

Magnetic susceptibility of the Suzuki phase formed in NaCl:Mn^{2+} in the 0.07–4.2-K temperature range

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The magnetic susceptibility of three different as-grown NaCl:Mn^{2+} crystals containing about 17000, 900, and 200 ppm of Mn^{2+} has been studied in the 0.07–4.2-K temperature range in order to investigate the magnetic properties of the Suzuki-phase microcrystals. The present data demonstrate that the Suzuki-phase precipitates Na_6MnCl_8 formed inside the host lattice undergo an anti-ferromagnetic phase transition at $T_N = 0.3$ K. Within the experimental uncertainty, the three samples have the same value of the paramagnetic Curie temperature $\Theta_S = 1.5 \pm 0.2$ K. On the other hand, the results for $T \leq 0.2$ K point out the existence of loose spins, corresponding to Mn^{2+} ions in which the internal field is smaller than that for normal Mn^{2+} ions in the bulk Suzuki phase. The ratio between the concentration of loose spins and that of normal Mn^{2+} ions in the bulk Suzuki phase increases when dopant concentration decreases, while the average internal field acting on the loose spins increases upon increasing dopant concentration. This phenomenon is tentatively associated with size effects, the loose spins corresponding to Mn^{2+} ions lying on (or near to) the surface of the precipitate. Finally, for the less doped sample it is shown that 20% of Mn^{2+} ions are dissolved in the NaCl host lattice while the remainder form the Suzuki phase.

INTRODUCTION

In doped ionic solids the formation of precipitates is a rather usual phenomenon which can appear even for low dopant concentration (less than 1000 ppm). The interest for studying precipitated phases embedded in host lattices arises from the following reasons.

(1) The composition and structure of the precipitates phases can be different from the corresponding to a known stable compound. Therefore we have the opportunity of exploring the properties of a new material inserted in a stable host lattice. A good example of this behavior is the so-called Suzuki phase¹ observed by x-ray diffraction or electron microscopy techniques in as-grown alkali-halide crystals doped with divalent cations, such as Cd^{2+} (Refs. 1–5), Mn^{2+} (Refs. 6 and 7), Fe^{2+} (Ref. 8), V^{2+} (Ref. 9), and Mg^{2+} (Refs. 5 and 10). In these cases attempts for growing single crystals of the Suzuki phase have been unsuccessful, and in general this phase can only be obtained as a precipitate inserted in the alkali-halide matrix. An exception to this behavior is, however, Li_8VCl_6 .⁹

(2) The precipitated phases are good candidates for detecting surface phenomena as well as examining the influence of size upon bulk properties. Since the discovery of the Suzuki phase in as-grown NaCl:Cd^{2+} samples, several studies have been carried out in order to explore its properties. In this sense Toman² was the first to investigate the influence of impurity concentration and cooling rate on the size of precipitates. Such work

pointed out that the size increases upon increasing dopant concentration; it also increases with decreasing cooling rate. This idea was later confirmed by the work of Spengler and Kaiser⁴ who at the same time were the first to explore the vibrational properties of the Suzuki phase in NaCl:Cd^{2+} through the Raman technique. Later, this technique was used for detecting the formation of the Suzuki phase in doped alkali halides.^{10–14}

Optical properties have also been explored for transition-metal divalent cations in the Suzuki phase. This is the case for the Suzuki phase formed in NaCl:Mn^{2+} where the excitation spectrum revealed¹⁵ the presence of a double exciton band, stressing the existence of the exchange interaction between close Mn^{2+} ions. Also the optical data pointed out that the $\text{Mn}^{2+}-\text{Cl}^-$ distance between a Mn^{2+} ion and the nearest Cl^- was slightly smaller than that for “free” Mn^{2+} ions truly dissolved in the NaCl lattice.

Finally, some optical bands showed at 12 K the existence of vibronic progressions consistent with Raman data.¹⁶ This kind of progression was also detected in NaCl:Ni^{2+} (Ref. 13) and more recently in NaCl:Co^{2+} (Ref. 14).

