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Calculation of the spin-polarized energy-band structure of $LaNi_5$ and $GdNi_5$

S. K. Malik
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

F. J. Arlinghaus
Physics Department, General Motors Technical Center, Warren, Michigan 48090

W. E. Wallace
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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Spin-polarized energy bands, the density of states, and the magnetic moments are calculated for the intermetallic compounds $LaNi_5$ and $GdNi_5$ with the use of the self-consistent augmented-plane-wave method. The calculations reveal a charge transfer of 1.5 electrons from La to Ni but no charge transfer from Gd to Ni. The calculated width of the 3*d* band and the calculated electronic specific-heat coefficient for $LaNi_5$ are in good agreement with the ultraviolet photoelectron spectroscopy results and measured electronic specific-heat data.

I. INTRODUCTION

$LaNi_5$ is the paradigm hydrogen storage material[1] and as such has attracted very considerable attention in recent years. Although the kinetic features of $LaNi_5$ as a hydrogen storage material have recently been clarified,[2] the characteristics which confer upon it a large capacity for hydrogen remain to be elucidated.

It is generally believed that two factors are involved in the energetics of hydrogen uptake, which, in turn, controls a metal's solvent power for hydrogen; there is a size factor and an electronic factor. The former has been stressed by Lundin *et al.*[3] The electronic factor is related to the bonding of hydrogen to the metal lattice. Hydrogen is absorbed dissociatively. The cleavage of the hydrogen bond is endothermal to the extent of ~ 400 kJ/mole H_2. Clearly, there must be a strong exothermal interaction with the lattice as hydrogen enters to compensate for this energy. This interaction has not been elucidated in any more than the most general terms; such as, for example, to assert that there is a strong La-H affinity in $LaNi_5$ hydride, etc. To acquire a deeper understanding, band-structure calculations are needed for the host intermetallic and also for its hydride. The present study represents the first step in this sequence for $LaNi_5$. To acquire a deeper understanding of the size effect, calculations were also made on $GdNi_5$, whose lattice is contracted $\sim 5\%$ compared to $LaNi_5$.

II. PRELIMINARIES OF CALCULATIONS

The compounds $LaNi_5$ and $GdNi_5$ crystallize in the hexagonal $CaCu_5$-type structure (space group D_{6h}^1). In this structure atoms occupy the following special positions: rare earth (1*a*) and Ni (2*c* and 3*g*). The calculational procedure employed is generally similar to that used in the earlier band-structure calculations[4] on YCo_5, $SmCo_5$, and $GdCo_5$. In the present study, as with the earlier study, no distinction is drawn for transition metals in the 2*c* and 3*g* sites. The Brillouin zone for the hexagonal $CaCu_5$ structure is a hexagonal prism (see Ref. 4).

In the augmented plane wave (APW) method[5] one uses a crystal potential which is divided in two parts, one centered on the ion cores and the other in the region between the ions. The potential is assumed to be spherically symmetric within nonoverlapping spheres centered on each atom of the unit cell, and constant in the remaining region outside the spheres. The radius of sphere around each atom is decided as follows: For the case of Ni, it was chosen to be half the nearest-neighbor Ni-Ni distance. The sphere radius around the rare-earth atom was chosen to be equal to the *R*-Ni nearest-neighbor distance minus the sphere radius around the Ni atom.

The most important ingredient of the calculations is the starting trial potential. A good choice of this may facilitate quick convergence. The starting trial potential for each compound was derived from the superposition of free-atom charge densities. The latter of these were calculated by a spin-polarized (i.e., different orbitals for different spins) Hartree-Fock method using a modification of the Herman-Skillman atomic structure program. The outer electron configurations of various atoms for these calculations were chosen as follows:

$$\text{Ni: } 3d\uparrow^4, 3d\downarrow^5, 4s\uparrow^{0.5}, 4s\downarrow^{0.5} ,$$

$$\text{La: } 4f^0, 5d\uparrow^{0.5}, 5d\downarrow^{0.5}, 6s\uparrow^1, 6s\downarrow^1 ,$$

$$\text{Gd: } 4f\uparrow^7, 5d\uparrow^{0.5}, 5d\downarrow^{0.5}, 6s\uparrow^1, 6s\downarrow^1 ,$$

where the arrows signify spin-up and spin-down orientations.

The exchange interaction between the electrons is represented by an exchange potential of the Slater $X\alpha$ type, with the exchange for each spin s given by

$$V_x^s = 6\alpha(3\rho_s/4\pi)^{1/3} ,$$

where ρ_s is the corresponding charge density. The earlier spin-polarized energy-band calculations for $R\mathrm{Co}_5$ (R = Y, Sm, and Gd) compounds had suggested[4] that $\alpha = 1$ was the most reasonable choice for those compounds. This value of α was used in the present calculation, which may slightly overestimate the exchange interaction.

