Ferromagnetism below the Stoner limit in La-Doped SrB_6

T. Jarlborg
DPMC, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Genève, Switzerland
(Received 5 January 2000)

Spin-polarized band calculations for $LaSr_7B_{48}$ show a weak ferromagnetic state. This is despite a low density of states (DOS) and a low Stoner factor. The reason for the magnetic state is found to be associated with a gain in potential energy in addition to the exchange energy, as a spin splitting is imposed. A DOS with an impuritylike La band is essential for this effect. It makes a correction to the Stoner factor and provides an explanation of the recently observed weak ferromagnetism in doped hexaborides.

PACS numbers: 75.50.Cc, 71.15.Mb

Recent experimental work on doped hexaborides shows many surprises [1,2]. Among the unexpected properties is the observation of a very weak ferromagnetic state that persists up to large temperatures when small amounts of Ca are replaced by La in the hexaboride system, $La_xCa_{(1-x)}B_6$ [3]. This is surprising since the density of states (DOS) at the Fermi energy, $N(E_F)$, and the Stoner factor are expected to be small in this system. Band calculations [4] in the local density approximation (LDA) [5] on SrB_6 and CaB_6 confirm that the DOS is low, with E_F falling in a valley of the DOS, and spin-polarized calculations for EuB_6 show a very weak spillover of the spin density from the Eu-*f* spin to the rest of the valence band. Electronic structure calculations based on the local (spin) density approximation, either by spin-polarized calculations or by calculations of the Stoner factor $\bar{S}$, are in general able to detect if a system is ferromagnetic or not [6–8]. Because the Stoner factor for $La_xSr_{(1-x)}B_6$ is far below the limit for magnetism, it is tempting to suggest that the observed magnetism is not a band magnetism, but something else, perhaps excitonic [9] or a polarization of the dilute electron gas [3,10]. However, for Ce it is found that the Stoner factor underestimates the tendency towards magnetism, because the stabilization energy does not come only from exchange, and the Stoner criterion has to be corrected for a potential energy [11]. Even if this correction is small in Ce, there is nothing in principle that prevents a large correction to the Stoner model in other systems. In this Letter we show that $LaSr_7B_{48}$ is such a system. We find that the exchange-split band structure triggers charge transfers that contribute to the gain in total energy via the Coulomb interaction.

Electron energies are calculated by the linear muffin-tin orbital method using the LDA. The structure of SrB_6 is simple cubic, with one Sr in the corner and a B_6 octahedron in the center. The internal parameter z which determines the shortest distance from one of the B atoms to a cube surface is in these calculations 0.215 of the lattice constant. Additional "empty" spheres are inserted at the cube edges, between the Sr atoms, in order to account for nonsphericity of the potential in the open part of the structure. Calculations were made for the basic unit cell, a double cell, and a large supercell of eight cubes (two cube lengths in the x, y, and z directions), containing totally 56 atoms and 24 empty spheres. Nonequivalent sites are treated independently, which permits all possible charge transfers to be monitored. The basis set for the largest unit cell includes s, p, d for the atoms, and s, p for empty spheres. The small cells also include *f* states for the Sr sites. The occupied *f* part is always very small, even for the La-impurity site. The lattice constant is fixed at 7.93 a.u. in each calculation. No lattice relaxation around the La impurity is considered. The number of k points varies from 286 to 20 irreducible k points for the unit cells of 10 and 80 sites, respectively.

The band structure for undoped SrB_6 agrees well with the one in Ref. [4]. The paramagnetic (non-spin-polarized) DOS from the supercell calculation for $LaSr_7B_{48}$ is shown in Fig. 1. The La band forms a separate band near E_F below the rest of the Sr-*d* band, making the real space

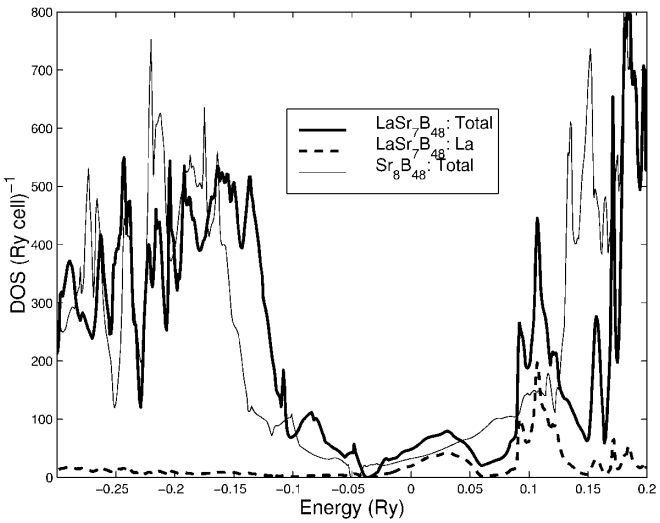

FIG. 1. Paramagnetic, total, and partial La DOS near E_F for $LaSr_7B_{48}$ and total DOS in Sr_8B_{48} as obtained from tetrahedron integration for 20 k points. The zero energy is at E_F for $LaSr_7B_{48}$ and at the energy corresponding to one additional electron above E_F for Sr_8B_{48}.

