A.8: Revealing superstructure ordering in $Co_{1+x}MnSb$ Heusler alloys and its effect on structural, magnetic and electronic properties

Half metallic (HM) ferromagnets with 100% spin polarization of electrons at Fermi level (E_f) are efficient spin injector materials for spintronic applications. Heusler alloy based half metals have attracted interest because of their high Curie temperature (T_C) and structural compatibility with conventional semiconductors. In this family, Co-Mn-Sb is an interesting system. In literature, there are some inconsistencies reported on the calculated and measured structural and magnetic properties of this alloy system. Although, from density functional theory (DFT) calculations, CoMnSb was reported to be a half metal in the optimized $C1_b$ structure (*F-43m* space group) and the superstructure phase (*Fm-3m* space group), it actually synthesized in the superstructure with larger lattice parameter compared to its theoretically calculated optimized superstructure phase and was measured to be metallic. Further, its full Heusler alloy counterpart Co_2MnSb, although it is predicted to be HM in $L2_1$ structure (*Fm-3m* space group), stabilizing into a mixed phase of $Co_{1.5}MnSb$ ($L2_1$) and face-centered cubic (fcc) Co. Also, there was no study on the intermediate compositions. These observations have motivated us to perform a combined experimental and theoretical study of $Co_{1+x}MnSb$ (where the nominal compositions x = 0, 0.25, 0.5, 0.75 and 1 have been named as CMS-1, CMS-2, CMS-3, CMS-4 and CMS-5, respectively) to understand the progressive evolution of the crystal structure and physical properties as a function of Co content.

By meticulously examining the crystal structure of the $Co_{1+x}MnSb$ system through synchrotron XRD measurements and Rietveld refinement, we find that all the arc-melted polycrystalline samples crystallize in the superstructure phase with *Fm-3m* symmetry (Figure A.8.1). With increasing Co content, the vacant set of *32f* sites in the superstructure get progressively filled with the Co atoms, but the maximum Co that is accommodated in the $Co_{1+x}MnSb$ phase correspond to x = ~0.45. The excess Co atoms, which do not occupy the lattice site segregate out of the main phase and precipitate at the grain boundaries. This is confirmed from detailed optical and scanning electron microscopy studies. All the samples are found to be ferromagnetic in nature (Figure A.8.2), well above the room temperature and the saturation magnetization (M_s/*f.u*) at 2 K increases slightly with increasing Co content.

To understand the experimental results, DFT based electronic structure calculations have been performed. The results show that the total magnetic moment per formula unit increases with increasing Co content, which is primarily due to the increase in partial moment of the Co atoms and the change of Mn moment is minimal. However, the electronic structure indicates that in spite of the large magnetic moment, none of the alloys are half metallic.

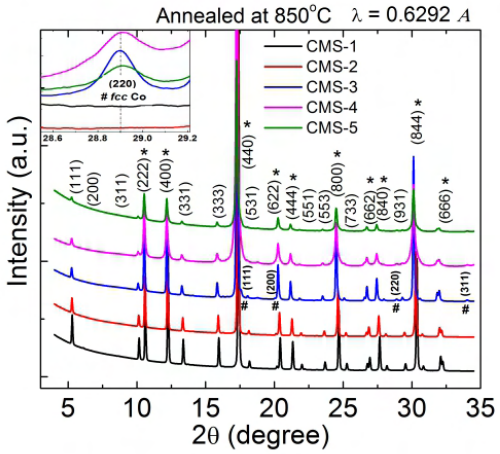

Fig. A.8.1: Room temperature powder XRD patterns of the CMS-1 to CMS-5 samples, annealed at 850 °C. The peak positions marked with (*) correspond to the fcc Co phase. To clearly indicate the existence of the fcc Co in the XRD profiles of the samples CMS-3, CMS-4 and CMS-5, the (220) peak is expanded and shown in the inset.

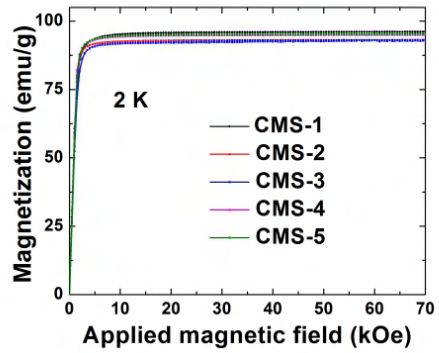

Fig. A.8.2: M vs. H curves at 2 K for fields up to 70 kOe.

Further, the combined experimental and DFT studies indicate that the actual synthesized CoMnSb sample has slight excess of Co and Sb composition, which is accommodated in the vacant sites of the superstructure and results in the increase in the lattice parameter and saturation magnetic moment, as compared to the calculated stoichiometric CoMnSb superstructure. The calculations also indicate that this minor deviation of stoichiometry destroys the half-metallicity in the CoMnSb superstructure. For more details please refer to *Phys. Rev. B, Vol. 105, p 184106 (2022)*.

In conclusion, $Co_{1+x}MnSb$ samples show superstructure ordering, but the maximum Co accommodated in the lattice is x ~ 0.45. Although the calculated CoMnSb superstructure exhibits half-metallicity, the actual synthesized sample does not, which is due to its off-stoichiometry.

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