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Identification and Quantification of Boron Dopant Sites in Antiferromagnetic Cr_2O_3 Films by Electron Energy Loss Spectroscopy

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Cr_2O_3 is antiferromagnetic in bulk but ferromagnetic on the (0001) surface. Bulk Cr_2O_3 has two degenerate antiferromagnetic states that can be switched by an electric field, which also switches the (0001) surface magnetism [1], creating the potential for voltage-controlled magnetic data storage and spintronic data processing. However, the magnetic ordering (Néel) temperature of pure Cr_2O_3 is too low for microelectronic applications. Boron substituting for oxygen in Cr_2O_3 to form BCr_4 tetrahedra increases the exchange energy of neighboring Cr atoms from the favorable hybridization geometry [2], increasing the Néel temperature.

We have combined electron energy loss spectroscopy (EELS) fine structure and density functional theory (DFT) calculations to determine the structure of B dopants in Cr_2O_3 thin films. EELS is highly sensitive to the nature of chemical bonds and to an atom's coordination environment. Especially for doped oxides when the dopant is surrounded by strong backscattering O atoms, EELS is dominated by scattering events within the local neighbours that can be explained by a molecular approach [3]. We find B in BCr_4 tetrahedra, but also in distorted BO_3 triangles. The BO_3 triangles can be identified by manipulating the electron momentum transfer ($\boldsymbol{q}$) in EELS, which changes the differential cross sections for the 1s-π^* and 1s-σ^* transitions. BCr_4 tetrahedra can be identified and also quantified by linear combination of simulated B K edges to reproduce the experimental π / σ ratios.

Figure 1(a) is a HAADF STEM image of a 2.5% B doped Cr_2O_3 film on Al_2O_3 substrate. Both the B and O atoms are invisible due to relatively weak high-angle scattering cross section. Figure 1(b) is a map of the B K edge intensity, showing a uniform distribution of B in the Cr_2O_3 film. Figure 1(c) is the B K edges acquired from plan view (top) and cross section (bottom) zone axes. The 194 eV peak corresponds to the 1s-π^* transition and the 203 eV peak corresponds to the 1s-σ^* transition [4]. The typical geometry of the B sp^2 hybridization forms BO_3 triangles with σ bonds parallel to the BO plane and π bonds normal to the BO plane [3]. The B K edges show clear orientation dependence because of the significant directionality of unoccupied 2p states of the BO_3 sp^2 structure. As illustrated in Figure 1(d), with the large EELS collection angles used in this experiment, the π intensity is proportional to the projection of the momentum transfer $\boldsymbol{q}$ onto the corresponding orbital orientations [4]. This indicates the BO_3 plane is normal to the [0001] direction.

Figure 2(a) is the possible B dopant structures, relaxed by DFT. All the structures shown have relatively low formation energies (±2 eV) calculated by Zhang-Northrup formalism [5] under film growth conditions, so they are thermodynamically accessible. The simulated BO_3 structures are either planar or slightly distorted, but all of them are normal to the [0001] directions, which matches with the EELS results in Figure 1(d). The existence of BCr_4 can be confirmed by the distinct π / σ ratios from multiple-scattering EELS simulation in Figure 2(b), especially on the plan view zone. The bounds of the

functional BCr_4 out of the total B can be probed by linear combination of simulated BCr_4 K edges with each BO_3 K edge to reproduce experimental π / σ ratios, which is shown in Figure 2(c). Only 12%-43% B dopants form BCr_4 tetrahedra and increases Néel temperature. Further calculation shows that the other BO_3 structures can frustrate the bulk antiferromagnetic order and suppress the interface exchange bias. To make B doping more efficient, posting annealing under low oxygen partial pressure will favor the formation of BCr_4, and co-doping is also a promising approach to stabilize BCr_4 [5].

