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High-temperature ferromagnetism of sp electrons in narrow impurity bands: application to CaB_6

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Abstract

Ferromagnetism with high Curie temperature T_c , well above room temperature, and very small saturation moment has been reported in various carbon and boron systems. It is argued that the magnetization must be very inhomogeneous with only a small fraction of the sample ferromagnetically ordered. It is shown that a possible source of high T_c within the ferromagnetic regions is itinerant electrons occupying a narrow impurity band. Correlation effects do not reduce the effective interaction which enters the Stoner criterion in the same way as in a bulk band. It is also shown how, in the impurity band case, spin wave excitations may not be effective in lowering T_c below its value given by Stoner theory. These ideas are applied to CaB_6 and a thorough review of the experimental situation in this material is given. It is suggested that the intrinsic magnetism of the B_2 and O_2 dimers might be exploited in suitable structures containing these elements.

1. Introduction

There is great interest in the possible existence of ferromagnetism well above room temperature in materials which have no transition metal or rare earth metal components. Such high temperature ferromagnetism has been reported in various carbon systems such as fullerenes [1–5] and graphite [4, 6, 7] and also in systems such as CaB_2C_2 [8] and CaB_6 [9, 10] containing boron. The electrons involved in the ferromagnetism are s and p electrons, rather than d or f. The saturation moment in these systems is invariably very small and it is generally believed that the ferromagnetism is associated with defects or impurities. It is natural to suggest that the ferromagnetism may merely be due to magnetic impurities such as Fe but this appears to be ruled out experimentally in some cases [6, 11]. It is also difficult to see how local magnetic moments associated with dilute Fe impurities could be coupled strongly enough to be ferromagnetically ordered above room temperature. In fact, the same problem exists for local magnetic moments arising from any other form of defect. We believe that the most likely source of high temperature ferromagnetism is itinerant electrons occupying a narrow impurity band.

In this paper we investigate how itinerant electron ferromagnetism in a narrow impurity band differs from the usual situation in the 3d band of transition metals. In the next section we discuss the criterion for ferromagnetism and the magnitude of the Curie temperature T_c within Stoner theory. It is pointed out that the size of the effective on-site interaction parameter which appears in the theory is not limited by the width of the impurity band, as one might expect naively from Kanamori's [12] T -matrix theory of electron correlation. A formal argument concerning this point is given in section 3. It is well known that in transition metals, and in very weak itinerant ferromagnets such as ZrZn_2 , Stoner theory overestimates T_c by a large factor. Instead T_c is determined by low-lying spin fluctuations which are not included in Stoner theory [13]. In section 4 we argue that this is not necessarily the case in impurity-band ferromagnets so that T_c may in fact be close to its Stoner value.

In all the carbon and boron-based ferromagnets the experimental situation is quite unclear with many conflicting results. To illustrate this we take the example of CaB_6 and in section 5 many experiments on this system are reviewed. An attempt is made to build up a picture of the system based on the present theory of impurity-band ferromagnetism. In section 6 we draw some conclusions.

2. Stoner theory of impurity band ferromagnetism

A condition for ferromagnetism in an itinerant electron system is the familiar Stoner criterion

$$I_{\text{eff}}N(E_F) > 1, \quad (1)$$

where $N(E_F)$ is the density of one-electron states per atom per spin at the Fermi level in the paramagnetic state and I_{eff} is an on-site interaction parameter. This criterion is not satisfied for most of the 3d metals or for any of the 4d metals. Even for the ferromagnetic metals Fe, Co and Ni it is only satisfied by a small margin ($I_{\text{eff}}N(E_F) \geq 1.2$) [14]. The reason for this is that the large on-site Coulomb interaction is reduced to an effective interaction $I_{\text{eff}} \simeq W/5$, where W is the width of the d band, owing to a correlation effect [12]. Rather than experience the strong on-site interactions two electrons (or holes) avoid coming on the same site as far as possible and thereby increase their kinetic energy due to increased spatial confinement. Since $N(E_F) \simeq 5/W$ we have $I_{\text{eff}}N(E_F) \simeq 1$. The situation is quite different when ferromagnetism occurs in a narrow impurity band. In this case $N(E_F) \simeq n_{\text{imp}}/W_{\text{imp}}$ where n_{imp} is the fraction of impurity atoms and the width W_{imp} of the impurity band can be very small. Also, even if the bare interactions for sp electrons are strong enough for the Kanamori effect to operate, the kinetic energy increase due to increased spatial confinement of holes is governed by the full width of the valence band, not by the width of the impurity band. Thus $I_{\text{eff}} \gg W_{\text{imp}}$ and this is shown formally in section 3 by considering the T -matrix for itinerant electrons in the impurity band. The Stoner criterion $I_{\text{eff}}N(E_F) > 1$ demands that $n_{\text{imp}}I_{\text{eff}}/W_{\text{imp}} > 1$ and this can be easily satisfied if W_{imp} is sufficiently small.

In Stoner theory the Curie temperature T_c is given by

$$I_{\text{eff}} \int dE \left(-\frac{\partial f}{\partial E} \right) N(E) = 1 \quad (2)$$

where $f(E) = \{\exp[(E - \mu)/k_B T_c] + 1\}^{-1}$. μ is the chemical potential and $N(E)$ is the density of states per atom per spin in the band. For simplicity we consider a half-filled impurity band with constant density of states $N(E) = n_{\text{imp}}/W_{\text{imp}}$ in the range $-W_{\text{imp}}/2 < E < W_{\text{imp}}/2$. Here it is assumed that each impurity atom introduces one state of each spin into the band and provides one electron (or hole). Owing to the assumption of half-filling, $\mu = 0$ at all temperatures so that equation (2) gives

$$k_B T_c = W_{\text{imp}} / [4 \tanh^{-1}(W_{\text{imp}}/I_{\text{eff}}n_{\text{imp}})]. \quad (3)$$

The right-hand side is a monotonic decreasing function of W_{imp} , so letting $W_{\text{imp}} \rightarrow 0$ we have

$$k_B T_c < I_{\text{eff}} n_{\text{imp}} / 4. \quad (4)$$

To obtain a Curie temperature above room temperature, with a typical value of $I_{\text{eff}} = 1$ eV, we require $n_{\text{imp}} > 0.1$. Assuming that there is complete spin alignment in the ground state, which for the rectangular band considered here occurs whenever the Stoner criterion $n_{\text{imp}} I_{\text{eff}} > W_{\text{imp}}$ is satisfied, the saturation moment is therefore greater than $0.1 \mu_B/\text{atom}$. If there is only partial spin alignment in the ground state the argument of section 4 supporting applicability of the Stoner model fails and low energy spin fluctuations are likely to reduce T_c far below the Stoner value. We conclude that room temperature ferromagnetism and a uniformly distributed saturation moment much less than $0.1 \mu_B/\text{atom}$ are incompatible.