Despite efforts of this kind devoted to explore structural, vibrational, optical, or electric properties associated with the Suzuki phase, less attention has been paid to its magnetic properties for cases when a transition-metal cation is involved. This kind of study is however, very attractive because of the structure of the Suzuki phase depicted in Fig. 1. In fact, for a Suzuki

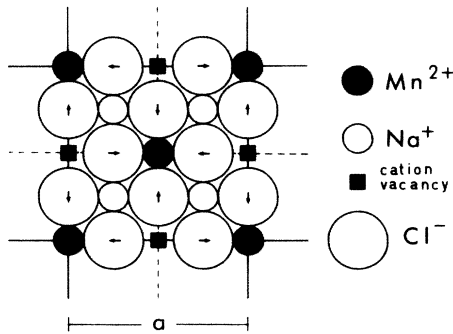


FIG. 1. (100) projection of the unit cell of the Suzuki phase in NaCl:Mn^{2+} which corresponds to the stoichiometry 6NaCl:MnCl_2 . The lattice parameter a is just twice that of the NaCl lattice. The distance between a Mn^{2+} ion and a nearest Cl^- ion is 2.58 Å.

phase formed in NaCl the divalent cations display a fcc lattice, the distance among the nearest cations being 7.97 Å.

This distance is then 1.9 times higher than that occurring between the nearest Mn^{2+} ions in the RbMnF_3 lattice ($T_N = 83$ K). As the exchange interaction in magnetic insulator compounds depends very strongly on the distance between the nearest magnetic ions,¹⁷ we can expect for the Suzuki phase in NaCl:Mn^{2+} an ordering temperature below 4.2 K.

Furthermore, it should be noted that in the absence of exchange interactions between next-nearest magnetic cations the fcc lattice displayed by the Mn^{2+} in the Suzuki phase would give rise to topological magnetic frustration.¹⁸

In preliminary work carried out on the Suzuki phase formed in NaCl:Mn^{2+} , it was determined that the corresponding susceptibility between 1 and 4.2 K measured using an external field $H = 80$ Oe follows a Curie-Weiss law $\chi = C / (T - \Theta_S)$ with $\Theta_S = -1.5$ K in agreement with estimations from structural data and the experimental EPR peak-to-peak bandwidth $\Delta H_{\text{p.p.}} = 135$ Oe measured at room temperature. Although this experimental result suggests the existence of a possible antiferromagnetic transition it was not detected at that time.

The present work reports a strong evidence of an antiferromagnetic transition. For achieving this goal we have studied the magnetic properties of three different samples of NaCl:Mn^{2+} containing 17 000, 900, and 200 ppm (and called I, II, and III, respectively, throughout this work) by means of susceptibility and magnetization measurements in the 0.07–4.2 K temperature range and magnetic fields up to 2500 Oe. These measurements make it possible to determine the different contribution to the macroscopic susceptibility appearing in our samples.

In fact, besides the contribution of “normal” Mn^{2+} lying in the bulk Suzuki phase as well as that of possible free Mn^{2+} ions truly dissolved in the NaCl lattice other contributions arising from loose spins (lying, for instance, in the surface of the precipitate) or from super-

paramagnetism of small precipitates could also be present in the macroscopic magnetization. It can be expected however that this kind of effect is less important as the Mn^{2+} concentration increases and thus the most doped crystal is, in principle, the best candidate for investigating the magnetic properties of the bulk Suzuki phase.

EXPERIMENTAL PROCEDURE

Samples of three different as-grown NaCl:Mn^{2+} crystals containing about 200, 900, and 17 000 ppm of Mn^{2+} (determined by atomic absorption spectrophotometry) have been studied through this work. The crystals were grown at the Departamento de Optica (Universidad Autónoma de Madrid) by means of the Czochralski method in an inert atmosphere, the cooling rate being about 300 °C/h. The studied samples were previously checked through optical¹⁵ and EPR techniques.¹⁹ Both techniques are consistent with the presence of the Suzuki phase in our samples.

The magnetization $M(H, T)$ measured for different magnetic fields, H , was determined by means of an extraction method using the experimental setup of the Centre de Recherches pour les Très Basses Températures (Grenoble, France) whose sensitivity allows detection down to about 50 ppm of Mn^{2+} at 0.1 K. From $M(H, T)$ the differential susceptibility for different values of H

$$\chi(H, T) = \frac{M(H + \Delta H, T) - M(H, T)}{\Delta H} \quad (1)$$

was derived.

RESULTS

Figure 2 depicts the differential susceptibility, $\chi(H, T)$, in the temperature range 0.07–4.2 K for sample I. The initial susceptibility $\chi(0, T)$ above 0.8 K clearly follows a Curie-Weiss law

$$\chi(0, T) = \frac{C_S}{T - \Theta_S},$$

where $\Theta_S = -1.5$ K and $C_S = 13 \times 10^{-4}$ emu K/(g Oe). The value of Θ_S is in agreement with a previous determination of Θ_S for the Suzuki phase.¹⁹ On the other hand, from the C_S value can be inferred a concentration of Mn^{2+} ions, forming the Suzuki phase, N_S , equal to 17 400 ppm through the relation

$$C_S = \frac{35}{3} N_S \frac{\mu_B^2}{k_B}. \quad (2)$$

At $T = 0.35$ K, $\chi(0, T)$ clearly shows a maximum which can, in fact, be associated to the existence of an antiferromagnetic phase transition. It should be remarked that below 0.2 K $\chi(0, T)$ begins to increase when the temperature decreases. More precisely below 0.35 K the experimental points corresponding to $\chi(0, T)$ can be fitted by the equation

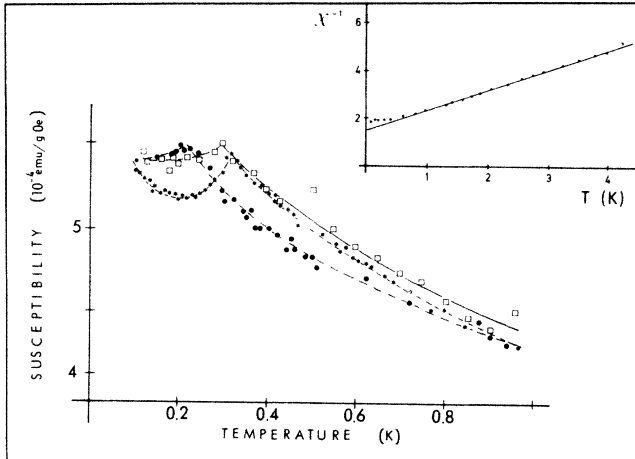


FIG. 2. Magnetic susceptibility $\chi(H, T)$ as a function of temperature in the 0.07–1-K range for sample (I) containing about 17000 ppm of Mn^{2+} . $\chi(H)$ has been determined for $H=0$ (*), 1000 (□), and 2000 Oe (●) and ΔH is always equal to 200 Oe. In the insert is shown $\chi^{-1}(0, T)$ in the 0.07–4.2 temperature range. $\chi^{-1}(0, T)$ is given in units of 10^3 (gOe)/emu.

$$\chi(0, T) = \chi_0 + \alpha_S T + \frac{C_L}{T - \Theta_L}, \quad (3)$$

the numerical values of the χ_0 , α_S , C_L , and Θ_L parameters being given in Table I.

It is worth pointing out here that Eq. (3) governs the magnetic susceptibility of dilute antiferromagnetic insulators below the order temperature T_N and also that of insulator spin-glasses below the freezing temperature, T_f . Examples of this behavior have been found in $\text{ZnCr}_{2x}\text{Ga}_{2-2x}\text{O}_4$ (Refs. 20 and 21), $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ (Ref. 22), and in the anisotropic spin-glass Fe_2TiO_5 (Ref. 23).

In such cases the typical meaning of Eq. (3) is the following. The first two terms (involving χ_0 and α_S parameters) depict the typical antiferromagnetic phase or spin-glass contribution while the last term reflects the existence of loose spins.

