The 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 a 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 ($T_C$), have been followed by several theoretical and experimental studies. For instance, it has been speculated that the FM could be of excitonic origin, be a spontaneous polarization of the dilute electron gas, or be caused of special conditions around impurities and thereby lead to band magnetism. The band structure of the pure hexaboride, 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, $E_F$. These results are in contrast to a recent independent GW-calculation by Kino et al. 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. This conclusion was supported by Mori and Otani who found that the FM signal could be removed by a treatment of the crystals, and suggested that that the FM is due to iron impurities. Other defects such as vacancies have been suggested as well. Possible vacancies of whole B$_6$-clusters were anticipated in calculations by Monnier and Delley who showed that a sizable FM moment surrounded such a vacancy in a supercell of CaB$_6$. They suggest that the observation of weak ferromagnetism in dilute doped hexaborides is caused either by a surface or interface effect, since the B$_6$ vacancy is modeling the natural cleavage planes in polycrystals, or by some amount 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 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 modeled by the Fermi-Dirac distribution, but no thermal disorder of the lattice is taken into account. As in ref., we consider a 3x3x3 supercell with one B$_6$ vacancy in Sr$_6$ so that the total cell is Sr$_{27}$B$_{156}$. The missing B$_6$ atoms form empty MT-spheres, and the calculations include additional empty spheres in the open part structure. The cell contains 19 nonequivalent MT-spheres, 4 Sr, 8 B and 7 empty ones. Other details of the calculations are as in ref. The density-of-states (DOS) functions near $E_F$ for the non-polarized case, are shown in Fig. 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 developed already when using 4 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 already when using only 4 k-points. The Stoner factor is calculated to be 1.05, just above the limit for ferromagnetism, 1.0, indicated by the horizontal line in fig. 1. The broken line shows the partial DOS from the six equivalent B-atoms closest to the B$_6$-vacancy. It is seen that roughly 1/3 of the total DOS at $E_F$ comes from these sites although they represent only about 3 percent of the total number of atoms in the cell. In the spin-polarized calculations (at low T), when using 4 k-points, one finds a magnetic moment, $m = 2.1 \mu_B$ per cell, in agreement with ref. This moment decreases to about 1.8 $\mu_B$ when the number of k-points is increased to 10 for the same temperature. This type of magnetism is a standard Stoner magnetism, where the large DOS on the 6 B-atoms nearest to the vacancy contribute most to the Stoner instability, cf. Fig 1. Similarly, about 40 percent 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 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 4 k-points, show first a gradual decrease of $m$ at low T, while the curve drops sharply as T is approaching 700 K, as shown in Fig 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, the typical behavior for ferromagnets is that the temperature at which S goes below the critical value for ferromagnetism,
is generally much larger than the Curie temperature ($T_C$) for real materials. 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. The atomic displacements from thermal vibrations at 700 K can be of the order 0.25 a.u. (corresponding to 7-8 percent of the B-B distance) for a material with a Debye temperature of 350 K, while large smearing effects on DOS peaks appear already at a lower degree of disorder. 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 $T_C$ values from both of these mechanisms. These results and recent experimental reports motivate 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 yet not clear.

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FIG. 1. Total DOS of Sr$_{27}$B$_{156}$ near $E_F$, using 4 and 10 k-points. The broken line is the partial DOS on B$_6$ closest to the vacancy. The vertical line indicate the limit for Stoner magnetism.

FIG. 2. Calculated magnetic moment ($\mu_B$ per cell) as function of temperature for Sr$_{27}$B$_{156}$. 