ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 3, pp. 415–418. © Pleiades Publishing, Ltd., 2014.
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Features of Exchange Interactions in Double Perovskites

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Received June 24, 2013

Abstract—Magnetic susceptibility of double perovskites $Sr_2BB'O_6$ (B = Sc, Fe, Cr; B' = Sb, Nb, W) and their dilute solid solutions has been studied. The complex changes of $Sr_2BB'O_6$ magnetic properties have revealed temperature-dependent distortions of crystalline structure and local ordering of 3*d* elements atoms in different spin states.

DOI: 10.1134/S1070363214030013

Diverse properties of double perovskites $A_2BB'O_6$ (with A = Sr; B = 3*d* element; B' = Sb, Nb, or W) stimulate their systematic studies. These oxides were previously classified as antiferromagnetics with ordered location of B and B' atoms. Recently their surprising magnetic and transport properties (ferrimagnetic, ferromagnetic, and ferroelectric) have been observed, and therefore they have been recognized as promising multiferroics and materials for magnetoelectronic devices [1–3]. The collected experimental data have shown that the materials properties are strongly dependent on electronic and magnetic ordering of the crystalline structure that are in turn determined by chemical composition of the double perovskite. The origin of unusual physicochemical behavior of the perovskites has not been elucidated so far. It has been commonly suggested that the electronic configuration of element B can play a decisive part along with different types of redistribution of electron density between the atoms in B positions. In the presence of B element with partially filled e_g orbitals and element B' having vacant orbitals, unique possibility to promote strongly multiferroic behavior appears [1]. Another factor could be the presence or the absence of different types of disordering of the complex oxide crystal lattice due to both change in the composition of B sublattice and the replacement of the element in positions B' [4]. Positions B' can be occupied by atoms of *p*- as well as *d*-elements (for example, Sb, Nb, Mo, or W), whereas positions B contain atoms of transition elements; oxides with iron as B element has been mostly studied. With *d*-elements in positions B and B', the properties of the oxide are significantly complicated.

Another interesting feature of double perovskites has been discussed in [5]: using Sr_2FeSbO_6 and Sr_2FeNbO_6 as examples, it has been shown that the material magnetoresistivity is determined by its morphology. In the case of monocrystal, the effect is significantly suppressed as compared with polycrystalline samples. That points at importance of the grain size and the intergrain boundary in determining the oxide behavior. According to low-temperature neutron diffraction data, at 100–300 K both oxides were paramagnetic, and their magnetic susceptibility followed the Curie–Weiss law; however, the oxides behavior was different at low temperature [6]. The Weiss constant was negative (–58 and –276 K, respectively), and magnetic moment was 3.86 and 5.92 μ_B, respectively. In the case of iron niobate, transition from paramagnetic state to that of spin glass has been observed below 20 K; iron antimonate became ordered antiferromagnetic below 35 K. As discussed in [5], the antimonate structure remained ordered, whereas in the niobate structure disordering of Fe(III) and Nb(V) between octahedral (or orthorhombic distorted) positions of the crystal lattice appeared. However, Feng et al. have reported only partial ordering (20%) of Fe/Sb in the antimonates. Even for antimonates with transition element B and *p*-element B', being the simplest case of replacement, changes of structural parameters upon substitution of 3*d*-element has not followed the general trend, and the corresponding reference data are contradictory [4].

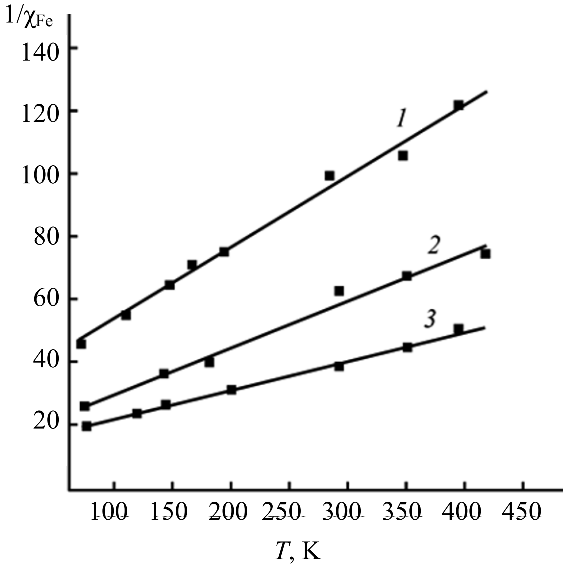

Fig. 1. Reciprocal paramagnetic part of magnetic susceptibility of $Sr_2Fe_xAl_{1-x}SbO_6$ solid solutions as a function of temperature. x, mole fraction: (*1*) 0.01, (*2*) 0.05, and (*3*) 0.09.

