ductivity will exist in finite one-dimensional systems, but only that it connot be ruled out a priori on the basis of the logarithmic divergence of $M$. In two dimensions for $T \neq 0$, $M$ similarly has a logarithmic divergence.

[1]W. A. Little, Phys. Rev. 134, A1416 (1964).
[2]R. A. Ferrell, Phys. Rev. Letters 13, 330 (1964).
[3]L. Gor'kov, Zh. Eksperim. i Teor. Fiz. 34, 735 (1958) [translation: Soviet Phys.-JETP 7, 505 (1958)].

## BAND STRUCTURE AND MAGNETISM OF GADOLINIUM METAL

J. O. Dimmock
Lincoln Laboratory,* Massachusetts Institute of Technology, Lexington, Massachusetts

and

A. J. Freeman
National Magnet Laboratory,† Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received 18 November 1964)

The type-$4f$ rare-earth metals have been viewed traditionally as consisting of trivalent atomic cores, including the $4f$ shell, plus three conduction electrons per atom. Previous theoretical work[1] has attempted to explain the available experimental data by assuming that the three conduction electrons occupy essentially free-electron bands perturbed perhaps by a fairly small crystal potential. Much of this theoretical work depends critically on the assumed free-electron nature of the conduction bands. However, it has been difficult to explain by means of the free-electron model the large saturation magnetization[2] of Gd ($7.5\mu_B$/atom) and especially the large electronic specific heat[3] of the rare-earth metals which indicates a density of states at the Fermi surface some eight times that given by the free-electron model.

This Letter reports briefly some results of a nonrelativistic augmented plane wave[4] (APW) calculation of the electronic energy bands in gadolinium metal. The calculated conduction bands differ markedly from those of the free-electron model, and instead closely resemble those of the transition metals. This is due to the fact that bands originating from atomic $5d$ and $6s$ states overlap and are strongly mixed. The bands near the Fermi surface are of mixed $s$-$d$ character and yield a density of states about three times that given in the free-electron model. This accounts for the large observed saturation magnetization of Gd metal and may account for the high electronic specific heats of rare-earth metals.

The one-electron potential, used as input for the APW calculation, was obtained from a superposition of spherically symmetric atomic potentials. Results have been calculated for two different atomic starting potentials: The first was determined from free-atom Hartree-Fock-Slater (HFS) wave functions[5] for the configuration $Gd^0$ $4f^7 6s^2 5d$, while the second was obtained from analytic Hartree-Fock wave functions[6] for the configuration $Gd^{+1}$ $4f^7 6s^2$ plus an atomic $5d$ wave function. The conduction bands obtained using these two potentials were practically identical indicating that they do not depend critically on the potential. We report here the results determined from the HFS potential which was chronologically the first potential used.

Energy eigenvalues were calculated at 45 points in 1/24 of the first Brillouin zone. The calculated $E(k)$ curves for the conduction bands of gadolinium metal along the major symmetry directions are shown in Fig. 1. The strong deviation of these bands from those of a free-electron or nearly free-electron model can be seen in the high density of relatively flat bands, which are largely of $d$ character. The calculation also yields a very narrow $4f$ band (width ~0.05 eV) about 0.8 Ry below the bottom of the $5d$-$6s$ bands. (This separation, however, was found to depend strongly on the potential used and is consequently not very reliable.) The very narrow width of the $4f$ band indicates that the $4f$ electrons are, as expected, highly localized.

The density of states of the conduction bands was obtained by dividing the Brillouin zone into 192 identical hexagons, each characterized by the energies calculated at its center. A histogram representing the computed den-

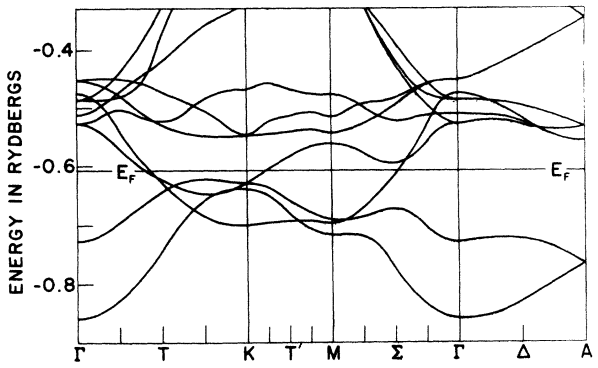


FIG. 1. Calculated $E(k)$ curves for the conduction bands of gadolinium metal along the major symmetry directions.