 0031-9007/00/85(1)/186(4)$15.00

distribution of this band localized near the La impurity. This is an example of an "excluded" band as in the spin-down bands of Heusler alloys [12]. The process of "exclusion" can be helped if the band is an impurity band, associated with atoms of low concentration in a different host. A similar example of a separate or excluded band is for a dilute V impurity in the oxide insulator $SrTiO_3$, where a narrow V band appears at the top of the band gap in $Sr_8VTi_7O_{24}$. This is in contrast to the equivalent concentration of a Nb impurity in the same oxide, where the Nb band merges well with the Ti band [13]. Such examples show that it is difficult to predict *a priori* when localized bands will form. The total $LaSr_7B_{48}$ DOS at E_F, $N(E_F)$, about 48 (states/cell)/Ry, is concentrated on the single La site, with $N_{\mathrm{La}}(E_F) \sim 19$ (states/cell)/Ry; cf. Table I. On the remaining 55 sites, each Sr has on average 1.0 and each B roughly 0.4 (states/cell)/Ry, respectively. By comparison, a rigid-band model obtained by adding one electron to the band structure without the La impurity (cf. Fig. 1) gives very different values: Of the total DOS, 32 (states/cell)/Ry, each Sr has 1.4 and each B, 0.25 states/Ry. Clearly, La behaves like a localized impurity site with a very large local $N_{\mathrm{La}}(E_F)$, much larger than on Sr. The additional valence electron remains located on the La, as can be seen in Table II. By comparing the charges in the undoped and doped supercells one finds that the remaining Sr_7B_{48} spheres receive no additional charge. The difference in charge between the two systems is never larger than 0.01 electron per Sr or B site. The derivative of the DOS becomes very large, about 1400 (states/cell)/Ry^2, from which 700 comes from the La site, compared to about 30 for each Sr site when the rigid-band model is applied to the undoped band structure. This asymmetric and uneven distribution of the DOS near E_F is a condition for real space charge transfers as T increases and as an exchange splitting is imposed. The transfer goes in both cases to the La site from the rest of the system.

Spin-polarized calculations for pure SrB_6, and for a double cell $SrLaB_{12}$, do not give stable moments of a significant size. The supercell calculation of $LaSr_7B_{48}$ using 20 k points finds a small moment of $0.10\mu_B$/cell at low temperature. The ferromagnetic state is about 10 m Ry/supercell lower in total energy than the paramagnetic solution. If fewer k points are used, one finds that the (paramagnetic) DOS and its energy derivative near E_F are larger, cf. Table I. The spin moment increases to $0.24\mu_B$/cell for the lowest number of k points, with a total energy 11 m Ry lower than the paramagnetic state. The moment is always largest on La, with more than 50% of the total moment on and near the La impurity. The moment on B sites far from the impurity is negligible. This fact and the uneven distribution of local DOS show that a rigid-band picture of dilute La-doped hexaborides does not apply. The bands near E_F are modified by the spatially nonuniform perturbation of the potential around the impurity site.

TABLE I. Paramagnetic DOS values (states/cell Ry, and states/cell Ry^2), spin-polarized exchange splitting on La ξ (m Ry), and magnetic moment on La and total (μ_B), as functions of the number of k points. To the impurity site are counted also the contributions from the six closest empty spheres.

k points	$N(E_F)$	N_{La}	N'_{La}	ξ_{La}	m_{La}	m_{tot}
4	98	50	2100	7	0.17	0.24
10	52	23	830	4	0.10	0.15
20	48	19	730	3	0.07	0.10