The observed magnetizations in graphite and C_{60} are of the order $10^{-3} \text{ A m}^2 \text{ kg}^{-1} \simeq 2 \times 10^{-6} \mu_B/\text{C atom}$ but typically an order of magnitude larger in CaB₆. We must conclude that the magnetization is very inhomogeneous with perhaps only a fraction 10^{-4} of the sample ferromagnetically ordered. Some evidence for this inhomogeneity in CaB₆ is discussed in section 5.

3. The effect of electron correlations

As we discussed in the previous section, renormalization of the effective Stoner interaction due to correlation effects is of crucial importance for understanding itinerant-electron ferromagnetism. Formally, this renormalization can be taken into account via the T -matrix approach [12, 15] which is exact for the case of small electron (or hole) concentration but is qualitatively adequate for arbitrary band filling. We start with the general many-body Hamiltonian:

$$\begin{aligned} H &= H_t + H_U \\ H_t &= \sum_{\lambda\lambda'\sigma} t_{\lambda\lambda'} c_{\lambda\sigma}^\dagger c_{\lambda'\sigma} \\ H_U &= \frac{1}{2} \sum_{\{\lambda_i\}\sigma\sigma'} \langle \lambda_1 \lambda_2 | v | \lambda'_1 \lambda'_2 \rangle c_{\lambda_1\sigma}^\dagger c_{\lambda_2\sigma'}^\dagger c_{\lambda'_2\sigma'} c_{\lambda'_1\sigma}, \end{aligned} \quad (5)$$

where $\lambda = im$ are the site number (i) and orbital (m) quantum numbers, $\sigma = \uparrow, \downarrow$ is the spin projection, c^\dagger, c are the Fermi creation and annihilation operators, H_t is the hopping Hamiltonian, and the Coulomb matrix elements are defined in the standard way

$$\langle 12 | v | 34 \rangle = \int d\mathbf{r} d\mathbf{r}' \psi_1^*(\mathbf{r}) \psi_2^*(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \psi_3(\mathbf{r}) \psi_4(\mathbf{r}'), \quad (6)$$

where we define for brevity $\lambda_1 \equiv 1$ etc. Following Galitskii [15] let us take into account the ladder (T -matrix) renormalization of the effective interaction:

$$\begin{aligned} \langle 13 | T^{\sigma\sigma'}(i\Omega) | 24 \rangle &= \langle 13 | v | 24 \rangle - \frac{1}{\beta} \sum_{\omega} \sum_{5678} \langle 13 | v | 57 \rangle G_{56}^{\sigma}(i\omega) \\ &\times G_{78}^{\sigma'}(i\Omega - i\omega) \langle 68 | T^{\sigma\sigma'}(i\Omega) | 24 \rangle, \end{aligned} \quad (7)$$

where $\omega = (2n + 1)\pi k_B T$ are the Matsubara frequencies for temperature $k_B T \equiv \beta^{-1}$ ($n = 0, \pm 1, \dots$). Using the spectral representation for the Green's function

$$G_{56}^{\sigma}(i\omega) = \int_{-\infty}^{\infty} dx \frac{\rho_{56}^{\sigma}(x)}{i\omega - x}, \quad (8)$$

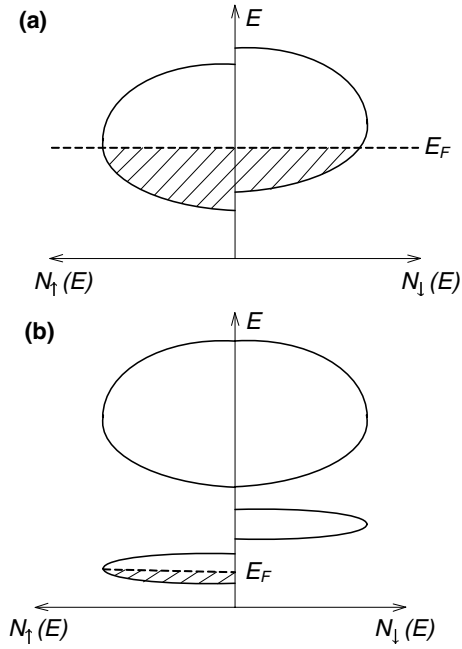


Figure 1. Schematic density of states for (a) a weak itinerant ferromagnet and (b) the ferromagnetic impurity band model.

substituting equation (8) into (7) and calculating the sum over Matsubara frequencies in the usual way [16] one can rewrite equation (7) in terms of the spectral density matrix $\hat{\rho}(x)$:

$$\begin{aligned} \langle 13 | T(E) | 24 \rangle &= \langle 13 | v | 24 \rangle + \sum_{5678} \langle 13 | v | 57 \rangle \langle 57 | P(E) | 68 \rangle \langle 68 | T(E) | 24 \rangle, \\ \langle 57 | P(E) | 68 \rangle &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \frac{1 - f(x) - f(y)}{E - x - y} \rho_{56}(x) \rho_{78}(y) \end{aligned} \quad (9)$$

where E is the *real* energy. In this section we neglect spin polarization since the effective exchange parameter I_{eff} in the Stoner criterion (1) should be calculated in the paramagnetic phase.

If we take into account only on-site Coulomb interaction (the Hubbard approximation) then the T -matrix turns out to be also diagonal in site indices and the matrix equation (9) holds assuming that 1, 2, ..., 8 label only orbital indices and $\hat{\rho}(x)$ is local (on-site) spectral density.

For simplicity, we will consider further the case with one orbital per atom and thus omit orbital indices. The effective interaction I_{eff} is given by $T(E)$ with E corresponding to the sum of energies of two occupied electron states [12]. Then from (9) we have $I_{\text{eff}} = v/(1 - Pv) = -1/P$ for large v . Hence in the bulk-band case (figure 1(a)) $I_{\text{eff}} \simeq W$ [12]. The energy spectrum for the impurity band model is shown schematically in figure 1(b), with a broad main band (region I) and a narrow impurity band (region II). The figure shows an impurity band split from the bottom of the main band but the present considerations are identical for the case of holes in an impurity band split from the top of a valence band, as in the model of CaB_6 proposed in section 5.1. To estimate different contributions to the function $P(E)$ one should take into

account that

$$\begin{aligned}\int_I \int_I \frac{dx dy}{x+y} \rho(x) \rho(y) &\sim \frac{1}{W} Z_{\text{band}}^2, \\ \int_{II} \int_{II} \frac{dx dy}{x+y} \rho(x) \rho(y) &\sim \frac{1}{W_{\text{imp}}} Z_{\text{imp}}^2, \\ \int_I \int_{II} \frac{dx dy}{x+y} \rho(x) \rho(y) &\sim \frac{1}{W} \ln\left(\frac{W}{W_{\text{imp}}}\right) Z_{\text{band}} Z_{\text{imp}},\end{aligned}\quad (10)$$

where

$$\begin{aligned}Z_{\text{imp}} &= \int_{II} dx \rho(x), \\ Z_{\text{band}} &= \int_I dx \rho(x) = 1 - Z_{\text{imp}}\end{aligned}\quad (11)$$

are total spectral weights of the impurity and main bands, respectively.