sity of states $N(E)$ is given in Fig. 2. The density of states for the free-electron model is superimposed for comparison. As seen from this figure the 5*d* bands have a width of about 0.5 Ry, and yield a high density of states. The Fermi energy, for three electrons per atom, is $E_F = 0.25$ measured from the bottom of the band as compared with a value of 0.54 Ry for the free-electron model. At the Fermi energy, the calculated density of states is large, $N(E_F) = 1.8$ electrons per atom per eV compared with the free-electron value of 0.6 $eV^{-1}$. This is due to the fact that the electron bands in the vicinity of the Fermi surface are of mixed *s*-*d* character and are consequently much flatter than would be expected from a free-electron model.

Let us consider the magnetic properties

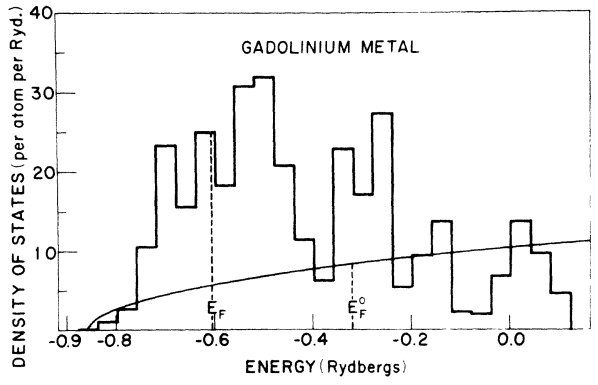


FIG. 2. A histogram representation of the density of states in electrons per atom per Ry. The parabolic curve is the prediction of the free-electron model.

of gadolinium. Saturation magnetization measurements[2] give $7.5\mu_B$ per Gd atom in the metal or $0.5\mu_B$ more than expected for an $^8S$ ion. It is common to assume that this additional moment arises from a polarization of the conduction electrons. Using our computed density of states and a simple model in which the conduction electrons are polarized by exchange with the localized 4*f* electrons, one may estimate the exchange integral $J$ required to produce this additional moment. For gadolinium the induced moment is given by $\mu = \frac{7}{2}JN(E_F)\mu_B$. For $N(E_F) = 1.8$ $eV^{-1}$ we find $J = 0.08$ eV. This $J$ is about 5 times smaller than that computed[7] between atomic 4*f* and 5*d* electrons but agrees with values of $J$ (0.05-0.10 eV) calculated between a localized 4*f* electron and a plane wave.[8,9] (Orthogonalized plane-wave calculations, on the other hand, give[9] $J = 0.04$-$0.07$ eV.) From these estimates, we conclude that the "extra" magnetization in Gd can arise very easily from a reasonable exchange between the magnetic 4*f* electrons and the *s*-*d* conduction electrons at the Fermi energy largely because of the size of our computed $N(E_F)$. Further, with this picture of *s*-*d* conduction electrons occupying a band having a high density of states, one sees a strong qualitative resemblance to the transition metals and the role of *d* electrons in understanding the origin of magnetism in these materials. The difference is that in the rare-earth metals the bulk of the magnetization is carried by the 4*f* electrons which, however, lie well inside the atom and play no further direct role in interatomic exchange.

From our calculated $N(E_F)$ we obtain an electronic specific heat contribution of $\gamma = 4.2$ mJ/mole deg$^2$, which may be compared with an average measured value[3] of about 10 mJ/mole deg$^2$ for the 4*f* rare-earth metals with triply ionized cores, and with a free-electron value of 1.3 mJ/mole deg$^2$. Thus while our calculated $N(E_F)$ is some three times larger than the free-electron value, the calculated $\gamma$ is smaller than experiment by about a factor of two. Crude estimates for Gd indicate that this difference could arise from electron-phonon contributions[10] to an apparent $N(E_F)$ deduced from measured $\gamma$ values. As pointed out by Krebs,[10] this enhancement is expected to be appreciable when the electron energy differs considerably from the free-electron case which we found to be the case

in Gd. Further theoretical work, including calculations for La, and other rare-earth metals, is in progress to answer this and other questions.

We are indebted to R. E. Watson who participated fully in almost all phases of this work. We are grateful to J. H. Wood for making the APW programs available to us and for many helpful discussions, and to A. Furdyna and R. Sheshinski for their help with many phases of the computations.

*Operated with support from the U. S. Air Force.