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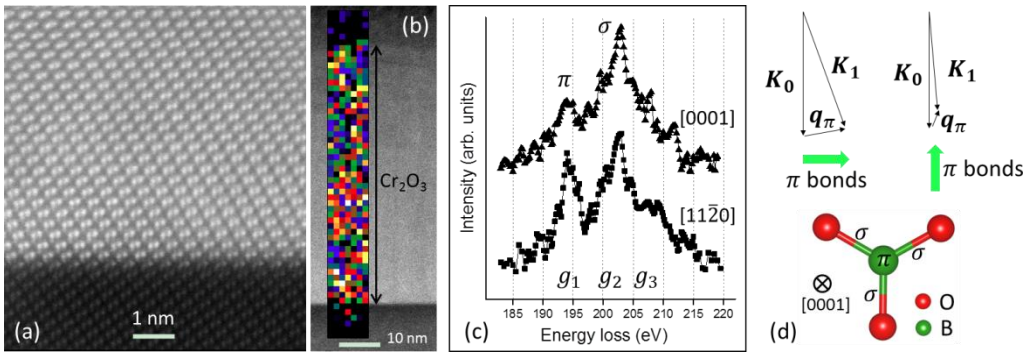

Figure 1. (a) HAADF STEM image of a B doped Cr_2O_3 film on Al_2O_3 substrate. (b) EEL spectrum guide image showing the whole 80 nm thick Cr_2O_3 film with B K edge intensity map superimposed. (c) B K edges from plan view and cross section zone axis. (d) Schematic illustration of EELS momentum transfer and the suggested orientation of BO_3 triangles.

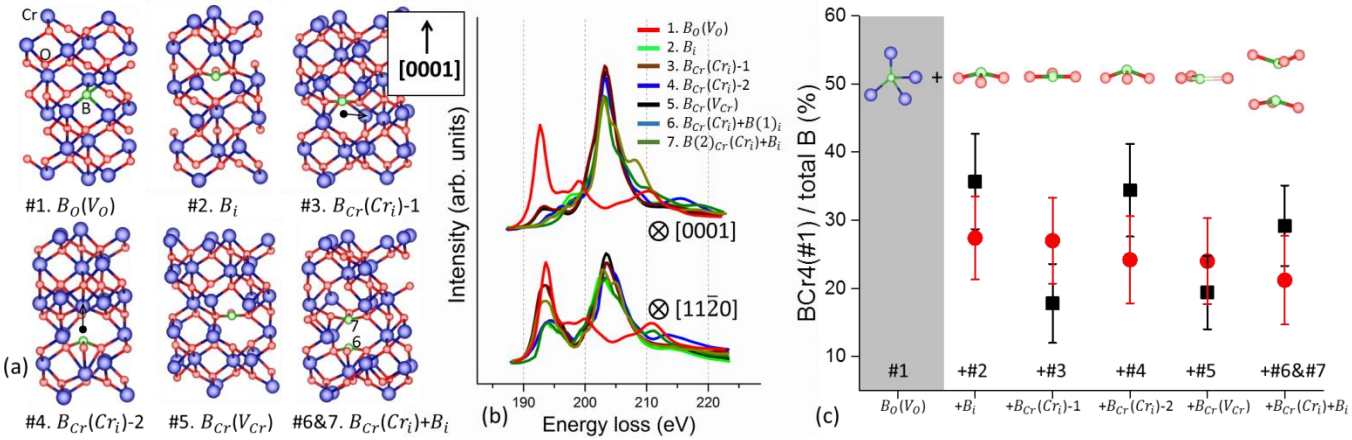

Figure 2. (a, and b) Calculated B dopant structures and corresponding EELS from multiple scattering simulations. (c) Quantification of the functional BCr_4 tetrahedra (#1. $B_O(V_O)$) / total B by linear combination of simulated BCr_4 K edges with each BO_3 triangles K edges to reproduce the experiment π / σ ratio. Black symbols are from the cross section data, and red symbols are from plan view data.

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