Electronic Structure Calculations for Cr$_{1-x}$Al$_x$

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Abstract:

Cr$_3$Al shows semiconductor-like behavior, attributed to a combination of antiferromagnetism and chemical ordering. We present a detailed study of chemical ordering in Cr$_3$Al. Using density functional theory within the Korringa Kohn Rostoker (KKR) formalism, we consider five possible Cr$_3$Al structures. The chemically ordered, rhombohedrally distorted X-phase has the lowest energy and should therefore be the ground state found in nature. The D0$_3$ structure has the highest energy and should not occur. While KKR indicates a pseudogap in the X-phase density of states, calculations using full potential linear muffin tin orbital and plane wave techniques show a narrow band gap.

Summary of Research:

The nature of a gap in Cr$_3$Al is currently of interest. Experimental results in the literature are suggestive of either a semimetal or degenerate semiconductor [1]. A full gap might suggest further study of Cr$_3$Al as a potential thermoelectric material [2]. In addition, recent theoretical work has predicted that Cr$_3$Al with binary Heusler (D0$_3$) ordering is almost completely spin polarized and that Mn-doped D0$_3$ Cr$_3$Al would behave as a true half metal with applications in spintronics [3]. While no evidence of D0$_3$ ordering has been shown in Cr$_3$Al, the Cr-Al phase diagram is not well established [4]. Thus, a study of the nature of a gap in Cr$_3$Al and how it is affected by chemical ordering is warranted.

We will explore here the three structures shown on the proposed phase diagram for Cr$_3$Al: bcc solid solution, C11$_p$ Cr$_2$Al + bcc Cr two-phase system, and X-phase Cr$_3$Al structure [4]. Also included are an off-stoichiometric C11$_p$ Cr$_3$Al structure, seen experimentally for films grown at 500-600°C [5] and the D0$_3$ (Heusler) structure. These structures are shown in Figure 1.

DFT calculations were done on the Intel cluster at the Cornell NanoScale Facility. All structures were evaluated using the AkaiKKR code, so the results for the different structures could be compared directly. This technique was chosen for its ability to treat site disorder, which was necessary for the bcc solid solution and off-stoichiometric C11$_p$ Cr$_3$Al structures. Disorder is treated using the coherent potential approximation (CPA) [6].

The total energy per atom is shown in Table 1. The X-phase structure has the lowest energy, suggesting that it is the low temperature stable phase for the Cr$_3$Al stoichiometry, confirming the proposed phase diagram [4].
The bcc solid solution, C11, Cr2Al + bcc Cr two phase system, and C11, Cr3Al structure have the next lowest energies, consistent with their being stable phases at higher temperatures. Finally, the D0₃ structure has a significantly higher energy.

The table also shows the density of states (DOS) at $E_F$. The lowest DOS($E_F$), as calculated by KKR, occurs for X-phase Cr₃Al due to barely overlapping bands at $E_F$ [5]. DFT calculations often underestimate the band gap in materials, sometimes showing overlapping bands in materials known to have a full band gap. Therefore, to complement the KKR calculations, we performed calculations using a plane wave approach (Quantum Espresso) and a full potential linear muffin tin orbital approach (FP-LMTO) [7, 8].

Figure 2 compares the calculated DOS for the three approaches. It is clear that, overall, the approaches produce similar features in the DOS near $E_F$. Quantum Espresso predicts a small but complete gap of 200 meV and FP-LMTO predicts a smaller gap of 40 meV.

Figure 2 shows the density of states for X-phase Cr₃Al calculated using the three approaches.

The bcc solid solution, C11, Cr₂Al + bcc Cr two phase system, and C11, Cr₃Al structure have the next lowest energies, consistent with their being stable phases at higher temperatures. Finally, the D0₃ structure has a significantly higher energy.

Thus, the semiconductor-like behavior in Cr₃Al can be explained by X-phase ordering leading to a gap in the DOS. It is likely that a perfect crystal of X-phase Cr₃Al would be a true narrow-gap semiconductor with a band gap greater than 40 meV. However, real samples thus far show the X-phase occurring in very small domains presumably separated by anti-phase boundaries [9]. Disorder could smear the band edges or introduce defect states. The experimental observations of Cr₃Al are consistent with a small but finite DOS($E_F$) [1].

A band gap can only occur in a material with an even number of valence electrons per unit cell in order to completely fill the valence band. So how can Cr₃Al, with 21 electrons per formula unit, have a band gap? The gap is possible because the primitive unit cell of the X-phase, shown in Figure 1, is actually Cr₆Al₂, having 42 valence electrons per unit cell. This aspect of the X-phase structure sets it apart from the other structures, which, although they may have a low DOS($E_F$), have an odd number of valence electrons per unit cell and therefore must have partially filled bands crossing $E_F$.

This study of the chemical ordering of Cr₃Al has important implications for materials design of transition metal compounds. The energy calculations indicate the D0₃ structure should not occur under equilibrium conditions. This may represent a lower limit on the number of valence electrons in the unit cell for the Heusler structure. Heusler alloys are usually studied with 22-31 valence electrons in the formula unit, while Cr₃Al has 21 [10]. Similar compounds containing transition metals from the left side of the periodic table should be studied for X-phase type ordering.

References: