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MAGNETIC PROPERTIES OF PRECIPITATED PHASES IN Mn$^{2+}$ DOPED ALKALI HALIDES

M. Moreno, F. Rodriguez and J. C. Gomez Sal

D.C.I.T.T.Y.M., Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain

Abstract. - The susceptibility and specific heat data on NaCl: Mn$^{2+}$ in the 0.07-4.2 K range reflect the existence of an antiferromagnetic phase transition at $T_N = 0.2$ K. Below $T_N$, the susceptibility reveals the presence of loose spins associated to Mn$^{2+}$ in (or near) the surface of the Suzuki phase precipitates. The E.P.R., susceptibility and optical, measurements performed on RbCl: Mn$^{2+}$ indicate that the nature of the precipitates is not MnCl$_2$, RbMnCl$_3$, Rb$_2$MnCl$_4$ or Rb$_2$MnCl$_7$, but the distorted MnCl$_6^{4-}$ units must share some common Cl$^-$ ions in order to explain the values $\theta_p = -124$ K and $T_N = 72 \pm 5$ found for this new material inserted in RbCl.

The precipitated phases formed in alkali halides crystals doped with magnetic divalent cations such as Mn$^{2+}$ ($S = 5/2$), offer an excellent opportunity for exploring new magnetic materials as well as the effects related to the precipitate size. The composition and structure of the microcrystals forming the precipitates do not correspond necessarily to a known compound. The present work is focused on the magnetic properties of precipitated phases formed in as grown NaCl: Mn$^{2+}$ and RbCl: Mn$^{2+}$ crystals.

As regards NaCl: Mn$^{2+}$ it gives rise to the so-called Suzuki phase which has been explored by different spectroscopic techniques [1, 2]. The presence of two exciton transitions in the optical spectra [2] as well as the observation of only one isotropic lorentzian band in the E.P.R. spectrum [3] are both consistent with the existence of Mn$^{2+}$ ions coupled through superexchange interactions with values of the exchange constant $|J|$ about 0.03 K. This value is qualitatively consistent with the very long Mn$^{2+}$-Mn$^{2+}$ distance (7.97 Å) between two Mn$^{2+}$ ions in the nearest position. In order to deep more into the magnetic properties of the Suzuki phase in NaCl: Mn$^{2+}$ we have performed magnetization and specific heat measurements in the 0.07-4.2 K range as well as small angle neutron scattering (S.A.N.S.) experiments. The magnetic susceptibility of three different NaCl doped Mn$^{2+}$ samples (17 000, 900 and 200 ppm) containing the Suzuki phase has been studied for several applied magnetic fields. When $T > 0.5$ K the reciprocal susceptibility of Suzuki phase in all the samples follows a Curie-Weiss law leading always to a $\theta_p = -1.5 \pm 0.2$ K. Specific heat measurements show a very sharp peak at 0.2 K which strongly supports the existence of an antiferromagnetic phase transition [4] (Fig. 1). The entropy change associated to such a peak is in agreement with that expected for a $S = 5/2$ ion. Below $T_N$, each sample shows a different magnetic behaviour, the susceptibility referred to one Mn$^{2+}$ increases when the Mn$^{2+}$ concentration decreases. Furthermore the susceptibility curves also depend on the magnetic field, as is shown in figure 2 for the 900 ppm sample. This complex behaviour has been interpreted as due to the presence of "loose spins" (Mn$^{2+}$ ions lying in/or near to the microcrystal surfaces which experience a smaller internal field). In fact the susceptibility curves of figure 2, show that as far as the magnetic field increases the contribution coming from the loose spins decreases progressively due to saturation effects. For $H = 2, 2$ kOe the curve is almost due to the bulk antiferromagnetic Suzuki phase contribution, showing the maximum at the Néel temperature. The relative concentration of loose spins estimated for each samples suggests a relation between the Mn$^{2+}$ concentration and the microcrystal size of the Suzuki phase. Preliminar S.A.N.S. experiments
Fig. 2. – Magnetic susceptibility $\chi(H,T) = \Delta M/\Delta H$ as a function of the temperature for NaCl: Mn$^{2+}$ (900 ppm) containing the Suzuki phase: a) $H = 0$ Oe, $\Delta H = 100$ Oe, b) $H = 500$ Oe, $\Delta H = 500$ Oe, c) $H = 1000$ Oe, $\Delta H = 500$ Oe, d) $H = 2000$ Oe, $\Delta H = 500$ Oe.

performed on samples with 17 000 and 900 ppm suggest the presence of precipitates greater than 1 000 Å size. Further work is now in progress.

The case of as grown RbCl: Mn$^{2+}$ crystals is rather different to NaCl: Mn$^{2+}$. In that system the optical spectra of the precipitated phase point out that its nature does not correspond neither to MnCl$_2$, RbMnCl$_3$, Rb$_2$MnCl$_4$ or Rb$_3$Mn$_2$Cl$_7$ compounds nor to the Suzuki phase [5]. This conclusion is supported by E.P.R. data. At room temperature the E.P.R. spectrum is composed of an isotropic truncated lorentzian shape band having $\Delta H_{pp} = 23$ G. Below about 90 K however $\Delta H_{pp}$ increases dramatically (Fig. 3) associated to the existence of a magnetic phase transition transition

with a Néel temperature $T_N = 72 \pm 5$ K [5]. The present results indicate that the precipitated phase must be formed by distorted MnCl$_6^{2-}$ units sharing some common Cl$^-$ ions. The susceptibility measurements carried out on this system in the 40-200 K temperature range point out that the system follows a Curie-Weiss law with $\theta_p = -124$ K (Fig. 4) which supports the existence of an important antiferromagnetic exchange between close Mn$^{2+}$ ions. The susceptibility data do not show however a clear evidence of a magnetic phase transition in our system. The present situation which has been found in the study of some ionic compounds [6] stresses the importance of performing complementary E.P.R. measurements through which magnetic phase transitions can be better detected.

Fig. 3. – Variation of the E.P.R. bandwidth, $\Delta H_{pp}$ vs. temperature. Experimental point errors are ± 1 G for $\Delta H_{pp}$ and ± 3 K for $T$.

Fig. 4. – Reciprocal susceptibility of RbCl: Mn$^{2+}$ vs. temperature. Experimental data were corrected for the diamagnetic susceptibility of RbCl.