J. Phys. C: Solid State Phys. **20** (1987) L421–L424. Printed in the UK

LETTER TO THE EDITOR

Low-temperature specific heat measurements for the Suzuki phase in NaCl : Mn^{2+}: evidence of a magnetic transition

J C Gomez-Sal†, M Moreno†, F Rodríguez†, A Revex‡ and J L Tholence‡
† Departamento de Optica y Estructura de la Materia, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain
‡ Centre de Recherches pour les Tres Basses Temperatures, CNRS, 166 X, 38042 Grenoble Cédex, France

Received 23 April 1987

Abstract. Specific heat measurements for an as-grown NaCl:Mn^{2+} crystal (Mn^{2+} concentration: 17000 ppm) containing the Suzuki phase have been carried out in the 0.1–10 K temperature range. The contribution due to the Suzuki phase shows a very sharp peak at 0.2 K which strongly supports the existence of an antiferromagnetic phase transition. The experimental entropy change associated with such a peak, equal to 16.6 J K^{-1} mol^{-1}, is very close to the molar magnetic entropy expected when $S = \frac{5}{2}$ ions are involved. To our knowledge this is the first time that relevant specific heat data on precipitated phases in insulator materials have been reported.

The formation of precipitated phases is a rather common phenomenon; it can happen when crystals of a *doped* compound are grown. Good examples of this behaviour are found in, for instance, alkali halide crystals doped even with small amounts (less than 1000 ppm) of divalent cations such as Cd^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+}. A review of this field of research can be found in [1].

One of the most interesting aspects of studying precipitated phases is the possibility of forming new materials, although these are placed in a well known host lattice. A good example of this is offered by the so-called Suzuki phase [2] formed in as-grown crystals of NaCl doped with, for instance, $CdCl_2$, $MnCl_2$ or $NiCl_2$ [2–5].

In this way, although the structure of the Suzuki phase precipitates has been well established in these cases, it has not been possible to grow Suzuki-phase single crystals: this phase has only been obtained in form of microcrystals within a NaCl lattice.

The physical properties of the Suzuki phase have received significant attention over recent years [6–10]. This interest of investigators has been encouraged by the simple crystalline structure of the phase (see figure 1). When the Suzuki phase involves a magnetic cation, the ordering of magnetic moments is an attractive point which deserves investigation for the following reason.

(i) The magnetic cations display a FCC lattice, which in the absence of exchange interaction between magnetic cations in next-nearest-neighbour positions would give rise to magnetic topological frustration [7].

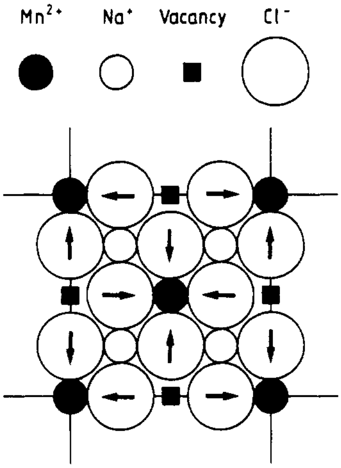

Figure 1. (100) projection of the unit cell of the Suzuki phase in NaCl:Mn^{2+}, which corresponds to the stoichiometry 6 NaCl:$MnCl_2$.

(ii) The distance between magnetic cations in nearest positions, R, is 7.97 Å for the Suzuki phase in NaCl:Mn^{2+}, which is nearly twice that found for $RbMnF_3$ ($T_N = 83$ K). As in the latter compound it has been determined [11] that the exchange energy depends upon R^{-15}, we expect that a magnetic phase transition in the Suzuki phase formed in NaCl:Mn^{2+} may occur at very low temperatures (below about 1 K).

Very recently, magnetic susceptibility experiments carried out on as-grown NaCl:Mn^{2+} crystals containing the Suzuki phase strongly suggest the existence of an antiferromagnetic phase transition at around 0.3 K [12]. In these experiments, however, the phase transition was obscured by the Curie–Weiss-like contribution of loose spins (lying probably on the surface of the precipitate) to the macroscopic susceptibility [13].

Owing to this, one has to investigate the existence of a magnetic phase transition in the Suzuki phase formed in NaCl:Mn^{2+} through specific heat measurements where the contribution of nearly free spins should in principle be less significant.

This technique may be useful for our present aim because the phenomenon occurs below 1 K, i.e., in the temperature region where the phonon contribution from the NaCl host lattice is smallest.

The sample used in the present experiment was taken from an as-grown NaCl:Mn^{2+} crystal obtained by the Czochralski method in an inert atmosphere by Dr E Dieguez and F Abella (Universidad Autónoma, Madrid). The crystal, containing 17 000 ppm of Mn^{2+} (as determined from atomic absorption spectrophotometry), has been used in previous magnetic susceptibility measurements that indicated that 96% of the Mn^{2+} ions formed the bulky Suzuki phase [12, 13].

The specific heat was determined by a heat pulse technique [14]. The sample was glued with Araldite onto a silicon plate sample holder. The heater (a Pt–W strain gauge) was directly glued onto the sample. A doped-silicon thermometer [15] was placed with Apiezon N grease onto the sample holder. The thermal leak to the heat sink (the mixing chamber of a dilution fridge) was ensured by using nylon pins. More details about the specific heat measurements can be found elsewhere [16].

