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LETTER TO THE EDITOR

Temperature dependence of magnetism near defects in SrB_6

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Abstract

The temperature (T) dependence of magnetic moments in SrB_6 is studied through spin-polarized band calculations for a supercell of $Sr_{27}B_{156}$ containing a B_6 vacancy. The magnetic moment decays rather quickly with T despite the fact that only electronic Fermi–Dirac effects are included. This result and the T dependence of moments near an La impurity can hardly explain the reports of a very high Curie temperature in hexaborides, but suggest that the magnetism is caused by some other type of impurity.

Early reports of weak ferromagnetism (FM) in lightly doped CaB_6 or SrB_6, associated with an unusually high Curie temperature (T_C) [1], have been followed by several theoretical and experimental studies. For instance, it has been speculated that the FM could be of excitonic origin [2], be a spontaneous polarization of the dilute electron gas [3], or be caused by special conditions around impurities and thereby lead to band magnetism [4, 5]. The band structure of the pure hexaboride [6], which is metallic when calculated within the density functional (DF) approach, has been questioned, since one GW calculation found a gap at the Fermi energy, E_F [7]. These results are in contrast to a recent independent GW calculation by Kino *et al* [8] where the ground state is metallic. Also, there are conflicting results concerning the interpretation of the experimental results on the weak magnetism. Quantum oscillations indicate that the FM state is not intrinsic to the bulk, but that impurities might be important [9]. This conclusion was supported by Mori and Otani [10] who found that the FM signal could be removed by a treatment of the crystals, and suggested that the FM is due to iron impurities. Other defects such as vacancies have been suggested as well [11]. Possible vacancies of whole B_6 clusters were anticipated in calculations by Monnier and Delley [12] who showed that a sizable FM moment surrounded such a vacancy in a supercell of CaB_6. They suggested that the observation of weak FM in dilute doped hexaborides is caused either by a surface or interface effect, since the B_6 vacancy is modelling the natural cleavage planes in polycrystals, or by a number of B_6 vacancies in pure crystals.

In the present letter, by use of the linear muffin-tin orbital (LMTO) band method in the local spin-density approximation, we study the variation of the magnetic moment around a

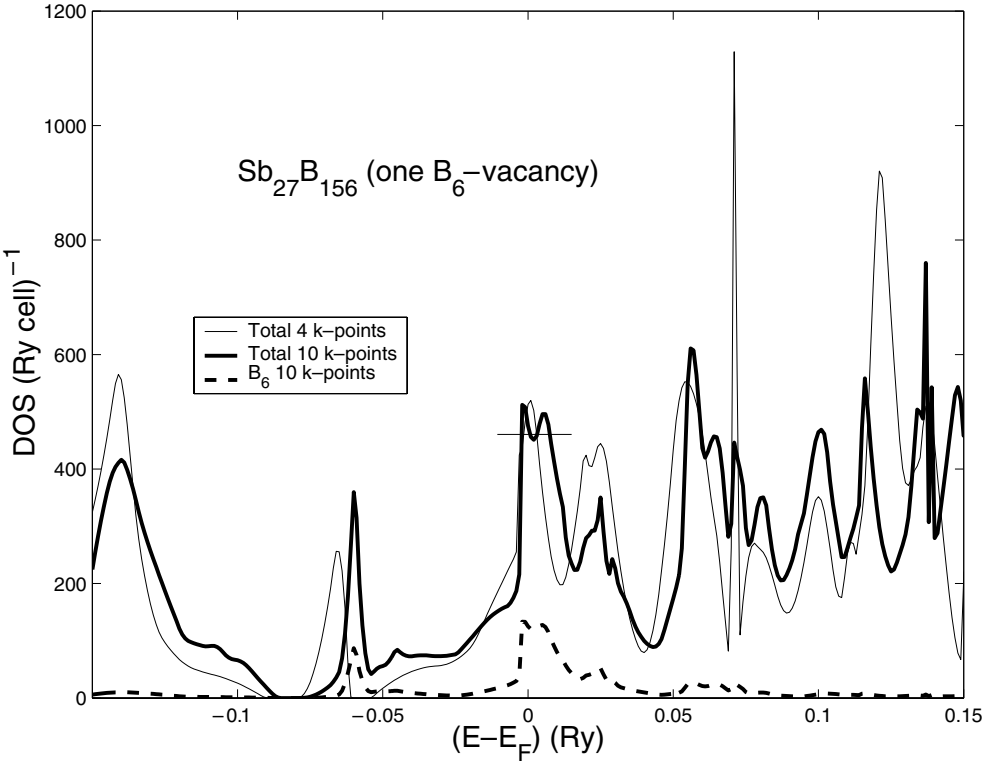

Figure 1. Total DOS of $Sr_{27}B_{156}$ near E_F, using four and ten k-points. The broken curve is the partial DOS on B_6 closest to the vacancy. The short horizontal line indicate the limit for Stoner magnetism.

B_6 vacancy in Sr_6 as function of temperature. This is done by self-consistent spin-polarized calculations, in which T-dependent electronic excitations are modelled by the Fermi–Dirac distribution, but no thermal disorder of the lattice is taken into account. As in [12] we consider a $3 \times 3 \times 3$ supercell with one B_6 vacancy in SrB_6 so that the total cell is $Sr_{27}B_{156}$. The missing B_6 atoms form empty muffin-tin (MT) spheres, and the calculations include additional empty spheres in the open part of the structure. The cell contains 19 non-equivalent MT spheres, four Sr, eight B and seven empty ones. Other details of the calculation are as in [5]. The density-of-states (DOS) functions near E_F for the non-polarized case, are shown in figure 1 for two sets of k-points (4 and 10) in the irreducible part of the Brillouin zone. It is seen that the essential features of the DOS are already developed when using four k-points, with only small differences in the fine details. In particular, the DOS peak at E_F is similar in the two sets of k-points, so that the criterion for Stoner magnetism should come out well even when using only four k-points. The Stoner factor (S) is calculated to be 1.05, just above the limit for FM, 1.0, indicated by the horizontal line in figure 1. The broken curve shows the partial DOS from the six equivalent B atoms closest to the B_6 vacancy. It is seen that roughly one-third of the total DOS at E_F comes from these sites although they represent only about 3% of the total number of atoms in the cell. In the spin-polarized calculations (at low T), when using four k-points, one finds a magnetic moment, $m = 2.1\ \mu_B$/cell, in agreement with [12]. This moment decreases to about 1.8 μ_B when the number of k-points is increased to 10 for the same temperature. This type of magnetism is the standard Stoner magnetism [13], where the

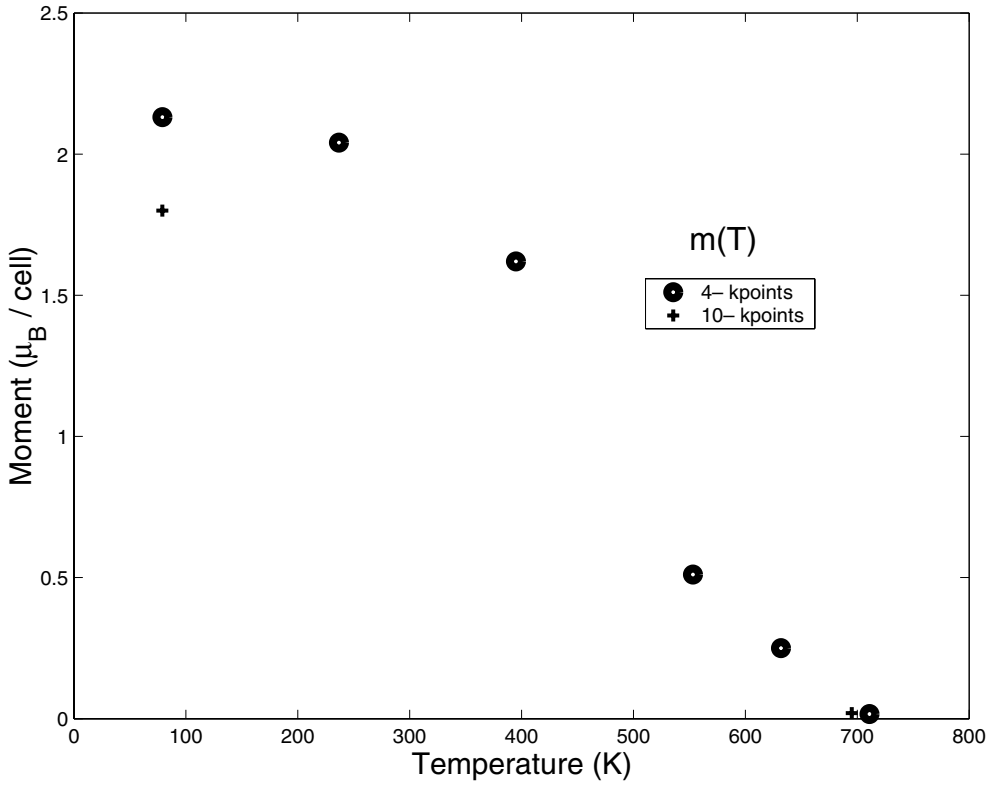

Figure 2. Calculated magnetic moment (μ_B/cell) as function of temperature for $Sr_{27}B_{156}$.