†Supported by the U. S. Air Force Office of Scientific Research.

[1]For example, see K. Yosida and A. Watabe, Progr. Theoret. Phys. (Kyoto) 28, 361 (1962). H. Miwa, Progr. Theoret. Phys. (Kyoto) 28, 208 (1962). R. J. Elliott and F. A. Wedgwood, Proc. Phys. Soc. (London) 81, 846 (1963); 84, 63 (1964). T. Kasuya, Treatise on Magnetism, edited by H. Suhl and G. Rado (Academic Press, Inc., New York, 1964), Vol. IIA.

[2]H. Nigh, S. Legvold, and F. H. Spedding, Phys. Rev. 132, 1092 (1963).

[3]L. D. Jennings, R. E. Miller, and F. H. Spedding, J. Chem. Phys. 33, 1849 (1960). A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. 109, 70 (1958). O. V. Lounasmaa, Phys. Rev. 126, 1352, 1357 (1962); 129, 2460 (1963); 133, A219 (1964).

[4]J. C. Slater, Phys. Rev. 51, 846 (1937); 92, 603 (1953). M. M. Saffren and J. C. Slater, Phys. Rev. 92, 1126 (1953).

[5]F. Herman and S. Skillman, Atomic Structure Calculations, (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[6]A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[7]A. J. Freeman and R. E. Watson, unpublished.

[8]T. A. Kaplan and D. H. Lyons, Phys. Rev. 129, 2092 (1963).

[9]R. E. Watson and A. J. Freeman, unpublished.

[10]K. Krebs, Phys. Letters 6, 31 (1963); R. E. Prange and L. P. Kadanoff, Phys. Rev. 134, A566 (1964).

## LOCALIZED MOMENTS OF MANGANESE IMPURITIES IN FERROMAGNETIC IRON

V. Jaccarino, L. R. Walker, and G. K. Wertheim
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 18 November 1964)

Most studies of hyperfine fields in ferromagnetic transition-metal alloys have been concerned with the spatial distribution of the fields and little attention has been given to the thermal variation of the latter. Recently,[1] however, it has been observed that the temperature dependence of the $Mn^{55}$ nmr frequency $\nu_T$ in a dilute (1.5% Mn) ferromagnetic FeMn alloy departs markedly from that of the magnetization $\sigma_T$ of the Fe host. In particular, $\nu_T$ decreases much more rapidly than $\sigma_T$ as may be seen in Fig. 1 where $\nu_T/\nu_0$ (open circles) and $\sigma_T/\sigma_0$ are plotted vs $T/T_c$.

We show here that an adequate explanation of the course of the Mn nmr may be obtained from the following assumptions: First, $\nu_T$ is proportional to the thermal average of the Mn moment $\langle S_T\rangle$; second, the Mn moment is localized, with a magnitude $S$ that is independent of temperature; third, the thermal average of the Mn moment is taken over its levels in the exchange field of the iron $H_T^{Mn}$; fourth, $H_T^{Mn}$ is substantially weaker than that exchange field $H_T^{Fe}$ which acts between the iron ions. From this we conclude that little, if any, of the Mn magnetization is induced by the iron host. As such the experiment and its interpretation provide information about the magnitudes of $S$ and $H_0^{Mn}$ and constitute the first example of a magnetized localized state in a ferromagnetic transition metal.

The simplest quantitative expression of these ideas is to equate $\nu_T/\nu_0$ with the Brillouin function $B_S(y)$, with

$$y=\frac{g\beta S}{kT}H_T^{Mn}, \tag{1}$$

and $H_T^{Mn}=H_0^{Mn}\sigma_T/\sigma_0$. Then for various values of $S$ and particular choices of $\zeta\equiv g\beta S\times H_0^{Mn}/kT_c$, families of curves may be generated, examples of which are shown in Fig. 2 for $S=\frac{1}{2}$ and $S=\frac{5}{2}$ for the values of $\zeta$ indicated. It is immediately apparent that the general shape of these curves, particularly for $0.5<\zeta<1$, resemble the behavior of the experimental data of Fig. 1. In particular, for $S=\frac{3}{2}$ and $H_0^{Mn}=3.7\times10^6$ Oe ($g=2.00$), a best fit to the experimental data could be obtained for which the average deviation $\Delta<0.5\%$. Less satisfactory agreement was found for $S=1$ ($\Delta>1\%$) and for other half-integral values of $S$ the fits were noticeably poorer.