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Geometrical frustration in an elemental solid: An Ising model to explain the defect structure of β-rhombohedral boron

Tadashi Ogitsu,[1,*] François Gygi,[2,3] John Reed,[1] Masafumi Udagawa,[4] Yukitoshi Motome,[4] Eric Schwegler,[1] and Giulia Galli[1,5]

[1]*Condensed Matter and Materials Division, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California 94551, USA*

[2]*Center for Applied Scientific Computing, Lawrence Livermore National Laboratory, Livermore, California 94551, USA*

[3]*Department of Applied Science, University of California, Davis, California 95616, USA*

[4]*Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan*

[5]*Department of Chemistry, University of California, Davis, California 95616, USA*

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Recently, it was reported that β-rhombohedral boron has a negative defect formation energy, which explains the presence of a macroscopic amount (4 at. %) of intrinsic defects. In this work, it is shown that the defects in boron have geometrical frustration described by an antiferromagnetic Ising model on an expanded kagome lattice, which is responsible for the reported macroscopic residual entropy. We suggest that the reported anomalies in the transport properties of β-boron are due to the hopping of boron atoms between nearly degenerate configurations.

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The elements are the basic constituents in condensed-matter physics, and most of the properties of the elements at ambient conditions have been understood in the 20th century. However, as recently pointed out in several studies,[1–6] the phase diagram of boron and its most stable allotrope under ambient conditions are still poorly understood. The interplay between the unusual chemistry of boron and its electron deficiency has been shown to be responsible for the presence of a macroscopic amount of intrinsic defects[7] in β-rhombohedral boron;[5,8] the presence of these defects reduces the internal energy as much as 30 meV/atom[5] (negative defect formation energy). As a consequence, β-rhombohedral boron is the most stable phase of boron[3–5] down to temperatures very close to zero;[5] however, no long-range ordering of these defects has ever been found experimentally, and theory suggests that there exists a macroscopic number of nearly degenerate ground-state configurations.[5] These findings are seemingly at odds with what one would expect based on the third law of thermodynamics. We propose that many of the peculiar properties of solid boron arise from the fact that this element has a nearly degenerate ground state *due to geometrical frustration*.

The most well-known example of geometrical frustration is proton disordered ice Ih reported by Pauling in 1935.[9] In the 1990s, spin systems represented by magnetic pyrochlore materials were shown to have geometrical frustration similar to that of ice.[10,11] In particular, the proton disorder in ice and spin magnetism in magnetic pyrochlore materials share the same underlying model,[10] the ferromagnetic Ising model on a corner sharing tetrahedron. This model, within the nearest-neighbor (NN) interaction approximation, has an exactly degenerate and disordered ground state with a macroscopic zero-point entropy that agrees surprisingly well with estimates based on experimental specific-heat measurements. However, recent studies support the notion that the measured macroscopic residual entropy corresponds to a nonequilibrium state due to slow dynamics at low temperature, and, thus, the third law of thermodynamics is unlikely to be violated.[11] Nevertheless, it was the identification of underlying model Hamiltonians that paved the way to the understanding of the complex behavior of frustrated systems.[9,10,12]

In this Rapid Communication, we report on the geometrical frustration in an elemental solid. In particular, we show that the imperfect atomic occupation in the elemental boron crystal, known as partial occupancy, can be modeled by an antiferromagnetic (AF) spin Ising model on an expanded kagome lattice;[13,14] the ground state of this model is exactly degenerate and disordered due to the competing effect between the AF interaction and the lattice geometry, i.e., due to geometrical frustration (see Fig. 2 and its caption). We also show that the rather peculiar transport properties of boron that have been reported over the past 40 years[15–18] can be rationalized by the presence of geometrical frustration.

Upon slow cooling, liquid boron solidifies into the β-rhombohedral phase,[19] which has an unusually large unit cell, approximately 320 atoms per hexagonal cell (hex cell hereafter). In this structure, six out of 20 crystallographic sites are only partially occupied [partially occupied site (POS)] with occupation rates varying from 2% to 75% from site to site (23 out of 320 atoms are at POS).[19] The topology of POS, determined by experiments, corresponds to a "quasi-two-dimensional" expanded kagome lattice[13] of the double layer type (Fig. 1).