In the disordered systems mentioned the loose spins correspond to magnetic ions whose internal field cancels, or at least whose associated energy is smaller than the

thermal energy $k_B T$. An indication of the average internal field acting on the loose spins is given by Θ_L . As expected for dilute antiferromagnetics it has been observed that when the concentration of magnetic ions decreases, Θ_L decreases, but the concentration of loose spins, N_L , increases.^{21,22} The value of N_L can be derived from the experimental C_L value through an analogous relation to Eq. (2) connecting N_S and C_S .

For sample I, Θ_L is found to be -0.1 K. Thus $|\Theta_L|$ is less than $|\Theta_S|$. It is worth stressing here that as our measurements are carried out down to 0.07 K, we are capable of distinguishing quite well the existence of loose spins with $\Theta_L \neq 0$ from that of free Mn^{2+} ions (dissolved, for instance, in the NaCl lattice), whose $\chi(0, T)$ should follow Curie's law.

The differential susceptibility $\chi(H, T)$ for $H \neq 0$ is consistent with the presence of the loose spins (Fig. 2). In fact, for $H=2000$ Oe, although $\chi(H, T)$ exhibits a maximum at 0.25 K, it does not increase significantly for $T < 0.25$ K, at variance with the behavior for $\chi(0, T)$ in the same temperature region. The assumption of the loose spins is thus supported by this fact, implying a magnetic spin moment of the order of $1\mu_B$. In other words this argument favors the idea that we are saturating nearly single ions rather than the total magnetic moment of a microcrystalline grain involved in a superparamagnetic situation.

In Fig. 3 data corresponding to sample II containing about 900 ppm are reported. For T higher than about 0.7 K, $\chi(0, T)$ follows Eq. (1) well, Θ_S being -1.7 ± 0.2 . This is the same as for sample I in view of the experimental uncertainties. However, the behavior of $\chi(0, T)$ for $T < 0.5$ is rather different from that of sample I and, in principle, no signs of a phase transition are seen in it as was previously noted.¹⁹ This situation is clarified by looking at $\chi(H, T)$ for $H \neq 0$. In this way for $H=2200$ Oe, $\chi(H, T)$ exhibits a maximum precisely at 0.3 K. Therefore the present facts suggest that $\chi(0, T)$ can also be understood through Eq. (3), although in this case the fraction of loose spins is increased with respect to that of sample I, masking the phase transition of the bulk Suzuki phase. Such a situation is, however, avoided by saturating the loose spins. The present interpretation is supported by the analysis of the experimental $\chi(0, T)$ curve for $T < 0.4$ K. Such a curve can also be explained through Eq. (3) but with a higher value of the N_L/N_S quantity and a smaller value of Θ_L as pointed out in Table I.

Regarding sample III which contains about 200 ppm

TABLE I. Values of the parameters involved in Eqs. (1), (2), and (3) derived for the three samples analyzed in the present work. χ_0 and C_S have the following values referred to a sample containing 1 ppm of Mn^{2+} ions forming the Suzuki phase. $\chi_0 = 2.4 \times 10^{-8}$ emu/(g Oe), and $C_S = 2.7 \times 10^{-8}$ (emu K)/(g Oe).

Sample	Nominal concentration (ppm)	Θ_S (K)	C_S (emu K)/(g Oe)	N_S (ppm)	Θ_L (K)	C_L (emu K)/(g Oe)	N_L/N_S (%)
I	17 000	-1.5 ± 0.2	13×10^{-4}	17 400	-0.1	35×10^{-4}	2.7
II	900	-1.7 ± 0.2	8.6×10^{-5}	1150	-0.08	3.5×10^{-6}	4.1
III	200	-1.3 ± 0.3	1×10^{-5}	130	-0.02	0.65×10^{-6}	6.5