The original Stoner model [6] can be applied together with *ab initio* paramagnetic band results in order to study the spin susceptibility or the onset of magnetism [7,8]. An applied exchange splitting, ξ, leads to a transfer from minority spins to majority spins, and a loss in kinetic energy $\Delta K = N\xi^2$, where N, the DOS at E_F, is assumed to be constant. The same spin transfer leads to a gain in exchange energy $\Delta E_x = N^2 I_s \xi^2$, where the exchange integral, I_s, can be calculated within LDA [7]. If $\Delta E_x \geq \Delta K$, there will be a total gain in energy and a ferromagnetic transition can occur: Eliminating factors of N and ξ^2 one obtains the Stoner criterion, $\bar{S} = NI_s \geq 1$. If a partial DOS is not constant near E_F, there will be a possibility of charge transfers as functions of ξ, and additional contributions to the total energy. As in Ref. [11], it is possible now to identify one subband, the La-impurity (mainly d) band, which has a large derivative of its DOS, $N'_{\mathrm{La}}(E_F)$. The total DOS at E_F is $N = N_{\mathrm{La}} + N_v$, where N_v is the rest of the DOS. By neglecting all other derivatives one can make a model of the charge transfers as functions of ξ and k_BT. From Ref. [11], we get the charge transfers $\Delta q_\xi = N_v N'_{\mathrm{La}} \xi^2 / N$ and $\Delta Q = N_v N'_{\mathrm{La}} \pi^2 (k_BT)^2 / 6N$, respectively, where it is assumed that $N'_{\mathrm{La}} k_BT$ and $N'_{\mathrm{La}} \xi$ are small.

Next we calculate the Coulomb energy associated with the charge transfer, $\Delta E(T) = U_0 \Delta Q$, from self-consistent paramagnetic calculations at different T. The charge density is $\rho(T, r) = \sum_{\vec{k},j} f(\epsilon^j_{\vec{k}}, E_F, T) \mid \Psi(\epsilon^j_{\vec{k}}, r)|^2$, where f is the Fermi-Dirac function, and $\Psi(\epsilon^j_k, r)$ is the wave function for point k and band j. The electronic total energy, E_{tot}, contains kinetic, Coulomb, and exchange-correlation terms:

$$E_{\mathrm{tot}}(T) = \int f \epsilon N(\epsilon)\, d\epsilon - \int \left(\frac{1}{2} V_e - \varepsilon + \mu\right) \rho\, d^3 r + E_M , \qquad (1)$$

where V_e is the electronic part of the Coulomb potential, E_M is the Madelung part of the electrostatic energy, and ε and μ are the exchange-correlation energy and potential, respectively.

The first term in Eq. (1), the kinetic term, becomes $E_K = \frac{\pi^2}{3} (k_BT)^2 N(E_F)$, giving the usual Sommerfeld term

TABLE II. Differences in valence charge (e^- per site) between doped and undoped SrB_6 supercells for selected sites calculated from 20 k points. The charge within the six closest empty spheres is assigned to the impurity site. There is not much variation among nonequivalent B sites.

Impurity site (La or Sr)	Sr near La	Sr far from La	B (average)
1.19	0.005	0.01	−0.005

in the specific heat $C_{\rm el} = \frac{\partial E_K}{\partial T} = \gamma T$. The difference, $E(T)$, between the fully calculated $E_{\rm tot}$ in Eq. (1) and E_K defines the nonkinetic contribution due to charge transfers:

$$E(T) = \int f\epsilon N(\epsilon)\, d\epsilon - E_{\rm tot}(T) = \int \left(\frac{1}{2}V_e - \varepsilon + \mu\right)\rho\, d^3r - E_M(T), \quad (2)$$

and

$$\Delta E(T) = E(T) - E(0). \quad (3)$$

Calculations of $E(T)$ need to be self-consistent because of relaxation, while E_K and the Stoner product are only moderately affected by nonlinear response effects from the system. At low T is ΔE nearly proportional to ΔQ, $\Delta E \approx U_0 \Delta Q$, while it saturates for higher T. The calculated parameter U_0 varies between 1 and 2.5 (Ry/e^-)/La for k_BT in the interval 0.5 to 15 m Ry, according to calculations using ten irreducible k points. The value of U_0 may seem large, because the charge transfer ΔQ is defined for the La site only, while ΔE involves contributions from the entire cell. The largest contribution to ΔE comes from the Madelung term, because of the sizable charge transfer to La. This value of U_0 is calculated without taking into account lattice expansion, but the mechanism of large charge transfers is expected to have an influence on thermal expansion and specific heat.