We have previously shown that the occupancy of POS, i.e., the distribution of unoccupied and occupied sites, can be mapped onto a generalized spin Ising model,[5]

$$H = \sum_i U_i S_i + \sum_{i,j} J_{i,j} S_i S_j + \sum_{i,j,k \in \mathrm{B}_{28}} T_{i,j,k} S_i S_j S_k + C, \quad (1)$$

where S_i is the occupation of site i, which takes values of either +1 (occupied) or −1 (unoccupied), U_i is the site-dependent local potential, $J_{i,j}$ is the pair interaction between sites i and j, $T_{i,j,k}$ represents the three body interactions, and C is a constant parameter. The sums over the first and the second terms in Eq. (1) are taken over all of the POS, while the sum over the third term is limited to the same B_{28} unit.

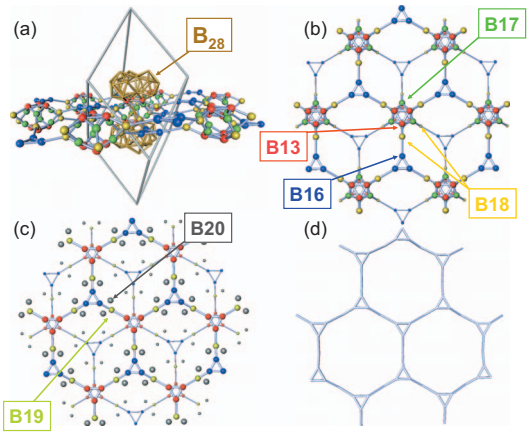

FIG. 1. (Color) The lattice structure of POSs in β-rhombohedral boron. (a) The POS forms a layered lattice structure at $z=0$ (not drawn) and $z=c/2$ (drawn), where c is the lattice parameter of a rhombohedral crystal. Two clusters made of 28 boron atoms (B_{28}, gold bonds) are connected by an interstitial atom and B13 vacancies (red spheres), and they are located in the middle of the rhombohedral cell. (b) and (c) depict the connectivity between B13 and B16–B20. B13 (red), B16 (blue), B17 (green), and B18 (yellow) are displayed in (b), and the rest, B19 (light green) and B20 (gray), are displayed in (c) separately for the sake of clarity. The viewpoint is along the z axis, and the size of spheres and bonds correspond to the offset in the z axis. (d) A single layer of this lattice, an expanded kagome lattice, is depicted, where the corners of the hexagonal lattice are decorated by triangles. Each POS lattice consists of two layers of expanded kagome lattices connected to each other through the B13 site. For a more detailed explanation, see Refs. 5 and 19.

The interaction coefficients U, J, T, and C were fitted to *ab initio* total-energy calculations of β-boron carried out for an extensive amount of independent POS occupation configurations and using different sizes of unit cells (rhombohedral cell and 1280 atom supercell). The resulting model reproduces the *ab initio* total energies to within a few meV/atom (see Ref. 5 for details) and favors the β phase over the α phase, in agreement with previous studies.[3,4] Remarkably, these calculations demonstrated that the presence of intrinsic defects significantly lowers the internal energy of β-boron due to the peculiar chemical properties of this element,[5] which tends to form three-center two-electron bonds.[5,8] Interestingly, all of the NN interactions in Eq. (1) (the β-boron Ising model hereafter) are AF except for the pairing occupation at B17 and B18 sites (see Fig. 1 for site definitions), which is reflected in the preferred NN correlations at low temperature.[5] Therefore, we first examine a version of the β-boron Ising model that retains only the interactions relevant at low temperature, that is, a NN AF Ising model on an expanded kagome lattice. The ground state of this model is essentially equivalent to that of the NN AF Ising model on the kagome lattice, which is known to be exactly degenerate and disordered due to geometrical frustration.[20,21] A simple mapping that shows the equivalence of the ground-state properties of these two models is illustrated in Fig. 2. The essence of geometrical frustration that leads to the massive degeneracy is described as follows. It is the combination of AF interactions and the triangle-based lattice geometry (expanded kagome lattice) that allows the system to have many