To proceed further, one has to specify our model for the impurity band. Let us consider for simplicity the Slater–Koster model of a single impurity, with non-degenerate band energy $\epsilon(\mathbf{k})$, \mathbf{k} being the quasimomentum, and on-site only impurity potential V ($V < 0$). Then the impurity site Green's function reads [17]

$$\begin{aligned}G_{00}(E) &= [F^{-1}(E) - V]^{-1}, \\ F(E) &= \frac{1}{N} \sum_{\mathbf{k}} \frac{1}{E - \epsilon(\mathbf{k})}\end{aligned}\quad (12)$$

where N is the number of atoms in the crystal. The energy of the impurity localized state E_0 and its spectral weight are determined by the equations

$$\begin{aligned}VF(E_0) &= 1, \\ Z_{\text{imp}} &= \left| \frac{d}{dE} [F^{-1}(E) - V] \right|_{E=E_0}^{-1} = \frac{1}{V^2 |F'(E_0)|}.\end{aligned}\quad (13)$$

For the case of shallow impurity levels

$$\varepsilon \equiv |E_b - E_0| \ll W, \quad (14)$$

where E_b is the energy at the bottom of the main band, one can use the asymptotic forms

$$F(E) \sim \frac{1}{W} \ln\left(\frac{W}{E_b - E}\right) \quad (15)$$

and

$$F(E) \sim \frac{1}{V_{\text{crit}}} + B \frac{\sqrt{E_b - E}}{W^{3/2}}, \quad (16)$$

for two-dimensional (2D) and three-dimensional (3D) cases, respectively. Here V_{crit} is the critical potential for which an impurity state splits from the band and B is a dimensionless constant. We consider the 2D and 3D cases because the top of the valence band in CaB₆ has strong quasi-2D character, as discussed in section 5.1. Substituting equations (15) and (16) into equation (13), one finds

$$Z_{\text{imp}} \sim \begin{cases} W\varepsilon/V^2, & 2\text{D} \\ 2W^{3/2}\varepsilon^{1/2}/V^2B, & 3\text{D}. \end{cases} \quad (17)$$

Taking into account equations (13), (15) and (16) one can eliminate V and rewrite this estimation in the final form

$$Z_{\text{imp}} \sim \begin{cases} \frac{\varepsilon \ln^2(W/\varepsilon)}{W}, & 2\text{D} \\ \sqrt{\frac{\varepsilon}{W}}, & 3\text{D} \end{cases} \quad (18)$$

taking $BV_{\text{crit}}^2/2 \sim W^2$. One can see that for the case of shallow levels the spectral weight of the impurity state is small. This estimation holds, at least in order of magnitude, also for the many-impurity case when the impurity band is formed. Thus one can conclude that all contributions (10) to $-P(E)$ are much smaller than $1/W_{\text{imp}}$ so that $I_{\text{eff}} \gg W_{\text{imp}}$. Thus the Kanamori renormalization of the effective Stoner parameter is not limited by W_{imp} as it is limited by W in the bulk case.

4. Spin waves in the impurity band model

In figure 1 we contrast two types of itinerant electron ferromagnet with small magnetization in the ground state. Case (a) shows schematically the situation in a very weak itinerant electron ferromagnet such as ZrZn_2 . The Stoner criterion is only just satisfied and a small exchange splitting between the majority (\uparrow) and minority (\downarrow) spin bands leads to the Fermi level E_F being positioned slightly differently in the two bands. Consequently, the majority spin Fermi surface is slightly larger than the minority spin one and the volume of \mathbf{k} space between the two Fermi surfaces is proportional to the ground state magnetization. The Curie temperature is determined by collective spin fluctuations rather than the single particle excitations of Stoner theory [13]. Well defined spin waves play a negligible role because they are confined to a very small region of the Brillouin zone. However, for sufficiently small wavevector \mathbf{q} they exist with energy Dq^2 . The spin wave stiffness constant D is small, being proportional to the magnetization [18].

The situation is different in case (b) where the small magnetization is associated with complete spin alignment of a low density of carriers in an impurity band. The dominant low-lying spin-flip excitations are now long-wavelength spin waves and we proceed to estimate D in this case. It is shown below that as long as complete spin alignment is maintained in the ground state D no longer tends to zero with the magnetization.

For simplicity we consider a one-band model with the disorder leading to the impurity band treated within the coherent potential approximation (CPA). We suppose that near the bottom of the band the Bloch-state energy $\epsilon(\mathbf{k})$ in the absence of disorder and local exchange splitting is given by

$$\epsilon(\mathbf{k}) = E_b + \frac{\hbar^2 k^2}{2m^*}. \quad (19)$$

Within the CPA the effect of disorder and exchange is contained in uniform potentials, for an effective medium, which depend on spin and energy. These potentials, or self-energies, $\Sigma_\sigma(E)$ for spin σ , would have to be determined self-consistently for a given detailed model, but here it is sufficient to assume that they give rise to exchange-split impurity bands as in figure 1(b).

The CPA Green's function for spin σ is of the form

$$G_{\mathbf{k}}^\sigma(E) = [E - \epsilon(\mathbf{k}) - \Sigma_\sigma(E)]^{-1} \quad (20)$$

with spectral representation (cf equation (8))

$$G_{\mathbf{k}}^\sigma(E) = \int dx \frac{\rho_{\mathbf{k}}^\sigma(x)}{E - x + i\eta} = \int dx \frac{\rho_{\mathbf{k},\text{imp}}^\sigma(x) + \rho_{\mathbf{k},\text{band}}^\sigma(x)}{E - x + i\eta}, \quad (21)$$

$\eta \rightarrow +0$. Here the spectral functions ρ_{imp} and ρ_{band} refer to the impurity band and main band respectively.

The spin wave stiffness constant is given by

$$D = \frac{1}{6\pi(n_{\uparrow} - n_{\downarrow})} \text{Im} \int_{-\infty}^{E_F} dE \sum_{\mathbf{k}} \left[G_{\mathbf{k}}^{\uparrow}(E) - G_{\mathbf{k}}^{\downarrow}(E) \right]^2 |\nabla_{\mathbf{k}} \epsilon(\mathbf{k})|^2 \quad (22)$$

where n_{σ} is the number of carriers of spin σ [19, 20]. This result was first derived for ferromagnetic alloys within the random phase approximation but is valid within any local approximation, where the self-energy is a function of energy only [21, 22].

