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Magnetic properties of the Suzuki phase formed in NaCl:Mn^{2+}

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Magnetic susceptibility measurements in the 0.07–4.2-K temperature range as well as electron-paramagnetic-resonance spectroscopy at room temperature have been carried out in order to explore the magnetic properties of a NaCl single crystal doped with Mn^{2+} (~ 900 ppm) containing the Suzuki phase. The magnetic susceptibility follows a Curie-Weiss law in the whole 0.07–4.2-K temperature range, Θ being equal to -1.7 K. This value, which indicates that the effective exchange coupling between Mn^{2+} ions is mainly antiferromagnetic, is not far from the estimations made through the experimental value $\Delta H_{\rm pp} = 135$ G of the peak-to-peak width of the electron-paramagnetic-resonance band at room temperature. The absence of an order temperature T_N, at least down to 0.07 K, implies that Θ / T_N is higher than 24. As the Mn^{2+} ions in the Suzuki phase display a fcc lattice in which the superexchange interactions among next-nearest Mn^{2+} ions are largely avoided, this absence of order is attributed to frustration.

I. INTRODUCTION

Ionic crystals doped with an impurity may give rise to the formation of precipitated phases even at low impurity concentrations. The composition and structure of such precipitates is not necessarily that of a known substance. In fact, in some cases the microcrystals which form the precipitates may exhibit a composition and structure different from any known compound. So such precipitates can be viewed as new materials in spite of the fact that they are formed only inside a well-known ionic matrix.

A good example of this is the so-called Suzuki phase[1,2] obtained in alkali halides doped with some divalent cations such as Cd^{2+} (Refs. 1 and 2), Mg^{2+} (Ref. 3), or Mn^{2+} (Ref. 4).

Figure 1 illustrates the (100) projection of the unit cell of such a phase whose Bravais lattice is fcc. It can be seen on Fig. 1 that in the Suzuki phase the vacancies are not defects but they are ordered as any other component of the perfect lattice.

Quite recently a good effort has been made in order to explore the vibrational[5-7] and optical properties[8] associated to the Suzuki phase. In this way, Raman spectroscopy has proved to be quite useful for identifying the Suzuki phase in as-grown NaCl:Mn^{2+} (Ref. 5) and NaCl:Cd^{2+} (Ref. 6) single crystals because such a phase exhibits first-order Raman peaks in contrast to the host matrix.

Furthermore, in NaCl:Mn^{2+}, where the Suzuki phase involves a luminescent cation the optical excitation spectra[8] reveal the presence of a double excitation peak at 231 nm characteristic of the Suzuki phase. The appearance of such double excitation peak has been related[8] to the existence of superexchange interactions among Mn^{2+} in close positions following the mechanism developed by Tanabe, Moriya, and Sugano.[9]

It is clear that the existence of exchange interactions among the Mn^{2+} ions forming the Suzuki phase should also influence the magnetic susceptibility of such a phase which up to now has not been explored.

Here we report magnetic susceptiblity and electron-paramagnetic-resonance (EPR) measurements on the Suzuki phase formed in NaCl:Mn^{2+}. This is, to our knowledge, the first study reported on the magnetic susceptibility of a *new* precipated phase in an ionic crystal.

The magnetic susceptibility measurements have been performed in the 0.07–4.2-K range. In fact, taking into account that the Mn^{2+}-Mn^{2+} distance between Mn^{2+} ions in closest positions is 7.97 Å (Fig. 1) and the superexchange

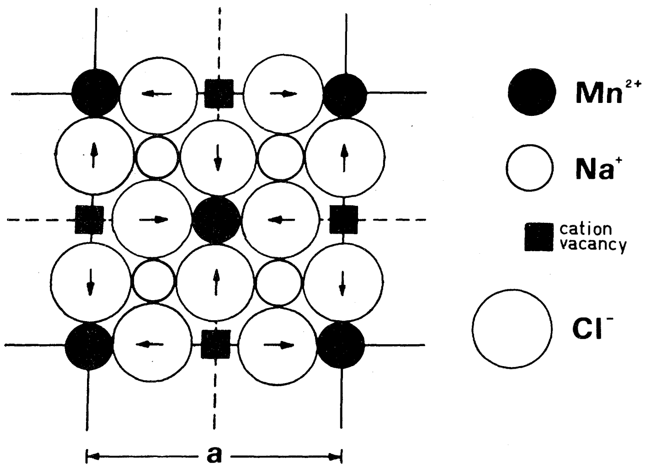

FIG. 1. (100) projection of the unit cell of the Suzuki phase in NaCl:Mn^{2+} which corresponds to the stoichiometry 6 NaCl:$MnCl_2$. The lattice parameter a is just twice that of the NaCl lattice. The distance between a Mn^{2+} ion and a nearest Cl^{-} ion is 2.58 Å (Ref. 4).

path involves two Cl^- ions we expect that the effects of the superexchange interaction on the susceptibility should be very weak and therefore better seen upon decreasing the temperature.