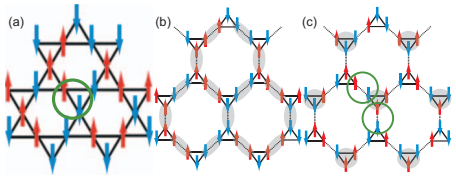

FIG. 2. (Color) In (a), one of the ground-state spin configurations of the AF Ising model on a kagome lattice is realized, which is described as "two-up, one-down" or "two-down, one-up" spin configurations that maximize the number of opposite spins on a triangle. The expanded kagome lattice is made by decorating the corners of the hexagonal rings with triangles (Ref. 13). If one duplicates the spins on the kagome lattice (a) onto the spins on an expanded kagome lattice, (b) is obtained. Choose half of the triangles in an alternating manner and flip the spins on the shaded triangles to get (c). The resulting spin configuration gives the ground state of the AF Ising model on an expanded kagome lattice, where, in addition to the AF intertriangle bonds, the "two-up, one-down" ground-state rule for the intratriangle bonds is preserved.

independent spin configurations with an equivalent number of AF pairs. An example is shown in Fig. 2(a), where flipping the pair of spins within the green circle does not change the total number of AF pairs; therefore, these two spin configurations are energetically degenerate. On an expanded kagome lattice [Fig. 2(c)], this corresponds to flipping two pairs of spins within the two green circles. By careful examination of Figs. 2(a) and 2(c), one will find that there are many ways to flip spins without breaking the ground-state rule. The number of such degenerate ground-state spin configurations in an AF Ising model on a kagome lattice is known to grow exponentially as a function of the system size,[20,21] which results in a macroscopic amount of zero-point entropy, $S_0 \sim 0.5R$ (R is the gas constant).[21] In the case of POS occupation in β-boron, by performing appropriate groupings on its atomic occupations (or spins), one can reduce the problem of finding the optimal atomic occupation to the AF spin Ising model on a double layer expanded kagome lattice; this model exhibits a large degree of degeneracy.[22] Here the origin of degeneracy is the same, the combination of AF interactions and the triangle-based lattice geometry result in many ways to flip spins without breaking the ground-state rule.

We now turn to the thermodynamic properties of the β-boron Ising model [Eq. (1)]. The model Hamiltonian, which was originally developed to quantitatively reproduce the first-principles density-functional theory total energies of β-rhombohedral boron,[5] required a large number of interaction parameters (40 in total).[22] Therefore, it is extremely challenging to examine it directly with an analytical approach. Here, we employed a numerical approach based on the replica exchange Monte Carlo (REMC) method, which was developed to overcome slow dynamics at low temperatures.[23] In this method, many MC runs on a discretized temperature grid are performed, and exchanges of configurations between adjacent temperatures are repeatedly attempted with an algorithm that ensures detailed balance.[23] As a consequence, all configurations repeatedly undergo high-temperature annealing cycles. In the present case, the occupation state at each site changed on average by 18%

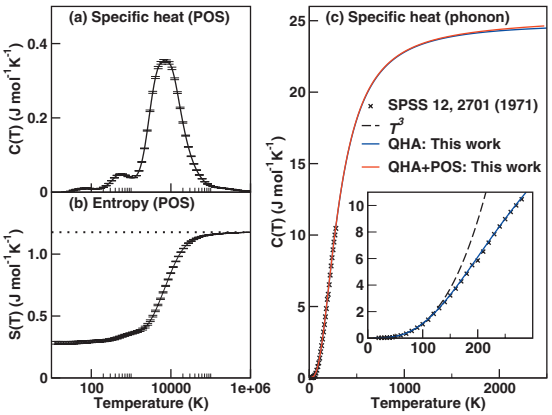

FIG. 3. (Color) (a) Specific heat of the Ising model fit to *ab initio* data, including error bars, as a function of temperature. (b) Entropy as a function of temperature calculated by thermodynamic integration from the high-temperature limit. The data were obtained for a $4\times4\times6$ supercell (4032 sites) derived from the rhombohedral cell. The solid lines in (a) and (b) are guides for the eyes. The horizontal dotted line in (b) is the high-temperature limit of the entropy $S(T\rightarrow\infty)=-R(p_{occ}\log p_{occ}+p_{unoc}\log p_{unocc})$, where, p_{occ} is the occupation rate (23/126), $p_{unocc}=1\text{-}p_{occ}$, and R is the gas constant. We obtained 1280 data points, and only 10% (with error bars) are plotted for clarity. (c) Measured specific heat (crosses) (Ref. 24), together with calculated phonon specific heat (blue line) and the sum of phonon and configurational specific heats (red line). The temperature range below 300 K is magnified in the inset. See the supporting material of Ref. 5 for the specific details of the phonon calculations.

after one REMC cycle at the lowest temperature, demonstrating the effectiveness of the approach.