In the case of complete spin alignment considered here, $n_{\downarrow} = 0$ and $G_{\mathbf{k}}^{\downarrow}(E)$ is real for $E < E_F$. By using Green's theorem on the \mathbf{k} sum we find

$$\begin{aligned} D &= \frac{1}{6\pi n_{\uparrow}} \text{Im} \int_{-\infty}^{E_F} dE \sum_{\mathbf{k}} \left[-G_{\mathbf{k}}^{\uparrow}(E) \nabla_{\mathbf{k}}^2 \epsilon(\mathbf{k}) - 2G_{\mathbf{k}}^{\uparrow}(E) G_{\mathbf{k}}^{\downarrow}(E) |\nabla_{\mathbf{k}} \epsilon(\mathbf{k})|^2 \right] \\ &= \frac{1}{6n_{\uparrow}} \int_{-\infty}^{E_F} dE \sum_{\mathbf{k}} \left[\rho_{\mathbf{k}}^{\uparrow}(E) \nabla_{\mathbf{k}}^2 \epsilon(\mathbf{k}) + 2\rho_{\mathbf{k}}^{\uparrow}(E) G_{\mathbf{k}}^{\downarrow}(E) |\nabla_{\mathbf{k}} \epsilon(\mathbf{k})|^2 \right]. \end{aligned} \quad (23)$$

Noting that $\nabla_{\mathbf{k}}^2 \epsilon(\mathbf{k})/6 = \hbar^2/2m^*$, and using the spectral representation of $G_{\mathbf{k}}^{\downarrow}$, we may write

$$D = D_0 + D_1 \quad (24)$$

where

$$D_0 = \hbar^2/2m^* \quad (25)$$

$$D_1 = \frac{1}{3n_{\uparrow}} \int_{-\infty}^{E_F} dE \sum_{\mathbf{k}} \rho_{\mathbf{k}}^{\uparrow}(E) \int_{-\infty}^{\infty} dx \frac{\rho_{\mathbf{k},\text{imp}}^{\downarrow}(x) + \rho_{\mathbf{k},\text{band}}^{\downarrow}(x)}{E - x} |\nabla_{\mathbf{k}} \epsilon(\mathbf{k})|^2. \quad (26)$$

To evaluate the energy integral in D_1 we approximate the denominator $E - x$ in equation (26) by $E_{0\uparrow} - x$, and further approximate it by $-\Delta = E_{0\uparrow} - E_{0\downarrow}$ in the integral involving $\rho_{\mathbf{k},\text{imp}}^{\downarrow}(x)$. Here $E_{0\sigma}$ is the energy at the centre of the σ spin impurity band and $\Delta = E_{0\downarrow} - E_{0\uparrow}$ is the splitting between the two impurity bands. Thus D_1 becomes

$$D_1 = -\frac{1}{3n_{\uparrow}} \sum_{\mathbf{k}} \left\{ \frac{\langle n_{\mathbf{k}}^{\uparrow} \rangle}{\Delta} \int dx \rho_{\mathbf{k},\text{imp}}^{\downarrow}(x) + \langle n_{\mathbf{k}}^{\uparrow} \rangle \int dx \frac{\rho_{\mathbf{k},\text{band}}^{\downarrow}(x)}{x - E_{0\uparrow}} \right\} \left(\frac{\hbar^2 k}{m^*} \right)^2, \quad (27)$$

where $\langle n_{\mathbf{k}}^{\sigma} \rangle = \int_{-\infty}^{E_F} dE \rho_{\mathbf{k}}^{\sigma}(E)$. To determine the \mathbf{k} dependence of $\langle n_{\mathbf{k}}^{\uparrow} \rangle$ and $\rho_{\mathbf{k},\text{imp}}^{\downarrow}$ it is sufficient to consider a single impurity with the on-site potential V , as in the previous section. Then

$$G_{\mathbf{k}}(E) = \frac{1}{E - \epsilon(\mathbf{k})} + \frac{t(E)}{[E - \epsilon(\mathbf{k})]^2} \quad (28)$$

with $t(E) = V/[1 - VF(E)]$ (cf equation (12)). For the case of a single impurity the contribution of the impurity level to the spectral density reads, similar to equation (13),

$$-\frac{1}{\pi} \text{Im} G_{\mathbf{k}}(E) = \frac{1}{[E_0 - \epsilon(\mathbf{k})]^2} \frac{-1}{F'(E_0)} \delta(E - E_0). \quad (29)$$

For a small density of impurities the δ -function broadens to the shape of the impurity band $\rho_{\text{imp}}(E)$ and we may write

$$\rho_{\mathbf{k},\text{imp}}^{\sigma}(E) = \frac{1}{[E_{0\sigma} - \epsilon(\mathbf{k})]^2} \rho_{\text{imp}}^{\sigma}(E) \left\{ \sum_{\mathbf{k}} \frac{1}{[E_{0\sigma} - \epsilon(\mathbf{k})]^2} \right\}^{-1}. \quad (30)$$

Now, $n_{\uparrow} = \int_{-\infty}^{E_F} dE \rho_{\text{imp}}^{\uparrow}(E)$ and $N_{\text{imp}} = \int_{-\infty}^{\infty} dE \rho_{\text{imp}}^{\sigma}(E)$, where N_{imp} is the total number of impurities and it is assumed that each impurity contributes one state to the impurity band. Using

these equations, together with equation (30), and assuming for simplicity that $E_{0\uparrow} \simeq E_{0\downarrow} \simeq E_0$ (i.e. $\Delta \ll E_b - E_0$), we obtain the contribution to D_1 of the first term in curly brackets in equation (27) in the form

$$-\frac{2\hbar^2}{3m^*\Delta} N_{\text{imp}} \left\{ \sum_{\mathbf{k}} \frac{1}{[E_0 - \epsilon(\mathbf{k})]^2} \right\}^{-2} \sum_{\mathbf{k}} \frac{\epsilon(\mathbf{k}) - E_b}{[E_0 - \epsilon(\mathbf{k})]^4}. \quad (31)$$

To estimate the \mathbf{k} sums in this expression we assume a constant density of states C per atom in the band $\epsilon(\mathbf{k})$. The first term in D_1 , given by (31), then becomes

$$-\frac{\hbar^2}{2m^*} \frac{2}{9} \frac{N_{\text{imp}}}{I_{\text{eff}} n_{\uparrow} C} \simeq -\frac{2}{9} \frac{\hbar^2}{2m^*} \quad (32)$$

if $n_{\uparrow} \simeq N_{\text{imp}}$ and $I_{\text{eff}} C \simeq 1$.

To estimate the second term in D_1 we assume that the bulk of the band is only weakly perturbed by the disorder so that $\rho_{\mathbf{k},\text{band}}(E) \simeq \delta(E - \epsilon(\mathbf{k}))$. Combining the result with equation (32), and using equation (25), we obtain

$$D = D_0 + D_1 \simeq \frac{1}{9} \frac{\hbar^2}{2m^*} = \frac{1}{9} D_0. \quad (33)$$

This is a crude estimate for an oversimplified model. The main point is that, as long as complete spin alignment is maintained, D is independent of the ground state magnetization. This contrasts with the standard case of very weak itinerant electron magnetism where D is proportional to the magnetization [18].