In order to extend the knowledge on behavior of compositionally diverse double perovskites, we prepared the oxides $Sr_2BB'O_6$ (B = Cr, Fe, Sc, Al, or Mg; B' = Sb, W, or Nb) and studied their magnetic susceptibility. According to X-ray diffraction data, the samples were of cubic crystal structure at room temperature.

Similarly to the above described case of iron oxides, magnetic properties of chromium antimonates and niobates were different. The starting oxides were checked to be free of ferromagnetic admixtures that could contaminate the measured data. The specific magnetic susceptibility of chromium antimonate depended on the magnetic force, in other words, a ferromagnetic contribution was detected. Such behavior was previously known for iron oxides; however, it was observed for the first time in the case of Ca_2CrSbO_6 [7] being unusual for chromium oxides in general. Magnetic susceptibility of chromium niobate Sr_2CrNbO_6 was independent of the magnetic force. The observed spin glass state was typical of all niobates of 3*d*-elements, but formation of local areas of magnetic ordering was unlikely in those cases.

Complex oxides Sr_2AlWO_6 and Sr_2ScWO_6 were prepared to be applied as potential diamagnetic matrices for magnetic dilution. Specific magnetic susceptibility of those samples was almost equal (0.154–0.155 cm^3/g at 293 K), and its temperature dependence was typical of diamagnetic materials, similarly to the earlier studied Sr_2AlSbO_6. Furthermore, we measured magnetic susceptibility of Sr_2MgWO_6 containing paramagnetic W(VI) atoms (as confirmed by temperature dependence of magnetic susceptibility following the Curie–Weiss law). Hence, crystal structure of the double perovskite was quite tolerant to changes of chemical compositions of B sublattice. That allowed magnetic dilution of tungstates containing 3*d*-element atoms in different oxidation states.

Experiments on magnetic dilution of iron, chromium, and manganese antimonates with Sr_2AlSbO_6 as diamagnetic solvent clarified the issue of disordering in double perovskites and its effect on the properties of ceramics. Solid solutions $Sr_2B_xAl_{1-x}SbO_6$ (B = Fe, Cr, or Mn; $0.005 \le x \le 0.100$) were prepared by ceramic method. Content of the paramagnetic element was determined by atom absorption spectroscopy. According to X-ray diffraction data, iron- and manganese-containing solid solutions revealed the solvent cubic lattice at room temperature.

Data on magnetic dilution of manganese antimonate were reported in our previous paper [8]. Changes in magnetic susceptibility and effective magnetic moment with temperature and the solution concentration revealed coexistence of two spin states of Mn(III) in the solutions. At about 250 K, a reversible transition from the low-spin state to the high-spin state was observed, pointing at the changed geometry of manganese atom surrounding with oxygen atoms. Fraction of the high-spin state increased with manganese concentration in the solution. As the low-spin state was observed only in dilute solutions, we concluded that the temperature-dependent distortions were local, i.e. regions with different cations ordering appeared in the lattice depending on temperature. In [9], crystal structure of Sr_2AlSbO_6 was studied in detail, and the regions of cations ordering were detected; they were recognized as appeared antiphase domains about 17 ± 1 nm in size.

Study of magnetic susceptibility of Sr_2FeSbO_6 solid solution revealed the ferromagnetic contribution as well, enhancing with higher iron concentration. Changes of magnetic susceptibility and magnetic moment with the solution concentration were typical of antiferromagnetic oxide. The magnetic moment extrapolated to infinite dilution (5.95 μ_B) coincided well with the respective value for Fe(III) and with data

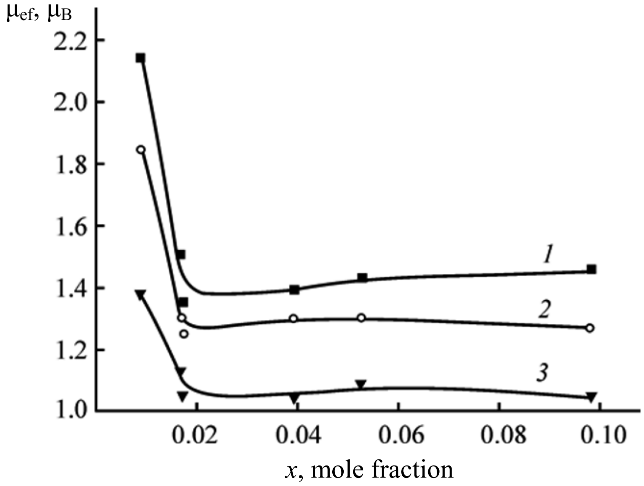

Fig. 2. Effective magnetic moment as afunction of composition of $Sr_2Cr_xAl_{1-x}SbO_6$ solid solutions. (*1*) 350, (*2*) 180, and (*3*) 100 K.