The specific heat of the β-boron Ising model was calculated on a temperature grid between 11.6 and 1.16×10^9 K [see Fig. 3(a)] at a fixed occupation rate $p_{occ}=23/126$, which corresponds to the experimental atomic density;[19] an analytical high-temperature expansion form ($\propto T^{-2}$) was used for extrapolation to infinite temperature. Thermodynamic integration was performed to calculate the entropy as a function of temperature, using infinite temperature as the reference point [see Fig. 3(b)]. Within the system sizes considered here, corresponding to $2\times2\times3$, $3\times3\times3$, and $4\times4\times6$ repetitions of the rhombohedral cell, we did not observe any evidence of phase transitions, and the calculated specific heat for each cell size was in agreement within statistical error bars. As can be seen in Fig. 3(b), the β-boron Ising model has a macroscopic amount of entropy, roughly $\frac{1}{4}$ of the high-temperature limit, at the lowest temperature of our simulation.[25] In our simulations, when the temperature decreases from the high T limit, first a large variation in the POS occupation rate is observed at 2000–10 000 K; most of the short-range correlations observed in our calculations develop in this temperature range. Subsequently, the interstitial B19/B20 occupation (see Fig. 1 for definition of specific sites) gradually decreases, while the number of B17–B18 pairs remains roughly constant. Below 200 K, the relative locations of B16 interstitials are gradually optimized against the orientation of B13 vacancies and its occupied pairs, such as a B17–B18 pair, or a B19. This sequence of geometrical arrangements corresponds to the three peaks observed in the specific heat.

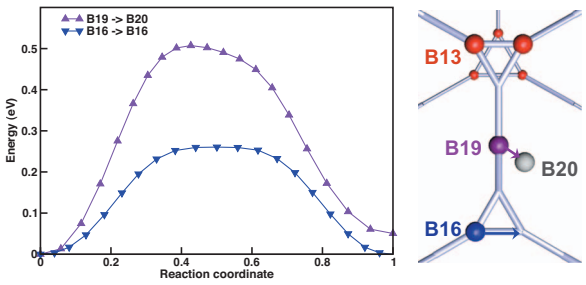

FIG. 4. (Color) The total energy (eV) per rhombohedral cell along the reaction coordinates of the two lowest-energy barrier paths. B16→B16 diffusion (blue arrow) corresponds to the intra-triangle diffusion along a symmetric direction with respect to the B19 atom. The B19→B20 diffusion (the purple arrow) takes place with the far-side B16 site occupied (as drawn).

The configurational constant volume specific heat $C(T)$ of spin ice has been measured precisely, and this contributed significantly to the development of the theory of frustration in spin ice.[11] Unfortunately, the $C(T)$ of β-boron has not been as extensively studied, and the separation of configurational and vibrational contributions has never been attempted. The vibrational specific heat calculated from our first-principles phonon density of states[5] is shown in Fig. 3(c) and is in excellent agreement with experiments,[23] including the T^3 behavior below $T=100$ K and the non-T^3 behavior above this temperature. A small scatter in the experimental data for $C(T)$ at $T\sim200$ K can be seen, although it is not clear if the scatter is within experimental uncertainties or if it corresponds to a dynamical temperature-induced change in POS configuration.

Apart from the specific heat, we found that there are several experimental evidences indicating that the POS atoms hop between adjacent sites over a wide range of temperature, and the potential relation to geometrical frustration has never been discussed before. For example, Tsagareishvili *et al.* performed internal friction experiments over a range of temperatures (77–1000 K) and found two clear peaks of inelastic response at $T=150$ K and at $T=530$ K,[16] indicating the presence of defect diffusion processes in β-boron. In addition, Werheit and Wehmoller measured the relaxation behavior in conductivity data and identified the presence of various relaxation mechanisms down to $T\sim100$ K, which was attributed to boron diffusion processes.[18]