The charge transfer towards La is a result of the increasing La DOS near E_F (Fig. 1). A very similar charge transfer pattern will result from a spin splitting, ξ, of the paramagnetic bands. The similarity between the two types of charge transfer permits us to write $\Delta E_\xi = U_0 \Delta q_\xi = U_0 N'_{\rm La} N_v \xi^2/N$. With this energy included, one obtains a modified Stoner criterion [11]:

$$\bar{S}_U = N I_s + U_0 N'_{\rm La} N_v / N^2 \geq 1. \quad (4)$$

The calculated Stoner product NI_s is 0.21, $N'_{\rm La} \sim 730$ per Ry^2 · cell, $N \sim 48$ and $N_v \sim 29$ (per Ry · cell), to give $\Delta q_\xi \approx 440\xi^2$ and $\Delta Q = 720(k_BT)^2$, with ξ and k_BT in Ry. The values make the Coulomb term in Eq. (4) very large, about 14. However, even if the Coulomb energy represents a major correction in this case, there are several facts indicating that other energies are involved as well. First, the exchange splitting ξ is not uniform over all sites. The spin-polarized calculation shows that ξ is finite only at or very near to La, and the energy of a variable ξ is not counted. Second, although the amount of charge transfer due to ξ and k_BT is similar, there are long tails of the Fermi-Dirac distribution which make the radial dependencies of Δq_ξ and $\Delta Q(T)$ different. Third, the effective derivative of the La DOS, $N'_{\rm La}(\epsilon, T)$ [taken as $\int(-df/d\epsilon)N'_f(\epsilon)\, d\epsilon$], is likely to be largest at low T, because the bare DOS does not have the same large derivative over a wide energy range. The mechanism of charge transfer and magnetism is therefore expected to disappear at some large T. This is confirmed in the spin-polarized results. By raising k_BT to 3 m Ry in the calculation with ten k points, the magnetic moment goes to zero. It is also interesting to note that the value of $N'_{\rm La}$ is larger in the calculation with fewer k points, as shown in Table I. The number of k points is insufficient for a good convergence in this case, but the variations of $N'_{\rm La}$ and the magnetic moment in the spin-polarized results as a function of the number of k points are similar.

The ξ^2 dependence of the charge transfer is a result of assuming at most a linear DOS variation in the simple model. In reality, there are more complex variations of the DOS and its derivatives around E_F. By imposing a ξ on the calculated bands rigidly, one finds that Δq_ξ is proportional to ξ^2 only below ~1 m Ry, it is linear around the interval 2–4 m Ry, and it saturates at about 0.007 e^-/La for ξ larger than about 5 m Ry. By comparing the energies for large ξ one can estimate the maximum ξ for a stable moment:

$$N^2 I_s \xi^2 + U_0 0.007 = N\xi^2. \quad (5)$$

With $U_0 = 1.5$, this gives $\xi = 16$ m Ry and a moment of $\sim 0.8\mu_B$ per cell. These values are much larger than the values from the stable spin-polarized solution, about 3 m Ry for ξ and $0.1\mu_B$ for the moment, located on La only. The model can reproduce the essential dependencies of the magnetic instability, and it helps to understand the reasons behind the transition. But for quantitative values one has to rely on the spin-polarized calculations.

The magnetic state in the supercell is fragile, and in a smaller cell not even stable. The fact that an insufficient number of k points can make the moment increase is not meant to represent the real physical situation. It serves to demonstrate that the moment depends on the derivative of the DOS, and thus to confirm the hypothesis that the charge transfer contributes to the stabilization of the magnetic state. This result should apply to any compound with favorable U_0 energies and DOS conditions at E_F, and many materials could be in this category, among which the doped hexaboride is one probable example. The magnetism is

in this case sensitive to other features in the electronic structure than what is normal for ferromagnets. A large Stoner factor needs a large DOS, usually a peak, which often is sensitive to disorder and thermal smearing. But a derivative of the DOS can be large in a fairly wide energy interval, aside from a peak in the DOS. The contribution to magnetism from charge transfer energies may therefore resist thermal effects well, and thereby be consistent with the observation of high Curie temperatures.

