. Lett.* **40** (1978) 193.
- [8] YOUNG, R. C., JORDAN, R. G. and JAMES, D. W., *Phys. Rev. Lett.* **31** (1973) 1473.
- [9] WILLIAMS, R. W. and MACKINTOSH, A. R., *Phys. Rev.* **168** (1968) 679.
- [10] WILLIAMS, R. W., LOUCKS, T. L. and MACKINTOSH, A. R., *Phys. Rev. Lett.* **16** (1966) 168.
- [11] STASSIS, C., KLINE, G. R., LOONG, C.-K. and HARMON, B. N., *Solid State Commun.* **23** (1977) 159.
- [12] JOHANSEN, G. and MACKINTOSH, A. R., *Solid State Commun.* **8** (1970) 121.
- [13] KOELLING, D. D., Unpublished.
- [14] HEDIN, L. and LUNDQUIST, B. I., *J. Phys. C* **4** (1971) 2064.
- [15] MORUZZI, V. L., WILLIAMS, A. R. and JANAK, J. E., *Phys. Rev. B* **15** (1977) 2854.

- [16] GLÖTZEL, D., *J. Phys. F* **8** (1978) L 163.
- [17] HARMON, B. N. and FREEMAN, A. J., *Phys. Rev. B* **10** (1974) 1979.
- [18] LEGVOLD, S., BEAUDRY, B. J., OSTENSON, J. R. and HARMON, B. N., *Solid State Commun.* **21** (1976) 1061.
- [19] HARMON, B. N., SCHIRBER, J. E. and KOELLING, D. D., Int. Phys. Conf. Ser. No. 39, *Transition Metals*, Lee, M. J. G., Perz, J. M. and Fawcett, E. eds. (Institute of Physics, Bristol) 1978, p. 47.
- [20] KOELLING, D. D. and HARMON, B. N., *J. Phys. C* **10** (1977) 3107.
- [21] VON BARTH, V. and HEDIN, L., *J. Phys. C* **4** (1972) 1629.
- [22] GUNNARSSON, O. and LUNDQÜIST, B. I., *Phys. Rev. B* **13** (1976) 4274.
- [23] MOON, R. M., KOEHLER, W. C., CABLE, J. W. and CHILD, H. R., *Phys. Rev. B* **5** (1972) 997.
- [24] FREEMAN, A. J. and DESCLAUX, J. R., *Int. J. Magn.* **3** (1972) 311.
- [25] ROELAND, L. W., COCK, G. J., MULLER, F. A., MOLEMAN, A. C., JORDAN, R. G. and MCEWEN, K. A., *J. Phys. F* **5** (1975) L 233.
- [26] WELLS, P., LANCHESTER, P. C., JAMES, D. W. and JORDAN, R. G., *J. Phys. F* **4** (1974) 1729.
- [27] SCHIRBER, J. E., SCHMIDT, F. A., HARMON, B. N. and KOELLING, D. D., *Phys. Rev. Lett.* **36** (1976) 448.
- [28] MATTOCKS, P. G. and YOUNG, R. C., *J. Phys. F* **7** (1977) 1219.