In order to examine the connection between the observed boron diffusion and the near degenerate POS configuration due to geometrical frustration, we have calculated the energy barriers between several different POS occupation configurations by using the elastic band method.[26] The structures used for these calculations correspond to the lowest-energy structures found in Ref. 5 from first principles. We have identified two low-activation diffusion paths connecting (near) degenerate low-energy POS occupation configurations (see Fig. 4): inter-B16 hopping and B19-B20 hopping, with barriers of 0.25 and 0.5 eV, respectively (see Figs. 1 and 4 for site definitions), in qualitative agreement with the experiment.[16] All the other diffusion paths, particularly, the ones that change the location of B13 vacancies, have high activation barriers (several eV), which are large enough to break an arbitrary bond in β-boron. An autocorrelation func-

tion analysis of the Ising-model Monte Carlo calculations, in addition to the calculated activation barriers, leads to the following conclusion. Hopping between B19 and B20 can still take place at $T \sim 600$ K [the temperature range corresponding to the middle peak in $C(T)$], while below $T = 200$ K, only inter-B16 hopping takes place. This suggests that the two diffusion processes at $T=150$ and 530 K, inferred from the internal friction experiments[16] correspond to these two hopping mechanisms. Based on our simulation results, we also suggest that the change in the optical absorption observed around $T=150 \sim 200$ K (Ref. 17) can be attributed to the inter-B16 hopping and the introduction of gap levels due to an unfavorable B16 occupation configuration.[5]

Based on existing experiments and our simulation results, we can speculate on the prospects of measuring the configurational entropy through specific-heat experiments. Although the experimental evidence of boron diffusion down to $T \sim 100$ K suggests that the configurational contribution can be estimated by specific-heat measurements, such a contribution is likely to be very small and a direct experimental observation will be challenging. At $T=100$ K, the calculated configurational specific heat is $C_V^{conf} \sim 0.009$ J mole^{-1} K^{-1}, while the vibrational contribution is $C_v^{vib} \sim 1.1$ J mol^{-1} K^{-1}. The total configurational contribution is less than 1%. Furthermore, from our boron diffusion barrier calculation, it is expected that only B16-B16 hopping will take place at such a low temperature. Therefore, it is likely that the actual configurational contribution to the specific heat is much less than 1% of the total. Nevertheless, the existing experimental observation of boron diffusion strongly suggests that the combination of various measurements on the transport properties might open a door to a complete understanding of the nature of geometrical frustration in elemental boron.

The fascinating question about elemental boron concerning its ordered ground-state structure at $T=0$ K remains an open question. Widom and Mihalkovic recently proposed a superlattice structure based on B17–B18 occupations as a candidate ground state. However, the resulting structure has an atomic density (321 atom/hexagonal cell),[4] that is, higher than the experimental value.[19] They also found numerous structures that are nearly degenerate in energy and, most interestingly, no evidence of a phase transition.[4] In this regard, their findings are consistent with the ones presented here.

In summary, we have demonstrated that the partial occupancy of β-rhombohedral boron is described by an AF Ising model on a double layer expanded kagome lattice, which possesses a degenerate ground state due to geometrical frustration. We have also provided computational evidence to support the interpretation that the experimentally observed boron diffusion processes correspond to dynamical reconfigurations of POS atoms between near degenerate ground states.

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*ogitsu@llnl.gov

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[25] The residual entropy of β-boron Ising model is $S_0 \sim 0.1$ R (R is the gas constant), while that of an AF Ising model on a kagome lattice is $S_0 \sim 0.5R$ (Ref. 21). The constant atomic density condition imposed on β-boron Ising model is likely to be responsible for the significant reduction in the zero-point entropy. We note that this S_0 value for the β-boron Ising model is normalized by the number of partially occupied sites so as to compare with that on a kagome lattice, while the values used in Fig. 3 are normalized by the total number of atoms so as to compare with the experimental specific heat. The conversion coefficient is $126/423 \sim 0.298$, where 126 is the total number of partially occupied sites (B13, B16–B20) and 423 is the total number of crystallographic sites (B1–B20). For the number of symmetry equivalent sites, see Ref. 19.
[26] We used PWSCF version 4 (www.pwscf.org) with the same calculation conditions reported in Ref. 5, except that the PBE GGA is used in this work.