When it comes to explaining the properties of the real hexaboride system from the band results, one has to rely on extrapolations. The very low doping ($x = 0.01$) for optimal magnetism in real $La_xCa_{(1-x)}B_6$ [3] is much smaller than the doping in the largest supercell ($x = 0.125$) studied here. Calculations for realistically large supercells are not possible at present. However, there are several indications that the mechanism favorable to magnetism will remain or even be stronger at lower doping. First, by increasing the La content to $x = \frac{1}{2}$ in a double cell $LaSrB_{12}$, one finds a more rigid-band-like La DOS than for the dilute impurity in the supercell, and the local La DOS resembles more the Sr DOS. Effects of charge transfers will therefore be less pronounced than for a single La impurity, and no magnetic state was found in this case. Second, the increasing La-La distance for less doping will maintain a narrow, impurity-like DOS localized on La. The Fermi energy will not cut this band in a rigid-band manner at a lower energy, where the DOS and its derivative are smaller, even though the number of electrons per average site decreases with lower doping. Instead, since the additional charge remains localized at the impurity, one expects the position of E_F to remain fixed relative to the La band, with large local values of N_{La} and N'_{La} even for lower doping. On the other hand, in the large volume far from the La site one expects that charges and DOS conditions will be as for the undoped material, not knowing about the effects of La in part of the system. Below a critical doping concentration there is not sufficient interaction across the conduction electrons for the local moments to order. Then one can speculate that N_v will approach N, where N only is the part of the DOS which is affected by the impurity, and the correction to the Stoner factor given by Eq. (4) will remain large to explain a local moment.

The non-rigid-band-like electronic structure around the dilute La impurity shows up in the distribution of the ferromagnetic moment. According to these results, it is mainly La and the nearest sites which take the major part of the total moment. B sites remain essentially nonpolarized. Alternative theories based on the excitonic mechanism [9] need to take into account the non-rigid-band effect of the La doping, where the local perturbation around an impurity can be favorable to formation of local electron-hole pairs. If a rigid-band mechanism did apply, one should expect a uniform distribution of both pairs and the moment. Theories of spontaneous ferromagnetism of the dilute electron gas have also been proposed [3,10]. However, the very large electron-gas parameter r_s necessary for this (≥ 30) is much too large. The total electron density should be considered (not only the part due to doping), and for this type of compound it corresponds to r_s smaller than 1.5 within the atomic sites and about 3 within the empty sites.

Some experiments can be suggested to verify if the La band is localized and if the moment is concentrated close to the La. Nuclear magnetic resonance from La should be able to probe the distribution of the magnetic moment. However, the low La concentration for the real magnetic system might be a problem for the intensity. Spectroscopic studies such as photoemission or soft x-ray emission would be useful even at larger La concentrations, before magnetism sets in. They could reveal if the DOS shows a localized La band similar to the DOS calculated here for $x \sim 0.125$, or if the DOS is more like a rigid-band image of the undoped DOS.

We have shown that ferromagnetism occurs in the supercell of $LaSr_7B_{48}$. This is despite the fact that according to the low Stoner factor, ferromagnetism should not appear. By doing the calculations with a different number of k points it has been possible to show that the actual derivative of the local DOS at E_F, which is necessary for charge transfers, scales with the stability of the magnetic moment. This demonstrates that the mechanism for ferromagnetism is not exclusively found in the exchange energy. The necessary condition of a localized, nonconstant La DOS near E_F, appears to be enforced as the doping decreases, making the mechanism of charge transfers persist at lower doping levels. A computational verification of this will need a very large unit cell or a Green-function method for the limit of dilute doping.

[1] H. R. Ott *et al.*, Z. Phys. B **102**, 337 (1997); H. R. Ott *et al.* (to be published).
[2] L. Degiorgi *et al.*, Phys. Rev. Lett. **79**, 5134 (1997).
[3] D. P. Young *et al.*, Nature (London) **397**, 412 (1999).
[4] S. Massidda *et al.*, Z. Phys. B **102**, 83 (1997).
[5] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[6] E. C. Stoner, Rep. Prog. Phys. **11**, 43 (1948); K. L. Hunt, Proc. R. Soc. London A **216**, 103 (1953).
[7] O. Gunnarsson, J. Phys. F **6**, 587 (1976); J. F. Janak, Phys. Rev. B **16**, 255 (1977).
[8] T. Jarlborg and A. J. Freeman, Phys. Rev. B **22**, 2332 (1980).
[9] M. E. Zhitomirsky, T. M. Rice, and V. I. Anisimov, Nature (London) **402**, 251 (1999); L. Balents and C. M. Varma, Phys. Rev. Lett. **84**, 1264 (2000); V. Barzykin and L. P. Gorkov, Phys. Rev. Lett. **84**, 2207 (2000).
[10] G. Ortiz, M. Harris, and P. Ballone, Phys. Rev. Lett. **82**, 5317 (1999).
[11] T. Jarlborg, Phys. Rev. B **58**, 9599 (1998).
[12] A. R. Williams *et al.*, J. Magn. Magn. Mater. **31–34**, 88 (1983).
[13] T. Jarlborg, Int. J. Mod. Phys. B **13**, 3525 (1999).