The EPR measurements have been carried out as a complementary tool. These measurements are able to indicate the existence of exchange interactions between Mn^{2+} ions well above the temperature region where the exchange effects manifest themselves in the susceptibility.[10] At the same time such measurements may provide us with a first *estimation* of the absolute value of the Curie-Weiss temperature, provided the structure of the precipitated phase be known[10,11] as it happens in the present case.[4] As it will be shown later, this estimation indicates that the good region of temperatures for good observation of the effects of exchange upon the susceptibility is in fact below liquid-helium temperature (LHeT).

EXPERIMENTAL

A NaCl:Mn^{2+} single crystal was grown by the Czochralski method in an inert atmosphere. The impurity content was measured by atomic absorption spectrophotometry. In the sample where the magnetic susceptibility and EPR measurements were carried out, the Mn^{2+} concentration was about 900 ppm.

The presence of the Suzuki phase in our as-grown sample was ascertained by means of Raman spectroscopy following the previous work by Calleja, Ruiz, Flores, and Velasco[5] and also by inspecting the excitation spectrum corresponding to an emitted light whose wavelength is $\lambda = 633$ nm as described in Ref. 8.

The magnetic susceptibility of our sample was derived from the initial slope of the magnetization curves performed in the 0.07–4.2-K temperature range. For each temperature, the magnetization was measured for the magnetic field varying between 160 and 850 G. The magnetization was determined through an extraction method in the experimental setup of the Centre de Recherches pour les Tres Basses Temperatures at Grenoble, France whose sensitivity allows one to detect at least 50 ppm of Mn^{2+} in the present temperature range. The EPR spectra were taken using a Varian *E*-12 X band spectrometer whose frequency was 9.18 GHz.

RESULTS AND DISCUSSION

As depicted in Fig. 2 the room-temperature EPR spectrum of our sample consists *only* of an exchange-narrowed band whose peak-to-peak width is $\Delta H_{pp} = 135$ G. No other paramagnetic species of Mn^{2+} are detected. When the temperature is decreased down to 120 K the band shape and the value of ΔH_{pp} are not modified.

This exchange-narrowed band can thus be reasonably associated with the presence of the Suzuki phase in our as-grown sample which, as already remarked, was previously verified through Raman and luminescence measurements.

At the same time the present EPR data point out that in our sample the concentration of Mn^{2+} ions dissolved in the NaCl lattice as Mn^{2+}-vacancy dipoles or Mn^{2+} ions with O_h symmetry is negligible compared to that of Mn^{2+} ions forming the Suzuki phase.

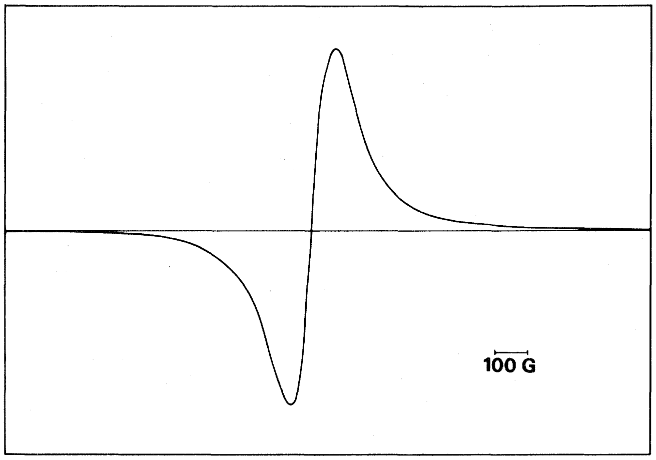

FIG. 2. Room-temperature EPR spectrum of the NaCl:Mn^{2+} sample containing the Suzuki phase. No signals corresponding to "isolated" Mn^{2+} ions or isolated Mn^{2+}-vacancy dipoles are seen.

In the as-grown NaCl:Mn^{2+} crystals, a very similar exchange-narrowed EPR band was first noticed by Forrester and Schneider[12] and also by Watkins,[13] who suggested, however, that it is due to manganese ions aggregated at or near internal boundaries or dislocations.

As the structure of the Suzuki phase is known (Fig. 1) we can derive from it the value of the second moment H_p^2 for a powder which is calculated to be 9.9×10^4 (G).[2] In this calculation we have omitted the $\frac{10}{3}$ factor,[10] a fact which will be justified *a posteriori*. The value of H_p^2 implies that in the absence of exchange effects the EPR line should have $\Delta H_{pp} = 630$ G assuming its shape is Gaussian. As this value is clearly higher than the experimental one $\Delta H_{pp} = 135$ G, the influence of exchange effects on the EPR band of the Suzuki phase is again stressed. Furthermore, following Anderson and Weiss theory[10] and the work by Gulley, Hone, Scalapino, and Silbernagel[11] on several Mn^{2+} salts we estimate an exchange field $H_e = 1250$ G, a value which supports *a posteriori* the neglect of the $\frac{10}{3}$ factor in our calculations.

If we only take into account the effective exchange interaction (written as $J\vec{S}_1\cdot\vec{S}_2$) between two Mn^{2+} ions in closest position, this value of H_e allows one to estimate the absolute value of J through the relation[10,14]

$$H_e^2 = 5.7\left(\frac{J}{g_0\beta}\right)^2 S(S+1) \tag{1}$$

with $S = \frac{5}{2}$ for the present case.

