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# Magnetic Susceptibility of $Li_{x}Mn_{1-x}Se$

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Measurements of magnetic susceptibility have been made on the  $Li_xMn_{1-x}Se$  system at temperatures ranging from 77 K to room temperature. The curves of the susceptibility obtained show a thermal hysteresis. The values of the effective magnetic moments per Mn atom decrease with increasing Li concentration. However, these values are lower than those expected on the consideration of  $Li_x^*Mn_x^{++}Mn_{1-2x}^{+}Se$ . The values of the paramagnetic Curie temperature increase with increasing Li concentration.

#### §1. Introduction

The details of the magnetic behavior of the  $\text{Li}_x \text{Mn}_{1-x}$ Se system are attributed to the double exchange interaction. An exchange mechanism has been proposed by Zener<sup>1)</sup> for these mixed valency materials. This interaction leads to a ferromagnetic coupling and in addition, to a low metallic-type electrical resistance. Heikes et al.<sup>2)</sup> have studied the behavior of magnetization of MnSe having Li content up to 11 at. % and found that ferromagnetism is induced in the  $\text{Li}_x \text{Mn}_{1-x}$ Se system. The magnetic behavior of this system has also been studied by neutron diffraction experiments.<sup>3)</sup> Kasaya has reported a typical anomaly in the variation of the resistivity<sup>4)</sup> and abrupt changes in the paramagnetic Curie points and the magnetization in the range 0.031  $\angle x \angle 0.053.^{5)}$ 

We report in this paper the results of magnetic susceptibility measurements on the samples of Li content x = 0.03, 0.05, 0.07, 0.085 and 0.10.

### §2. Experimental Procedures

The  $Li_xMn_{1-x}Se$  system has been prepared by reacting  $Li_2Se$ , Se and MnSe in the proper amounts at elevated temperatures. The elements Mn (99.995%, flakes), Se (99.999%, pellets) and Li (99.5%, flakes) were purchased from Mitsuwa Chemical Co., Ltd.  $Li_2Se$  and MnSe were prepared by solid-vapour reaction. Due to the known air sensitivity of the  $Li_2Se$  and the potential sensitivity of phases in the  $Li_xMn_{1-x}Se$  system, all operations were conducted using Blickman vacuum glove box back filled with welding grade argon. Materials in the single phase region of the  $\text{Li}_x \text{Mn}_{1-x}$ Se system were stable in air. In the range of composition of this system where  $0 \le x \le 0.11$ , the products of the powder sample were the single phase material of rock salt structure. X-Ray diffraction patterns were taken of the products. The results are shown in Fig. 1. The lattice parameter decrease linearly with increasing Li concentration. These values are in fair agreement with those determined by Johnston et al.<sup>6</sup>)

Magnetic susceptibility of the powder sample was measured by means of the automatic magnetic balance in the temperature range from 77K to room temperature. The temperatures of the specimen were determined by a gold cobalt-copper thermo-couple.



Fig. 1. X-Ray lattice parameter vs. Li concentration x.

## §3. Experimental Results and Discussion

The magnetic susceptibility vs. temperature curves for  $Li_{0.10}Mn_{0.90}Se$  are shown in Fig. 2. The data were taken at a field strength of 3820 Oe. The cooling and warming curves show a thermal hysteresis. For the data plotted in this figure, the sample had previously been cooled to 77K and then allowed to warm up to room temperature. The values of the susceptibility in the cooling process near the transition temperature are larger than that of warming process. In a cooling process, the ferromagnetic Curie temperature is at approximately 110K. All these curves obtained from the measurements of the susceptibility show a thermal hysteresis.

Figure 3 shows magnetization curve at 80K for  $Li_{0.10}Mn_{0.90}Se$ . The magnetization curve is easily saturated at about 1 kOe.

At temperatures except near the transition temperature, all the samples obey the Curie-Weiss relationship in a cooling process. Figure 4 shows the effective magnetic moment per Mn atom vs. Li concentration x. As for the pure MnSe, the value of the effective magnetic moment corresponds to Mn<sup>++</sup> ion within the experimental error.<sup>7)</sup> The values of the effective magnetic moment decrease with increasing Li concentration. Each Li substitution causes the formation of one Mn<sup>+++</sup> ion as represented in the formula  $\text{Li}_x^+\text{Mn}_x^{+++}\text{Mn}_{1-2x}^{++}$ Se. The values of the theoretical effective magnetic moments of Mn<sup>+++</sup> ions are 5.92  $\mu_B$  and 0  $\mu_B$ , respectively. If the orbital

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Fig. 2. Magnetic susceptibility vs. temperature for  $Li_{0,10}Mn_{0,90}Se$ .



Fig. 3. Magnetization vs. magnetic field at 80 K for  $Li_{0,10}Mn_{0,90}Se$ .



Fig. 4. Effective magnetic moment vs. Li concentration x.

moments are quenched, these values are  $5.92 \,\mu_B$  and  $4.90 \,\mu_B$ , respectively. However, the values of the effective magnetic moment obtained from the experiment in  $\text{Li}_x \text{Mn}_{1-x}$ Se are lower than those expected on the consideration that  $(1-2x)\text{Mn}^{++}$  and  $x\text{Mn}^{+++}$  in  $\text{Li}_x\text{Mn}_{x}^{+++}\text{Mn}_{1-2x}^{++}$ Se have even the magnetic moments of  $5.92 \,\mu_B$  and  $0 \,\mu_B$ , respectively.



Fig. 5. Paramagnetic Curie temperature vs. Li concentration x.

In Fig. 5 the paramagnetic Curie temperature vs. Li concentration x are shown. The paramagnetic Curie temperature increase with increasing Li concentration. Kasaya<sup>5</sup>) has pointed out that the abrupt change in the paramagnetic Curie temperature occurred near the concentration of x=0.031. But the curves obtained in this experiment do not show the abrupt change. The difference may be caused by the state of the sample. Kasaya had used the ceramic samples which was pressed into pellets before the reaction in the furnace. But, the powder samples used in the present work were not pressed into pellets. Further magnetic studies are now in progress. It will be reported elsewhere in the near future.

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