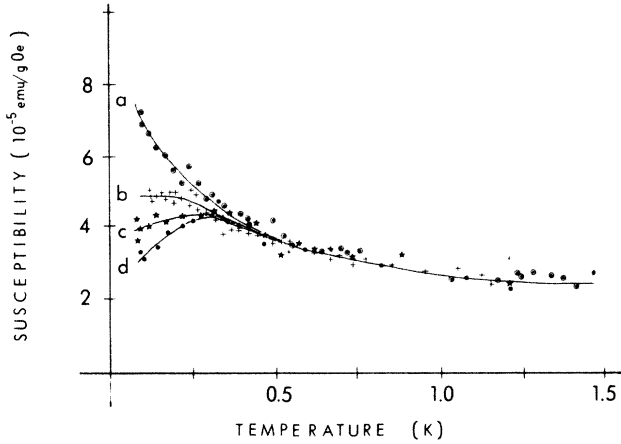


FIG. 3. Magnetic susceptibility $\chi(H, T)$ as a function of the temperature in the 0.07–1.5 temperature range for sample II (900 ppm of Mn^{2+}). (a), \odot , $H=0$ Oe; $\Delta H=100$ Oe (Ref. 19); (b), $+$, $H=500$ Oe; $\Delta H=500$ Oe; (c) \star , $H=1000$ Oe; $\Delta H=500$ Oe; (d) \bullet , $H=2200$ Oe; $\Delta H=500$ Oe.

of Mn^{2+} , the situation is more complex (Fig. 4). In fact, fitting the experimental results for $T > 0.7$ K to Eq. (1), the value of Θ_S obtained is -0.7 K, which is different from that corresponding to samples I and II.

However, the isotropic part of the EPR spectra of sample III is the same as the EPR spectrum of samples I and II: it consists of a truncated Lorentzian shape band with $\Delta H_{p.p.} = 135 \pm 5$ Oe at room temperature which has been identified as being due to the Suzuki phase.

By virtue of this fact, we interpret the experimental $\chi(0, T)$ curve in the $T > 0.7$ -K region assuming that it is essentially due to the simultaneous presence of the Suzuki phase as well as of isolated Mn^{2+} dissolved in the NaCl host lattice whose susceptibility $\chi(0, T)$ is governed by a pure Curie's law.

Fitting now the experimental results of Fig. 4 for $T > 0.7$ K to the equation

$$\chi(0, T) = \frac{C_S}{T - \Theta_S} + \frac{C_F}{T}, \quad (4)$$

it is found $\Theta_S = -1.3 \pm 0.3$ K, $C_S = 10^{-5}$ (emu K)/(g Oe), $C_F/C_S = 0.27$. In this equation the term C_F/T arises from the contribution of free Mn^{2+} ions dissolved in the NaCl host lattice.

It is worth pointing out that the value of Θ_S obtained through Eq. (4) is essentially the same as that corresponding to the paramagnetic Curie temperature of the Suzuki phase found in samples I and II. On the other hand, the values of C_S and C_F imply a concentration of Mn^{2+} ions forming the Suzuki phase $N_S = 130$ ppm while the concentration N_F of isolated Mn^{2+} ions is 35 ppm.

Also depicted in Fig. 4 is the curve $\chi_D(0, T)$ which results from subtracting the free Mn^{2+} contribution from the experimental susceptibility.

Despite the experimental uncertainty it is clearly seen

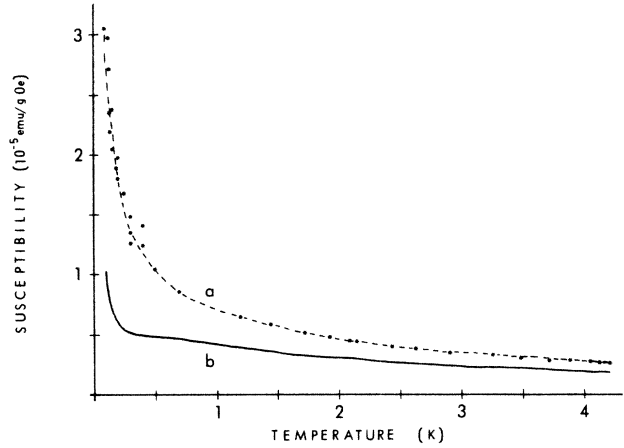


FIG. 4. (a) Experimental magnetic susceptibility $\chi(H, T)$ for sample III (200 ppm of Mn^{2+}) in the 0.07–4.2-K temperature range $H=0$ Oe; $\Delta H=100$ Oe. The disturbance seen in the vicinity of 0.4 K reflects the scatter of data rather than a real effect. (b) Magnetic susceptibility $\chi_D(H, T)$ corresponding to the Suzuki-phase precipitates in sample III derived from the experimental $\chi(H, T)$ as explained in the text.

how the referred curve increases when the temperature decreases for $T < 0.2$ K. At the same time no phase transition at $T_N = 0.35$ K is observed. Both facts are again ascribed to the presence of loose spins whose influence can be significant for $T < T_N$ while it can be negligible for $T > 0.7$ K.