large DOS on the six B atoms nearest to the vacancy contribute most to the Stoner instability (cf figure 1). Similarly, about 40% of the total moment in the spin-polarized calculations comes from these six B sites closest to the vacancy.

Spin-polarized calculations at different temperatures in the Fermi–Dirac distribution show that the moment goes to zero when T is increased to about 700 K. The two sets of k-points have been used at the lowest and highest T, and both sets give a vanishing moment at $T = 700$ K. Calculations for intermediate T, using four k-points, show first a gradual decrease of m at low T, while the curve drops sharply as T approaches 700 K, as shown in figure 2. This T dependence is understood from the fact that E_F falls on a narrow peak in the DOS, so that thermal smearing, due to electronic excitations, can reduce the effective DOS and the Stoner factor. Since T_C in the doped hexaborides is of the same order, 700 K, it is tempting to assign the observed T_C to the mechanism of Stoner magnetism due to the B_6 vacancy. However, typical behaviour for ferromagnets is that the temperature at which S goes below the critical value for FM is generally much larger than the Curie temperature (T_C) for real materials [14]. By taking into account additional smearing effects on the DOS coming from thermally induced disorder of the structure one obtains more realistic values of T_C in mean-field calculations [15]. The atomic displacements from thermal vibrations at 700 K can be of the order 0.25 au (corresponding to 7–8% of the B–B distance) for a material with a Debye temperature of 350 K, while large smearing effects on DOS peaks already appear at a lower degree of disorder [16]. The present calculations include only the T dependence via the Fermi–Dirac distribution and the effects from thermal disorder are expected to reduce the moment further. Therefore, it is difficult to

understand the high T_C in the real materials from the T dependence of the moments within the Stoner mechanism. One possibility would be that the local structure around a B_6 vacancy can somehow escape the effects of thermal disorder, in which case it is justified to consider only the effect Fermi–Dirac smearing. The position of E_F relative to the peak appears to be at the optimal place for the largest possible Stoner factor for this supercell, and an increased height of the peak at larger T would be opposite to the normal T dependence of the DOS.

Another mechanism leading to magnetism is due to a gain of Coulomb energy in addition to the exchange energy, by means of charge transfers. This mechanism can be activated if there is a large derivative N' of the DOS of an impurity band, leading to very small moments near the impurity [4]. This difference from the normal Stoner mechanism suggests that this weak magnetism could better resist changes in temperature and broadening of the DOS by disorder, since N' can be large within a wider energy interval compared with that of a peak in the DOS. However, the results from calculations for an La impurity in a $3 \times 3 \times 3$ cell give only a partial support to this expectation [5]. The DOS of this cell is such that N' is maximal a bit below E_F, and even if there is a small moment at 600 K, it tends to zero at low T. It is difficult to have a sizable moment both at low and high T. By optimizing the position of N' relative to E_F (and the amplitude of N) by a combination of the virtual crystal approximation and a non-conventional choice of linearization energies in the band calculation, it is possible to have a weak moment within some range of T. Such band results are not *ab initio*, but they are useful to show a correlation of moment and charge transfers. They also show that magnetism within this mechanism depends on fine details of the electronic structure near the impurity, which in turn suggests that such magnetism should be a result of circumstances. Furthermore, it is expected that thermal disorder should be as important for this type of magnetism as it is for the standard Stoner magnetism.

In conclusion, the band results confirm that weak magnetism is possible, either as standard Stoner magnetism around a B_6 vacancy or assisted by Coulomb energies near an La impurity, but it is more difficult to understand the high T_C values from both of these mechanisms. These results and recent experimental reports [9, 10] prompt similar electronic structure studies of the properties near iron impurities in these materials. However, the exact state of iron contamination, impurity sites or clustering on surfaces, is not yet clear.

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