A realistic estimate of D_0 , the first term in D , may be obtained within a multi-orbital tight-binding model (e.g., [22]). To make the calculation specific we consider the case of CaB_6 where, as discussed in the next section, we propose that ferromagnetism arises from the complete spin alignment of holes in an impurity band just above the valence band. The valence band is assumed to be formed largely from boron 2p orbitals and the Hamiltonian is of the form

$$H = H_0 + H_1, \quad (34)$$

$$H_0 = \sum_{\mathbf{k}} \sum_{\mu\mu'\sigma} V_{\mu\mu'}(\mathbf{k}) c_{\mu\mathbf{k}\sigma}^\dagger c_{\mu'\mathbf{k}\sigma},$$

where $c_{\mu\mathbf{k}\sigma}^\dagger$ creates an electron of spin σ in a Bloch state of wavevector \mathbf{k} formed from orbital μ . Here H_1 contains on-site Coulomb and exchange interactions and an additional one-electron term representing spin-independent diagonal disorder. For a cubic crystal, such as CaB_6 ,

$$D_0 = \frac{1}{6(n_{\uparrow} - n_{\downarrow})} \sum_{\mathbf{k}} \sum_{\mu\mu'\sigma} \nabla_{\mathbf{k}}^2 V_{\mu\mu'}(\mathbf{k}) \langle c_{\mu\mathbf{k}\sigma}^\dagger c_{\mu'\mathbf{k}\sigma} \rangle \quad (35)$$

where the expectation value is evaluated in the ferromagnetic ground state. If we assume only nearest-neighbour hopping, and the on-site orbital energy is taken as zero, $\nabla_{\mathbf{k}}^2 V_{\mu\mu'}(\mathbf{k}) = -R^2 V_{\mu\mu'}(\mathbf{k})$ where R is the nearest-neighbour distance. (We neglect the slight difference in distance between boron atoms within the unit cell of CaB_6 and between unit cells.) Hence, from equation (35),

$$D_0 = -\frac{R^2}{6(n_{\uparrow} - n_{\downarrow})} \langle H_0 \rangle = \frac{1}{12} R^2 W, \quad (36)$$

where W is the width of the valence band. The last equality follows since $\langle H_0 \rangle = 0$ for a completely full band and $n_{\uparrow} - n_{\downarrow}$ holes are removed from an impurity band formed from states at the top of the band with energy $W/2$. D_0 is an upper bound on D since the second term

in D is negative. For CaB₆ the B–B distance $R = 1.7 \text{ \AA}$ and the width of the valence band $W = 9 \text{ eV}$ [23]. Hence $D_0 = 2167 \text{ meV \AA}^2 = 3.47 \times 10^{-39} \text{ J m}^2$. At low magnon density the magnons may be regarded as non-interacting bosons with energy Dq^2 . The number of magnons excited per unit volume at temperature T is then $0.0586(k_B T/D)^{3/2}$. The volume per boron atom in CaB₆ is 11.88 \AA^3 so that at $T = 600 \text{ K}$ with $D = D_0$ the number of magnons excited per boron atom is 2.57×10^{-3} . The corresponding reduction in moment per boron atom is $5.14 \times 10^{-3} \mu_B$, which is much less than the minimum $T = 0$ saturation moment of $0.1 \mu_B$ discussed in section 2. Thus if $D = D_0$ spin waves are not the dominant excitations controlling T_c and the Stoner estimate of this quantity should be realistic. If, however, D is strongly reduced from D_0 , to $D_0/5$ say, the number of magnons excited is an order of magnitude larger and T_c could be reduced considerably from its Stoner value. Thus to obtain a Curie temperature well above room temperature we require $D \geq D_0/2$, say. Whether this is possible can only be decided by realistic calculations of D in a multiorbital impurity band model. This can certainly be done, but only if one knows the nature of the impurities or defects producing the impurity band. No reliance can be placed on the calculation for a simple one-band model discussed earlier in this section, which gave the estimate $D \simeq D_0/9$.

To conclude this section we point out why it should be much easier to achieve high temperature ferromagnetism in the impurity band system than in diluted magnetic semiconductors such as (Ga, Mn)As. In our impurity band model itinerant electron ferromagnetism is achieved through the high density of states in a narrow impurity band, which enables the Stoner criterion to be satisfied. In the diluted semiconductor ferromagnetic order is obtained by an exchange interaction between the local Mn moments which is mediated by spin polarized holes in the semiconductor valence band. In this case equation (35) for D_0 is still valid but the factor $n_\uparrow - n_\downarrow$ includes the moment of the Mn atoms. Thus, for the same number of spin aligned holes in the band (or impurity band) in both models, and similar bandwidth W and interatomic distance R , the relative value of D_0 is controlled by the $n_\uparrow - n_\downarrow$ factor. Hence in the diluted ferromagnetic semiconductor D_0 is reduced by a factor $M_{\text{band}}/(M_{\text{band}} + M_{\text{loc}})$ compared with the impurity band case. Here M_{band} and M_{loc} are the contributions to the saturation magnetization of band carriers and localized moments respectively. With $M_{\text{loc}} = 4 \mu_B$ for the Mn atom this factor can be small. The role of spin waves in reducing the Curie temperature of diluted ferromagnetic semiconductors has been discussed by Jungwirth *et al* [24]. The reason why local moments reduce D so strongly is that they provide no exchange stiffness, this being entirely due to the band carriers. This is like hanging weights on a spring without increasing its stiffness. The oscillation frequency is reduced.

5. Application to CaB₆

In this section we review most of the experimental data on CaB₆, doped and undoped, and try to build up a theoretical picture based on the impurity band model. Most other theories are based on homogeneous models where doping merely changes the number of electrons in the system. The first such model [9, 25, 26] assumes the system behaves as a low-density electron gas, which is predicted to become ferromagnetic for density less than about $2 \times 10^{20} \text{ cm}^{-3}$ ($r_s \geq 20$). Even favourable estimates of T_c [25] are far below room temperature. Another early model [27–30] is that of a doped excitonic insulator which was predicted long ago to be ferromagnetic [31]. Problems associated with lack of nesting between electron and hole Fermi surfaces and with structural instability have been discussed [29]. Hotta *et al* [32] show that the excitonic state is unlikely to be stable and also conclude that ferromagnetism in CaB₆ may require the local removal of cubic symmetry by defects.

Young *et al* [9] first observed high-temperature ferromagnetism with small saturation moment in La-doped CaB_6 , SrB_6 and BaB_6 . In $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ with $x = 0.005$ the saturation moment $M_s = 3.5 \times 10^{-4} \mu_B/\text{unit cell}$ and the Curie temperature $T_c = 600$ K. Subsequently, Ott *et al* [10] found $M_s = 2 \times 10^{-4} \mu_B/\text{unit cell}$ and $T_c = 900$ K for $x = 0.01$. According to the discussion of section 2 the magnetization must be very inhomogeneous with only a fraction 10^{-4} – 10^{-3} of the sample ferromagnetically ordered.