It may be emphasized that although the electrostatic part of the potential is independent of spin orientation, the spin-up and spin-down electrons do see different exchange potentials. The exchange potential for a given spin direction depends on the density of occupied states for that spin direction. The potential modifies the occupied states which in turn affect the potential. Thus, apart from the self-consistency criteria of potential and energy bands, another self-consistency requirement (and usually the most sensitive) is imposed: The difference between the number of electrons occupying the spin-up and spin-down states, which is the magnetic moment, must converge to a unique value. In every iteration, we compute the energy bands for each spin direction at a number of points in the Brillouin zone. In the first and subsequent few iterations, when the results are far from self-consistency, calculations were performed only at eight points in the Brillouin zone. When the results began to converge for eight points, the number of points was increased to 144 and the first self-consistent results were obtained. At the end of each iteration, the Fermi energy is determined by counting states—the states for either spin direction being occupied to a common Fermi level.

The eigenvectors for each state are used to compute the corresponding charge densities. The total charge density is then the sum of charge densities for all occupied states plus a constant charge density corresponding to the core states, the latter obtained from the Herman-Skillman free-atom calculations. Knowing the total charge density, the Poisson equation can be solved to obtain a new potential. As remarked in our earlier paper,[4] one cannot use the new potential as it is for the next iteration, since this causes instability and the process may fail to converge. One typically uses 75% of the initial potential and 25% of the final potential for the next cycle. For both the compounds, the convergence of potential, band energies, and the magnetic moment was achieved (see Table I).

III. RESULTS AND DISCUSSION

The converged energy bands for $\mathrm{LaNi_5}$ and $\mathrm{GdNi_5}$ are presented in Fig. 1, with the corresponding density-of-states curves shown in Fig. 2. The band results are similar in the two cases, dominated by the complex of nickel $3d$ bands.

The nickel $3d$ band complex is ~4 eV wide in both cases, for both spin-up and spin-down. The density-of-states curves are similar in shape for spin-up and spin-down. In both cases the energy-band curves reveal a completely filled majority-spin $3d$ subband, with the Fermi energy lying in a region of very low spin-down density. The $3d$ band complex lies in the middle of a typical parabolic s-p band.

In the $\mathrm{LaNi_5}$ case, no other bands are evident; the results may be approximated by a rigid shift or exchange splitting of about 0.35 eV. No occupied, separate lanthanum band is seen; most of the lanthanum electrons fill up the nickel d band. In the $\mathrm{GdNi_5}$ case there is a shift of ~0.5 eV, and extra bands appear at the top of the nickel d bands, arising principally from the gadolinium $5d$ levels. The

TABLE I. Lattice constants used, number of iterations required for self-consistency, and calculated spin moments.

	a (Å)	c (Å)	Number of iterations	Spin moment per formula unit
$\mathrm{LaNi_5}$	5.013	3.984	19	0.69
$\mathrm{GdNi_5}$	4.899	3.973	20	0.76

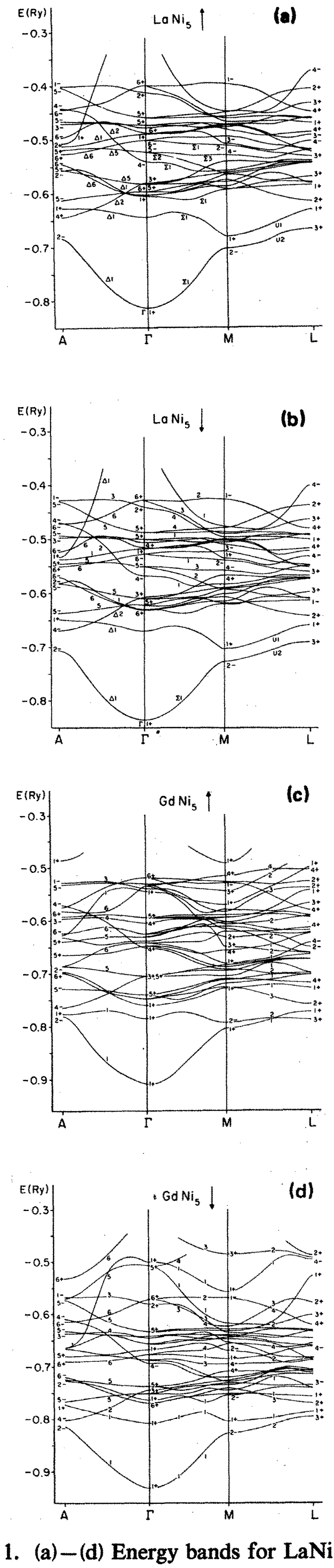

FIG. 1. (a)–(d) Energy bands for $LaNi_5$ and $GdNi_5$.

gadolinium contribution is hybridized with the nickel 3*d* band; since there are 50 nickel electrons and only three gadolinium electrons, the rare-earth contribution does not dominate anywhere. Examination of the separate contributions to the charge density shows a rare-earth portion almost everywhere, which is important in the aggregate.