The analysis of $\chi_D(0, T)$ for $T < 0.35$ K using Eq. (3) leads to the values $\Theta_L = -0.02$ K and $N_L/N_S = 6\%$ reported in Table I. This value of the fraction of loose spins supports a posteriori their neglect in the analysis of $\chi(0, T)$ in the region $T > 0.7$ K. On the other hand the values of Θ_L and N_L/N_S found for sample III support the idea when impurity concentration increases Θ_L increases but N_L/N_S decreases.

FINAL REMARKS

The experimental results reported in the preceding section offer good evidence for the existence of an antiferromagnetic phase transition for the Suzuki phase in $\text{NaCl}:\text{Mn}^{2+}$ at $T_N = 0.3$ K. This fact is consistent with EPR data carried out down to 7 K. In this way the bandwidth $\Delta H_{p.p.}$ associated with the EPR spectrum of the Suzuki phase remains unchanged from room temperature to about 20 K. Below this temperature, however, $\Delta H_{p.p.}$ begins to increase, its value at 7 K being 170 Oe, that is, about 25% higher than $\Delta H_{p.p.} = 135$ Oe measured at room temperature.

This increase of $\Delta H_{p.p.}$ can be associated with the critical divergence of $\Delta H_{p.p.}$ expected for insulator magnetic materials whose magnetic ions do not display a simple cubic or a body-centered cubic arrangement.²⁴ This kind of effect has recently been detected in the precipitated phase formed in as-grown $\text{RbCl}:\text{Mn}^{2+}$ crystals²⁵ and it is useful for determining the magnetic phase-transition temperature of a precipitated phase in-

volving magnetic ions. In the region $T > 0.7$ the contribution to $\chi(0, T)$ coming from the Suzuki phase follows a Curie-Weiss law.

The value of the paramagnetic Curie temperature, Θ_S , found for the three samples is essentially the same in view of the experimental uncertainties. Therefore $\Theta_S = -1.5 \pm 0.2$ K characterizes the Suzuki phase formed in as-grown NaCl:Mn²⁺ crystals. From the present work no evidence for a dependence of Θ_S upon precipitate size can be inferred such as has been detected for fine particles of MnF₂.²⁶

The analysis of $\chi(0, T)$ below the phase-transition temperature T_N clearly reveals the existence of loose spins in the microcrystals of the Suzuki phase formed in as-grown NaCl:Mn²⁺ samples. It has been shown that the fraction of the loose spins increases when the Mn²⁺ concentration decreases. This fact can be understood relating such a fraction to the size of the precipitate which depends on the impurity concentration for the same crystal growth conditions as was already pointed out by Toman² and Spengler and Kaiser.⁴ In other words, in the present case the loose spins are thought to arise from nearly free Mn²⁺ spins lying on (or near to) the surface

of the precipitate.

This fact then implies that, in our case, the appearance of loose spins is not only connected to the degree of dilution of a magnetic ion (such as it happens for ZnCr_{2x}Ga_{2-2x}O₄ or Cd_{1-x}Mn_xTe compounds) but rather to surface phenomena which are more significant as far as the size of the precipitate decreases.

Though the present data can be understood assuming that the spins on surface are essentially loose and the size of precipitates^{2,4,10} is of the order of 10³ Å, further work is necessary to check this assumption.

Also for confirming the magnetic phase transition of the Suzuki phase in NaCl:Mn²⁺ by means of another technique, specific-heat measurements have been performed.²⁷ Such measurements support the present results.

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