Young *et al* [9] found that ferromagnetism does not appear for $x > 0.02$. This has been confirmed recently by Cho *et al* [11] in $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ crystals with $x = 0.03$ and 0.04 grown using boron of 99.9% purity (3N). They did find ferromagnetism in nominally stoichiometric CaB_6 , as well as in $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ with $x = 0.005, 0.01$ and 0.02 . All these ferromagnetic crystals were grown using 3N boron. Cho *et al* [11] found no magnetism in boron-deficient CaB_6 (3N) and in no single crystal of CaB_6 (stoichiometric, boron rich or boron deficient or La doped) made using boron of 99.9999% purity (6N). Furthermore, the temperature-dependent resistivity $\rho(T)$ of CaB_6 (6N) exhibits semiconducting behaviour, corresponding to an energy gap much smaller than the 168 meV deduced by Vonlanthen *et al* [33] from their $\rho(T)$ data, whereas CaB_6 (3N) is metallic with $\rho(0)$ a factor of 10^{-4} smaller than in CaB_6 (6N). Hall effect measurements on ferromagnetic undoped CaB_6 crystals invariably indicate that electrons are the dominant carriers [34]. From the work of Cho *et al* [11] it appears that ferromagnetism is associated with charge carriers introduced by impurities in 3N boron. The removal of ferromagnetism by overdoping with La, which adds electrons to the system, suggests that ferromagnetism is associated with holes in the valence band, or in an impurity band close to the valence band. In a ferromagnetic region, with 0.3 aligned hole spins per unit cell, say, 2% La doping would remove 0.02 holes per unit cell, which might be enough to move the Fermi level out of a sharp peak in the density of states so that the Stoner criterion is no longer satisfied. Clearly if the magnetization were uniform the critical concentration for uniform La doping in this picture would be more like 0.002%. Boron deficiency would also be expected to remove holes from the valence band. However, Hall effect measurements [34], particularly those [35] on a ferromagnetic sample with $\rho(T)$ very similar to the CaB_6 (3N) crystal, indicate that electrons are present in the conduction band. This suggests that impurities or defects arising from 3N boron lead to a small band overlap. The major impurities in 3N boron were identified as C and Si, with negligible amounts of magnetic impurities such as Fe [11].

5.1. An impurity band model of ferromagnetism in CaB_6

The first assumption of the model, which seems essential for reconciling high T_c with very small average moment per atom, is the inhomogeneous nature of the magnetization. Ferromagnetic regions are assumed to have a moment of order $0.1 \mu_B/\text{B atom}$, about 1000 times the average value. As discussed in the previous section this is consistent with the high La doping concentration required to suppress ferromagnetism. Terashima *et al* [36] invoke spatially inhomogeneous magnetization in $\text{Ca}_{0.995}\text{La}_{0.005}\text{B}_6$ to try to understand their susceptibility data. In ferromagnetic resonance measurements on the same system Kunii [37] finds a magnetization which is three orders of magnitude larger than the value observed in static measurements. This could be consistent with our picture.

The second assumption of the model is that the saturation moment within a ferromagnetic region arises from complete spin alignment of holes in a narrow impurity band just above the valence band. Electrons are also present in an overlapping conduction band whose states, to a good approximation, do not mix with those of the valence band. The situation is shown in figure 2. Transport is dominated by the conduction band which may not be much influenced by the magnetic inhomogeneity of the valence band.

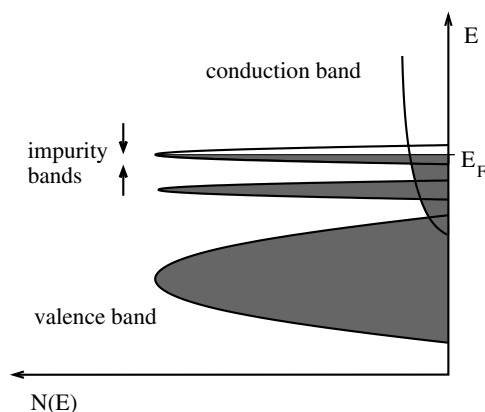


Figure 2. Sketch of the proposed electronic structure of ferromagnetic CaB_6 .

To proceed further it is necessary to describe the nature of the CaB_6 system. The crystal is cubic, with Ca^{2+} ions forming a simple cubic lattice. Each cubic unit cell is occupied by an octahedron of six boron atoms, but the distance between neighbouring B atoms in adjacent cells ($\sim 1.67 \text{ \AA}$) is considerably less than the distance between B atoms in one octahedron ($\sim 1.76 \text{ \AA}$) [23]. Thus the structure could be described as a Ca simple cubic lattice with B_2 dimers positioned at the centre of each square face and oriented perpendicular to that face. Dimerization is a marked effect, the interatomic spacing in the isolated B_2 dimer being 1.59 \AA , and it plays a significant role in our theory, as will be seen later. Clearly the interatomic spacing $2ua$ for dimers in the lattice can be varied uniformly without changing the cubic symmetry or the lattice constant a . Calculations by Massidda *et al* [23] predict that the bandgap in CaB_6 reduces by 0.5 eV for a 3.5% decrease in u with constant a . The bottom of the conduction band, at the point X in the zone, falls while the top of the valence band at X rises. Negative bandgap corresponds to band overlap. A change from a very small bandgap in the CaB_6 (6N) crystals of Cho *et al* [11] to band overlap in CaB_6 (3N) might occur by a slight contraction of the dimers induced by impurities in 3N boron. This impurity effect would not lead to uniform contraction and an impurity band might form just above the valence band. This contraction effect might be produced by many different impurities, so the mechanism leading to ferromagnetism is not confined to the CaB_6 (3N) crystals of Cho *et al* [11].

The formation of a shallow impurity band is favoured by the quasi-two-dimensional nature of the band-structure near the top of the valence band at the X point. All existing band calculations find a very flat band along $\text{X}\Gamma$, which leads to an almost discontinuous rise in the density of states at the top of the valence band. However, band calculations discussed in section 5.2 differ widely in their prediction of the sign and magnitude of the direct bandgap at the X point in CaB_6 .

The impurity band picture has similarities with the situation in ferromagnetic transition metals such as Ni and Co. The role of the transition metal d band is played by a narrow impurity band formed from boron p orbitals and in both cases there is a broad overlapping conduction band, this being formed largely from calcium d orbitals in the CaB_6 case. Magnetism in the transition metal d band is not unexpected since in the isolated atom the spins of electrons in degenerate d orbitals are aligned by the Hund's rule mechanism. An analogous situation in the boron p band becomes clear when one remembers, as discussed above, that the boron lattice may be regarded as formed from B_2 dimers, and that the isolated B_2 dimer has a ground state with total spin $S = 1$ [38, 39]. The two p electrons in B_2 occupy degenerate π_x and π_y

bonding orbitals, the z axis being the axis of symmetry of the dimer, and their spins are aligned according to Hund's rule. The only other magnetic second-row dimer is O_2 , the relevant orbitals now being the corresponding antibonding orbitals.