This estimation gives $|J|/k_B = 0.025$ K. Now using this value of J we are able to *estimate* the absolute value of the Curie-Weiss temperature. For this we assume the relation

$$\Theta = J/k_B ZS(S+1)/3 \tag{2}$$

given by the molecular field theory for the case in which only the exchange interaction between Mn^{2+} in closest positions is considered. As in the present case the Mn^{2+} ions in the Suzuki phase describe a fcc lattice; the number of Mn^{2+} ions in closest position to a given one is $Z = 12$. Now taking $S = \frac{5}{2}$ and putting $|J|/k_B = 0.025$ K in Eq. (2) we *estimate* $|\Theta| = 0.9$ K.

Therefore this estimation made using EPR data obtained at room temperature tells us that the suitable region of temperatures for good detection of the influence of exchange in the magnetic susceptibility is below LHeT.

The results of the magnetic susceptibility measurements performed on the same sample in the 0.07–4.2-K range are depicted in Fig. 3. It can be clearly seen in that figure that the magnetic susceptibility follows a Curie-Weiss law $\chi = C/T - \Theta$ in the *whole* 0.07–4.2-K temperature range with $\Theta = -1.7$ K and $C = 7.4\times 10^{-5}$ emu K/g.

This result is thus quite consistent with the presence of the Suzuki phase in our sample and indicates that the effective coupling between Mn^{2+} ions in such a phase is mainly antiferromagnetic as it usually happens in the Mn^{2+} salts. On the other hand, from the experimental value of the Curie constant C we derive a concentration of Mn^{2+} ions forming the Suzuki phase equal to 990 ppm.

As regards the experimental value of $|\Theta|$ we find a reasonable agreement with the previous *estimation* made from the EPR data at room temperature in view of the approximations involved in it.

Besides the evidence of antiferromagnetic coupling in the Suzuki phase precipitates the most significant fact contained in Fig. 3 is the absence of an order temperature T_N at least down to 0.07 K. In this sense there is not seen in Fig. 3 any sign of deviation with respect to the Curie-Weiss law in the region 0.07–0.1 K. These facts clearly mean that the ratio between $|\Theta|$ and T_N should be higher than 24, which is indeed a very large figure.

A reasonable but qualitative explanation of this peculiar behavior can be obtained looking at the crystal structure of the Suzuki phase. In fact, Fig. 1 points out that the Mn^{2+} ions display a fcc lattice as it happens for other Mn^{2+} salts such as MnO, for instance. Nevertheless, in the present case the superexchange interaction among Mn^{2+} ions in next-nearest positions should be much smaller than that among Mn^{2+} ions in nearest positions. This is consistent with the fact that in the Mn^{2+}-Cl^--Cl^--Mn^{2+} superexchange path among Mn^{2+} in next-nearest positions there is a vacancy placed in the middle position which moreover induces an inward relaxation of Cl^- ions towards the closest Mn^{2+} ion. This fact produces a Cl^--Cl^- distance in such a path equal to 6.12 Å while the Mn^{2+}-Mn^{2+} distance is 11.28 Å.

Therefore we can reasonably assume that in the Suzuki phase where the Mn^{2+} ions display a fcc lattice *only* the effective exchange interactions among nearest Mn^{2+} ions are important while the remainder can be neglected. Now it is worth recalling here that this situation avoids the existence of a perfect correlation at 0 K among the spins of magnetic ions.[15] In other words we think it is reasonable to associate the absence of an order temperature for the Suzuki phase (at least down to 0.07 K) to the phenomenon of frustration.

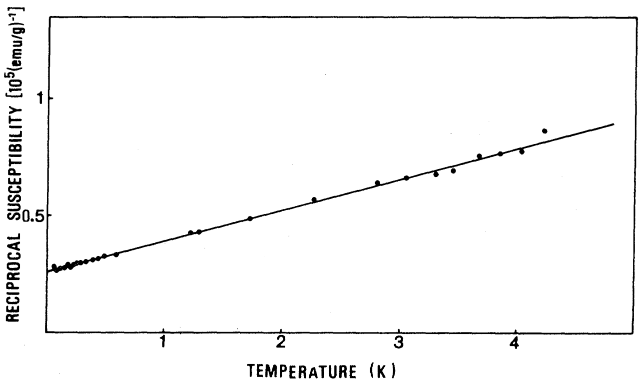

FIG. 3. Plot of the experimental reciprocal susceptibility vs temperature for the $NaCl:Mn^{2+}$ sample containing the Suzuki phase in the temperature range 0.07–4.2 K.

We have also explored the possible influence of the size of microcrystals in the present phenomenon. In this sense we have carried out susceptibility measurements in the 0.07–4.2-K range on an as-grown $NaCl:Mn^{2+}$ crystal containing only 200 ppm of Mn^{2+} and the results concerning the Suzuki phase are essentially the same as those reported for the crystal with ~900 ppm of Mn^{2+}.

Further work along this line is currently under way.

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