Pressure-induced metal-insulator transition in MgV$_2$O$_4$

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Abstract

On the basis of experimental thermoelectric power results and ab initio calculations, we propose that a metal-insulator transition takes place at high pressure (approximately 6 GPa) in MgV$_2$O$_4$.  

Key words: Spinels; first-principles calculations; metal-insulator transition

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Transition metal oxides often present an interplay between different degrees of freedom (orbital, spin and charge) resulting in the formation of different superstructures [1]. Among these, oxide spinels with chemical formula AB$_2$O$_4$, that present a frustrated pyrochlore lattice for the B cations (transition metal), are particularly interesting because they allow to study the importance of direct cation-cation interactions in a series with single-valent B-B interactions. The series AV$_2$O$_4$ (with A being Cd, Mn, Zn, Mg) approaches a metal-insulator transition when the V-V distance is reduced sufficiently. This can be observed in Fig. 1. A reduction in the absolute value of the thermoelectric power is evident in Zn and Mg samples, with respect to Mn and Cd samples. Moreover, typical activated behaviour is no longer present in Zn and Mg, and thermopower tends to a constant value at low temperature. This result is fully consistent with a scenario in which progressive electronic delocalization in cation-cation bonds occurs as the metal-metal distance is reduced across the series. These conclusions about partial electronic delocalization are also supported by the strong reduction in the magnetic moment observed from CdV$_2$O$_4$ to ZnV$_2$O$_4$, in spite of the constant V$^{3+}$[11].

The V-V distance, determined from a Rietveld refinement of the X-ray patterns, reduces along the series from 3.07 Å in the Cd compound to 2.97 Å for MgV$_2$O$_4$. On the basis of experimental considerations, the critical distance for the metal-insulator transition was estimated at about 2.94 Å [2]. One way to study this transition could be to apply pressure to the Mg compound since it is closest to the critical distance. An experimentally accessible pressure is expected to produce the transition.

For analyzing this, we have carried out density functional theory calculations on the compound MgV$_2$O$_4$ within a full-potential, all-electron approach by using the WIEN2k software [4]. Electronic correlations were taken into account by means of the LDA+U approximation [5].

We studied the cubic phase, with lattice parameter $a = 8.4378$ Å measured at room temperature. The atomic po-
Fig. 2. DOS plots for all the V and O levels in the unit cell for the experimental structure. The d-d character of the narrow gap of only 0.2 eV can be noticed. Upper (lower) panels show the spin-up (down) channel.

Fig. 3. DOS plots for all the V and O levels in the unit cell for an applied pressure of 8 GPa. Observe that metallicity occurs by overlapping of the d bands that come together due to the small V-V distance. Upper (lower) panels show the spin-up (down) channel.

sitions are: Mn (0.125, 0.125, 0.125), Cr (0.5, 0.5, 0.5) and O (0.260, 0.260, 0.260) in the space group Fd3m.

We performed total energy calculations to optimize the volume of the material within the generalized gradient approximation (GGA) in the so-called Perdew-Burke-Ernzerhof scheme. The ground state volume obtained by this procedure is in agreement with the experimental one (0.3% smaller). The value of the bulk modulus of 196 GPa is also consistent with previous results on oxide spinels. It is well known that the trigonal distortion of the oxygen octahedron surrounding the $V^{3+}$ cations varies with the V-V distance, and this changes slightly the oxygen positions. We made the approximation of keeping fixed the oxygen coordinates and only varying the cell parameters.

From our total energy vs. volume calculations, the predicted critical V-V distance (2.94 Å) is reached at about 5 GPa. For the equation of state around the minimum, we used fittings to a Murnaghan equation, leading to the same quantitative results for equilibrium volumes and bulk moduli. According to our calculations, the transition occurs very close to that distance, at some 6.5 GPa (V-V distance of 2.937 Å, in close agreement with the predicted result).

In Figs. 2 and 3 the transition from a narrow-band insulator to a metal can be observed. For the experimental structure (Fig. 2), the material is an insulator with a band gap of approximately 0.2 eV. The value of U was chosen to fit the experimental value of the band gap (it turns out to be about 3.1 eV within the so-called self-interaction corrected LDA+U method). The material shows the typical electronic structure of a Mott-Hubbard insulator with a d-d gap. Fig. 2 shows the total value of O and V total (including multiplicities) density of states inside the unit cell. Both the conduction and the valence band have a strong d character, being the O p contribution to those bands smaller, but non-negligible. Fig. 3 shows the density of states for the structure under an applied pressure of approximately 8 GPa. The reduced V-V distance leads to a stronger d-d interaction. At a high enough pressure, the valence and conduction bands eventually overlap yielding a metallic behaviour.

In summary, a metal-insulator transition is predicted along the series $AV_2O_4$, and should be obtained by applying pressure to the MgV$_2$O$_4$ compound. Experimentally, the tendency to metalicity can be observed by analyzing the variation in the Seebeck coefficients of the series as the V-V distance gets reduced. Ab initio calculations predict a critical pressure of some 6.5 GPa needed to produce the metal-insulator transition.

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