The calculated spin magnetic moments are given in Table I. To compare with experiment we must add contributions for the orbital moment and for the localized 4*f* moment. Reck and Fry show[6] that nickel metal has an unquenched orbital moment of $0.05\mu_B$. The filling up of the nickel 3*d* band in the RNi_5 compounds will probably lower that value further. We shall therefore ignore it. The Gd ion has a moment of $7\mu_B$ and this couples antiparallel to the spin moment, thus giving $6.24\mu_B$ for the total moment of $GdNi_5$. The experimental moment of $GdNi_5$ is $6.8\mu_B$ per formula unit, whereas $LaNi_5$ is reported to be paramagnetic.[7]

The main difference between the band structures of the RCo_5 and RNi_5 compounds is the extra five nickel electrons, which fill the minority-spin band much further, thus reducing the magnetic moment. Once again, the RNi_5 compounds are essentially nickel metal in a peculiar crystal structure, just as the RCo_5 compounds were very like cobalt metal. The similarity with elemental Ni is also observed in recent UPS results for $LaNi_5$.[8]

The most striking difference has to do with charge transfer. A naive model would predict that the three valence electrons of the rare-earth metal would fill up the holes in the minority-spin nickel 3*d* band. That would reduce the magnetic moment very nearly to zero. Calculations for the RCo_5 compounds showed[4] a transfer of only about one rare-earth electron in each case.

In $LaNi_5$, calculations of the charge distribution show that there is more charge transfer, about 1.5 electrons per lanthanum, with a much-reduced nickel moment. The total moment of $0.69\mu_B$ per formula unit is small and almost entirely due to the nickel. There is essentially zero moment induced at the lanthanum site. Thus, $LaNi_5$ is a very weak ferromagnet with large charge transfer and therefore an almost filled minority-spin band. This view conflicts with experiment for $LaNi_5$. Very careful experiments have been recently initiated to ascertain the magnetic status of $LaNi_5$ at low temperatures.

By contrast, there is almost no charge transfer in $GdNi_5$ from gadolinium to nickel. An apparently weaker exchange interaction on the nickel leads to

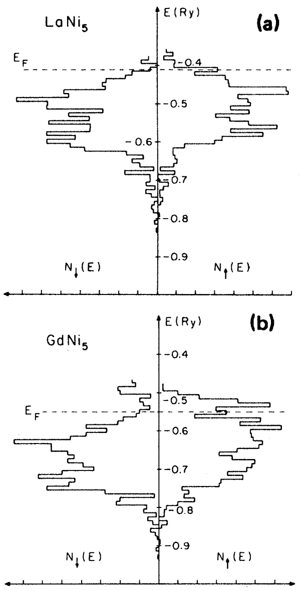

FIG. 2. Density of states for (a) LaNi$_5$ and (b) GdNi$_5$.

a smaller $0.23\mu_B$ moment per nickel atom. This is, however, opposed by a relatively large $0.4\mu_B$ induced moment on the gadolinium site, directed antiparallel to the nickel moment. This is a band effect in the Gd 5*d* band (which is not a separate band, however, but overlaps and hybridizes with the Ni 3*d* band).

IV. RELATIONSHIP TO EXPERIMENT

The data in Fig. 2 can be used to calculate the electronic specific-heat coefficient (γ), $(2\pi^2 k^2/3) \times N(E_F)$, for LaNi$_5$. $N(E_F)$ is calculated to be 26.0×10^{35} erg^{-1}(mole LaNi$_5$)$^{-1}$. From this, γ is evaluated to be 3.24×10^{-2} J mole^{-1}(K)$^{-2}$. This is to be compared with the experimental values in J mole^{-1}(K)$^{-2}$ of 3.43×10^{-2} by Nasu *et al.*[9] and 3.65×10^{-2} by Takeshita *et al.*[10] The agreement with the APW calculations is seen to be quite good. The enlarged value of the experimental quantities can readily be ascribed to electron-phonon enhancement effects.

The calculated width of the *d* band is 3.8 eV. The corresponding experimental values as determined by Weaver *et al.*[8] by photoemission studies is 3.6 eV. Hence, the calculated density of states at the Fermi level and the width of the *d* band are both in good agreement with experiment.

In summary, these calculations provide considerable insight into the behavior of *R*Ni$_5$-type compounds. They show the origin of the moment and reason for its variations. They also show the variability possible in charge transfer effects and the role this can play in the magnetic properties. These charge transfer effects are sensitive to the details of the crystal potential and are obtained only from detailed and self-consistent computations of the electronic structure.

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