5.2. Further discussion of theory and experiment

The picture described above is controversial for several reasons. The first controversial point to consider is whether CaB_6 is a semimetal (semiconductor), with a very small negative (positive) bandgap, or whether it is a semiconductor with a gap of order 1 eV. Following the pioneering band-structure calculation of Hasegawa and Yanase [40], using the local density approximation (LDA), Massidda *et al* [23] found that within the LDA the dimerization effect discussed above led to a small band overlap. However, the difference between small negative and positive bandgaps is within calculational error. The top of the valence band near X is formed from B bonding p orbitals and the bottom of the conduction band at X is dominated by Ca d orbitals. These states have a different parity on symmetry lines and the bands therefore cross each other there. Although mixing occurs at general points in the zone these two bands may therefore be considered approximately as independent of each other, even when they overlap. Rodriguez *et al* [41] have made similar calculations for SrB_6 and find quite detailed agreement with optical and transport data [42], which support the semimetallic picture. Further strong support for this picture comes from more recent data [43] on reflectivity and Hall resistivity. To obtain a reflectivity which relates to the bulk band-structure it was necessary to file the surface of the as-grown crystal to a depth of 10 μm and then polish it. According to our discussion of [11], CaB_6 and SrB_6 crystals are expected to be semimetallic if the boron used to make them is of substantially less than 6N purity. Hall *et al* [44] have made de Haas–van Alphen (dHvA) measurements on $Ca_{1-x}La_xB_6$, with $x = 0, 0.0025, 0.005$ and 0.01 , and on SrB_6 . The La-doped samples were ferromagnetic, except for $x = 0.01$, where in any case no dHvA oscillations were seen owing to impurity scattering. Orbits attributed to electron and hole pockets were seen in CaB_6 and SrB_6 but the hole pockets dropped out as electrons were added by doping with La. Electron and hole pockets have also been seen in the related divalent hexaboride EuB_6 by dHvA [45] and Shubnikov–de Haas experiments [46]. The calculations and data so far discussed in this paragraph are reasonably consistent with the picture we proposed in section 5.1. However, Denlinger *et al* [47] report angle resolved photoemission spectroscopy (ARPES) data, on cleaved (001) surfaces, showing an X-point bandgap of about 1 eV for SrB_6 and EuB_6 . The Fermi level is located just above the bottom of the conduction band. These authors interpreted the apparent discrepancy between their ARPES data and the bulk semimetal picture in terms of an electron-rich surface region, maybe 60 Å thick, within which the X-point bandgap varied rapidly due to variation of the dimerization parameter u between the bulk and surface. They postulated that broken dimer bonds at the cleaved (001) surface would allow octahedra near the surface to contract, thus increasing u and consequently the bandgap. Subsequently, Denlinger *et al* [48, 49] reinterpreted their large observed gap as characteristic of the bulk. This was largely in response to a band calculation for CaB_6 by Tromp *et al* [50], who used the GW approximation to obtain a bandgap of 0.8 ± 0.1 eV. The GW approximation generally yields larger, and more reliable, bandgaps than LDA. Denlinger *et al* support their new conclusion with results of x-ray absorption and emission spectroscopy although the band edges in these data are not clear-cut. Very similar ARPES data are reported by Souma *et al* [35]. A more recent band calculation for CaB_6 using the GW approximation is that of Kino *et al* [51, 52]. They find that over most of the zone the gap between conduction and valence bands is enlarged compared with the LDA case, as in [50], but that a small band overlap nevertheless occurs at the X point. The subtle reason for this exceptional situation is analysed and it is suggested that the discrepancy with [50] may be due to an improper treatment

of the core contributions in the pseudopotential plane-wave method by Tromp *et al.* A similar pseudopotential method, but with a non-local weighted density approximation (WDA), was recently used by Wu *et al* [53] to find the same bandgap as that of [50]. Kino *et al* [51, 52] point out that the difference between a very small negative and positive bandgap is within their calculational error. The question of semimetal, or small bandgap semiconductor, versus 1 eV bandgap semiconductor in the bulk is clearly not completely settled. However, there is strong evidence for the former scenario [43, 44, 51, 52] and we have adopted this viewpoint here.

The second controversial point we must consider is whether the small-moment ferromagnetism in these systems arises from spin alignment of charge carriers within ferromagnetic regions of the bulk or is associated entirely with magnetic impurities near the surface. It is also quite possible for these two sources of magnetism to coexist. The standard method of growing CaB₆ crystals uses an Al flux and Otani and Mori [54, 55] attribute ferromagnetism to Fe on the surface, the Fe being introduced as an impurity in the Al flux. They found that ferromagnetism disappeared completely from crystals of CaB₆ and Ca_{1-x}La_xB₆ after being kept in HCl solution for a few hours. They conclude that Fe was removed from the surface during the HCl treatment and that no bulk ferromagnetism exists in these samples. However, many workers have used the same Al flux to grow a number of crystals, some ferromagnetic and some not. For example, ferromagnetism never exists in overdoped Ca_{1-x}La_xB₆ with $x \geq 0.03$ [9, 11]. Cho *et al* [11] found that no crystal made with 6N boron was ferromagnetic, even though the same Al flux was used as for ferromagnetic 3N boron samples. However, in some of the latter samples it was found that chemical etching partially removed the magnetism, although no details are given. Thus bulk ferromagnetism and surface impurity ferromagnetism may coexist in these samples. Bennett *et al* [34] also find evidence for such coexistence in a ferromagnetic sample of CaB₆. The saturated moment M_s was reduced by 47% after a surface layer of thickness 6000 Å was removed by etching, but no further reduction occurred on removing an additional 6000 Å. These workers also found that in 16 different undoped CaB₆ crystals there was no correlation between M_s and the electron density deduced from Hall effect measurements. This is consistent with our picture that the bulk part of M_s is determined by the number of holes in the valence band, or an associated impurity band, whereas the Hall effect is dominated by conduction electrons. Young *et al* [56] report measurements of M_s for CaB₆ grown from Al flux which was deliberately contaminated with a wide range of concentrations of added Fe. There was no dependence of M_s on Fe concentration, from which the authors conclude that alien Fe–B phases are probably not the source of ferromagnetism in aluminium-flux-grown single crystals. This contrasts with the behaviour of CaB₆ sintered powders for which Matsubayashi *et al* [57] offer convincing evidence that the observed ferromagnetism is entirely due to FeB and Fe₂B phases on the surface, the Fe originating in the crucible used for synthesis. Young *et al* [56] propose that in aluminium-flux-grown crystals Fe impurities incorporated in the bulk are responsible for high-temperature ferromagnetism. It is assumed that the concentration of Fe is about 0.1 at.%, being determined by off-stoichiometry of the CaB₆. It seems that such a low concentration of Fe, considered purely as a magnetic defect, could only lead to ferromagnetism with a very low T_c . In fact Young *et al* report that inclusion of Co or Ni in the flux, in addition to Fe, leads to small-moment ferromagnetism with $T_c < 10$ K. They propose that Co and Ni enter CaB₆ in preference to Fe but do not explain why Fe should lead to a T_c 100 times larger than is produced by Co or Ni. It is possible that Fe is one of the defects which lead to a partially occupied impurity band just above the valence band, whereas Co and Ni do not. We have argued that such an impurity band can lead to high-temperature ferromagnetism; this is quite independent of whether or not the defects responsible for the impurity band are magnetic impurities. Meegoda *et al* [58] argue against any significant concentrations of Fe in the bulk on

the basis of depth profiling with Auger electron spectroscopy; for a CaB_6 crystal grown in a Al flux they find that Fe impurities are confined to a surface region with a depth of a few microns.

