



	Experiment title: Local magnetic moments of constituent atoms in $(\text{Fe}_{1-x}\text{Co}_x)_7\text{S}_8$: influence of composition, temperature, and high pressure	Experiment number: HC-2270
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Report:

The aim of the project was to study the nature, the details, and the peculiarities of magnetic state in the iron chalcogenide $(\text{Fe}_{1-x}\text{Co}_x)_7\text{S}_8$ system by means of core-to-core (ctc) and valence-to-core (vtc) x-ray emission spectroscopy (XES) at different external conditions (the proposal #p37148).

As is known, the shape of core-to-core XES ($K\alpha_{1,2}$ and $K\beta_{1,3}$ lines) is directly connected to the magnetic moment of an element studied. Within the limits of experimental error (≤ 0.1 eV) no temperature-induced changes of ctc-XES lineshape were detected in the range 10-700 K for both cobalt and iron in any compound. In illustration, the $K\alpha_{1,2}$ spectra of Fe_7S_8 at different temperatures are shown in Fig. 1. This fact points on the completely localized nature of local moments in this family of chalcogenides, and disprove the hypothesis of transition “localized moments \rightarrow band (Stoner) magnetism” upon cobalt doping put forward previously.

The iron and cobalt $K\alpha_{1,2}$ spectra of representative compounds obtained at room temperature are shown in Fig. 2 and 3; in the inserts, the $K\alpha_1$ FWHMs along with corresponding local moment values μ for all compounds are presented. The numerical values of $\mu_{\text{Fe,Co}}$ were extracted by means of usual reference technique (with pure iron, pure cobalt, FeS_2 and Co_7S_8 as reference samples). In this investigation, the formation of magnetic moments on Co atoms in these compounds have been established for the first time. The size of the moments allows one to suggest their “induced” nature. μ_{Fe} shows gradual reduction with increasing cobalt content. Also, the dependence of μ_{Fe} on lattice parameter c (the spacing between Fe layers) reveals two distinct branches: at small and intermediate lattice parameters μ_{Fe} is almost linearly proportional to c , while at highest lattice parameters a kind of “saturation” effect was discovered. Such behavior of μ_{Fe} resembles strikingly gradual collapse of a magnetic moment in an itinerant system upon applying external pressure.

In Fig. 4, the vtc-XES ($K\beta_{2,5}$ spectra) of iron in the $(\text{Fe}_{1-x}\text{Co}_x)_7\text{S}_8$ series are shown. The increasing sharpness of $K\beta''$ low-energy satellite reflects increasing overlapping between iron 3d and sulfur 3s orbitals upon increasing Co content, following by lattice contraction. The growing “hump” on the high-energy side of the spectra might suggest the increasing injection of electrons by Co to the valence band. *Ab-initio* calculations of the density of states near the Fermi level in these compounds will clarify this issue.

Finally, the high-pressure experiment on $(\text{Fe}_{0.6}\text{Co}_{0.4})_7\text{S}_8$, surprisingly, have revealed no transition to low-spin state for pressures up to 22 GPa, the highest value achievable in the utilized high-pressure cell. This is in drastic contrast to Fe_7S_8 and FeS cases, in which spin transitions occurs at $P \leq 6.5$ GPa. Such an effect can be attributed either to increased porousness of the crystal lattice due to the smaller atomic radii of Co with respect to Fe, or to increase of stiffness of atomic bonds upon Co doping. The future XES and EXAFS experiments at higher pressures could shed light on the exact physical nature of this result.