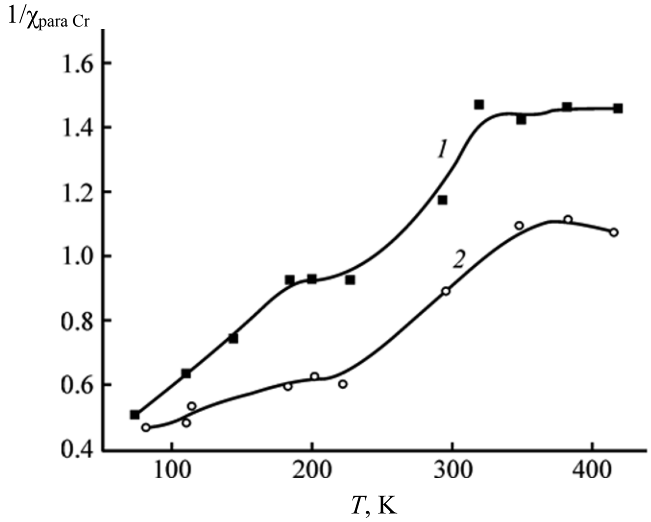

Fig. 3. Reciprocal paramagnetic part of magnetic susceptibility of $Sr_2Cr_xAl_{1-x}SbO_6$ as a function of temperature. x, mole fraction: (*1*) 0.1 and (*2*) 0.02.

from [6]. Temperature dependences of magnetic susceptibility followed the Curie–Weiss law, similarly to the case of pure oxide (Fig. 1). The Weiss constant was negative, of approximately –120 K in the cases of all studied solutions. Generally, the Weiss constant of solid solutions depends on the content of paramagnetic element; therefore, its decrease as compared to the Sr_2FeSbO_6 case pointed at competitive (ferromagnetic) contribution to the susceptibility. Detection of ferromagnetic exchange exclusively in dilute solutions confirmed the local character of distortions and formation of magnetically ordered regions in the solutions as well.

In the case of $Sr_2Cr_xAl_{1-x}SbO_6$, tetragonal distortions of the cubic structure (leading to significant deformation of oxygen octahedrons surrounding Cr atoms) were observed by X-ray diffraction even in dilute solid solutions. In contrast to the case of Sr_2CrSbO_6, magnetic susceptibility of the solutions was constant with the magnetic force. Moreover, the susceptibility values were much lower than could be expected for Cr(III) atoms in the $3d^3$ high-spin configuration. Changes of paramagnetic part of the susceptibility (with respect to 1 mol of Cr atoms) with concentration was typical of antiferromagnetics, however, its temperature dependence was more complex. Values of μ_{eff} extrapolated to infinite dilution (1.42–2.20 μ_B) were lower than those in the high-spin state (Fig. 2). Its changes at 80–450 K corresponded to the values calculated for the low-spin state (^{2}E term).

Temperature dependence of magnetic susceptibility of the samples revealed a sudden change at 180–300 K (Fig. 3), its value being a function of the solution concentration. The jump could be explained by a change of local surrounding of Cr(III): the phase transition from monoclinic Sr_2CrSbO_6 structure into cubic one was observed in the same temperature range [9]. Distortion of oxygen surrounding of chromium ions led to the change of the atoms spin state reflected in changes of magnetic properties.

To conclude, the experimental data collected in this work confirmed a strong influence of structure of regions of cations ordering on magnetic properties of double perovskite. Evidently, absolutely ordered virginal lattice could not be realized in the cases of 3*d*-elements antimonates.

EXPERIMENTAL

Complex oxides were prepared by ceramics method by annealing mixtures of the corresponding starting reagents at 1173 K during 200 h. Strontium carbonate was annealed at 1073 K beforehand, in order to remove adsorbed water and carbon dioxide. The so prepared samples were tested by means of X-ray diffraction and static magnetic susceptibility at 77–400 K [10].

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