From the above discussion we conclude that high-temperature ferromagnetism of CaB_6 and $\text{Ca}_{1-x}\text{La}_x\text{B}_6$ crystals exists as an inhomogeneous bulk effect. However, in as-grown crystals there is frequently a contribution from Fe impurities in a surface region which can be eliminated by suitable surface treatment. The bulk ferromagnetism is clearly associated with defects or impurities but, as in the case of impurities arising from use of 3N boron in [11], they need not be intrinsically magnetic. Jarlborg [59, 60] looked for ferromagnetism associated with various defects in SrB_6 by means of LDA band calculations. The point defects were centred in $2 \times 2 \times 2$ or $3 \times 3 \times 3$ periodically continued supercells, corresponding to defect concentrations $x = 0.125$ and 0.037 respectively. The point defects considered were La, In and Al impurities, and a vacancy, replacing one Sr atom. For the La case a moment of order $0.1 \mu_B \text{ La}^{-1}$ impurity was found for both sizes of supercell. However similar calculations for La in CaB_6 by Monnier and Delley [61], using the generalized gradient approximation (GGA), a variant of LDA, and a $3 \times 3 \times 3$ supercell, resulted in zero moment. Jarlborg emphasizes that for ferromagnetism it is essential that the Fermi level falls within an impurity band, which in the case of La is associated with the conduction band. No magnetism is found in the In, Al or vacancy cases. For In and Al doping with $x = 0.125$ Jarlborg finds an almost rigid upward shift of the energy bands relative to the Fermi level, by about 0.5 eV in the case of In, so that holes occupy the valence band. A similar effect also occurs for the Sr vacancy. For lower doping levels presumably no rigid shift would occur and the holes might occupy a narrow impurity band just above the valence band. Jarlborg does not consider any lattice relaxation around the impurity. Monnier and Delley [61] find a large magnetic moment of $2.36 \mu_B$ associated with removal of a complete boron octahedron; this moment is reduced to $1.32 \mu_B$ if the B_6 octahedron is replaced by Ca and is lost completely if B_6 is replaced by La or Al. They propose that the large moments associated with B_6 vacancies, created during growth due to kinetic effects, are the source of ferromagnetism. Fisk *et al* [62] take up this suggestion and estimate the density of such vacancies to be 10^{-4} – 10^{-3} per unit cell. However, no explanation is given of how such a low concentration of local moments could have a Curie temperature in the range 600–900 K (see also [63]).

From the above discussion of Jarlborg's works it appears that Al substituting for Ca or Sr, or a Ca or Sr vacancy, are possible sources of the impurity band required for ferromagnetism. Terashima *et al* [36] deduce from a low temperature resistivity anomaly, also seen by Vonlanthen *et al* [64], that their CaB_6 samples were contaminated with Al granules. It therefore appears that Al does enter the bulk during Al flux growth and might also substitute for Ca. Hall *et al* [44] find no evidence of Al inclusions in their samples, but Al as a substitutional impurity is presumably not ruled out. However, Monnier and Delley [61] find that the formation energies of a Ca vacancy and an Al substitutional impurity are both about 5 eV, so that the defect concentrations would be negligible if growth took place under conditions of thermal equilibrium. This is probably not the case since it is generally believed that hexaborides, including CaB_6 , have a tendency to self-doping by metal vacancies [10, 33, 36, 46, 64, 65]. It might be that certain non-magnetic impurities, including those in 3N boron which are apparently essential for ferromagnetism according to Cho *et al* [11], facilitate the formation of Ca vacancies or Al substitutional impurities by kinetic effects during growth, as suggested by Monnier and Delley [61] in connection with B_6 vacancies. On the other hand, we have already described how any impurity leading to more pronounced boron dimerization locally could lead to the desired impurity band. The effect of Fe impurities in the bulk on the electronic structure is unknown. The same can be said of C and Si impurities, which are probably introduced using 3N boron in the work by Cho *et al* [11].

We suggest that there are many ways in which a narrow impurity band can be formed just above the valence band and we believe that this is essential for ferromagnetism. The extremely inhomogeneous nature of the ferromagnetism which we propose might arise in two ways. One possibility is that the impurities or defects responsible for the impurity band might be distributed very inhomogeneously. A second possibility is that the impurity band is widespread but the Stoner criterion for ferromagnetism is only satisfied in regions with a particularly favourable impurity configuration.

6. Outlook

A ferromagnetic semiconductor with a Curie temperature T_c well above room temperature would have great potential for use in spintronic devices. A well explored route towards this objective involves Mn doped III–V compounds but the highest T_c obtained is well below room temperature. The reason for this failure to achieve high T_c is discussed at the end of section 4. The essential point is that although ferromagnetic order is induced by the large Mn moments they do not contribute to the exchange stiffness, which is provided by the spin-polarized band carriers. In fact, the Mn moments reduce the spin wave stiffness constant by a large factor. To achieve high T_c it seems essential that the band carriers themselves produce ferromagnetic order by their mutual interaction, without the aid of local magnetic moments. This requires a high density of states at the Fermi level, to satisfy the Stoner criterion, and this is most likely to be achieved in a narrow impurity band. However, the estimate of T_c in section 2 indicates that room temperature ferromagnetism is unlikely unless the number of completely spin-polarized carriers in the impurity band exceeds 0.1 per bulk atom. It is not clear whether this can be compatible with a sufficiently narrow impurity band. Assuming that this scenario is possible, at least in some regions of the sample, it is argued in section 4 that spin wave excitation may not significantly reduce T_c from its Stoner value. If this mechanism is responsible for the ferromagnetism observed in some carbon systems and in CaB₆, the very small observed magnetization indicates that ferromagnetic order exists only in a very small fraction of the total volume of the crystal. Clearly, before any spintronic application can be envisaged, it is necessary to find a way of producing the conditions for impurity band ferromagnetism more uniformly throughout the specimen.

In section 5.1 we pointed out that the CaB₆ structure may be regarded as built from B₂ dimers. The isolated dimer is magnetic, with a moment of $2 \mu_B$; of course, this large moment does not survive in the CaB₆ structure, where the bonding levels broaden to form the valence band as electrons hop between bonding orbitals of adjacent dimers. It would be interesting to find a boron structure with more pronounced dimerization, and narrower bands formed from the bonding orbitals, than in CaB₆. If such a structure exists its magnetic properties, doped and undoped, could be interesting. The same can be said of any structure containing O₂ dimers, linked by hopping between the antibonding orbitals of the dimer in this case.

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