Figure 2 depicts the specific heat measured for both the sample plus addenda and the

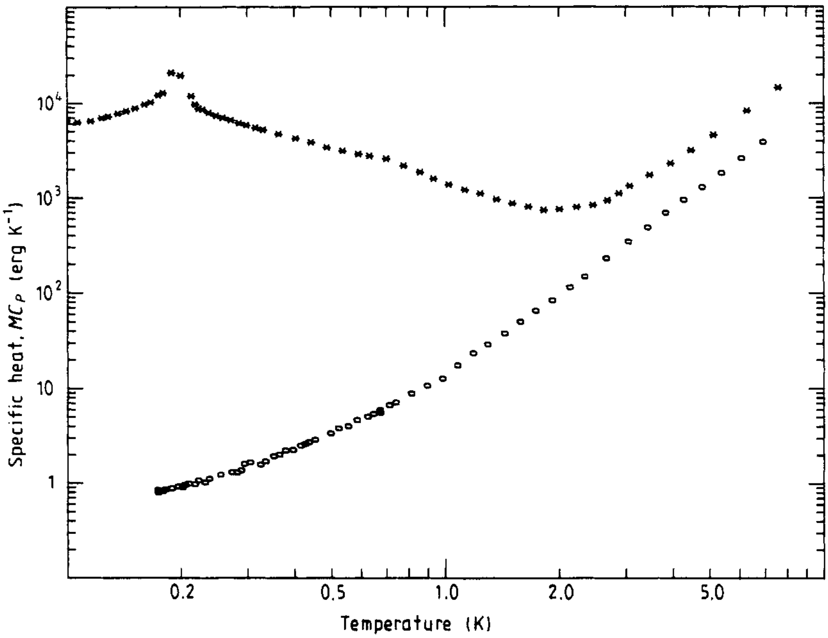

Figure 2. Specific heat versus temperature; addenda + $NaCl:Mn^{2+}$ (*) and addenda alone (□). M is the mass of $NaCl:Mn^{2+}$ (309.4 mg).

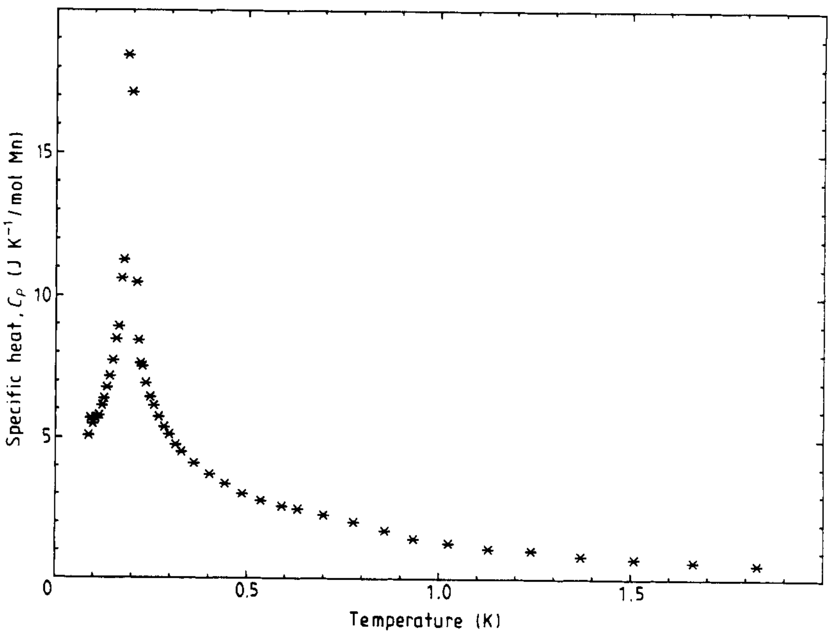

Figure 3. The specific heat of the Suzuki phase versus temperature.

addenda alone in the temperature region 0.1–10 K. It can be seen in the figure that for $T < 1$ K the contribution of the addenda is negligible. On the other hand the difference between the two curves of figure 2 in the 3–10 K temperature region strictly represents the contribution due to NaCl phonons.

From these data, the contribution to the specific heat of the sample arising from the Suzuki-phase precipitates within the NaCl host lattice can easily be derived. This contribution is shown in figure 3. A very sharp peak can be seen in figure 3 at 0.2 K; this is obviously attributable to the existence of a second-order phase transition in the Suzuki phase at that temperature.

The entropy at 2 K derived from the experimental data shown in figure 2 is equal to 16.6 J K^{-1} for one mole of manganese ions forming the Suzuki phase.

This figure is very close to the molar magnetic entropy $S = R \ln (2S + 1)$ for $S = \frac{5}{2}$ (corresponding to Mn^{2+} ions) which is equal to 15.0 J K^{-1}. This strongly supports the assertion that there is a magnetic phase transition for the Suzuki phase formed in $NaCl:Mn^{2+}$.

Because of the sharpness of the anomaly found in the specific heat measurements, we believe that the ordering temperature is now more accurately determined than from previous magnetic susceptibilities where the contributions of loose spins mask the phase transition.

In conclusion, to our knowledge this is the first time that clear evidence of a magnetic phase transition in a precipitated phase has been obtained through specific heat measurements.

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