Systematics in the modulated phases of $(N(CH_3)_4)_2MnCl_4$

1991 J. Phys.: Condens. Matter 3 3387

(http://iopscience.iop.org/0953-8984/3/19/017)

J. Phys.: Condens. Matter 3 (1991) 3387–3391. Printed in the UK

LETTER TO THE EDITOR

Systematics in the modulated phases of $[N(CH_3)_4]_2MnCl_4$

Nozomu Hamaya†‡, Susumu Shimomura†‡ and Yasuhiko Fujii†‡
† Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan
‡ Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan§

Received 27 February 1991

Abstract. X-ray scattering studies of $[N(CH_3)_4]_2MnCl_4$ under pressure reveal strong indications of the existence of several new commensurate phases with long periods. The wave vectors of these phases are found to constitute a set of the Farey-tree series. Structure branching and other features in the observed P–T phase diagram are in good agreement with the predictions of the axial next-nearest-neighbour Ising (ANNNI) model.

A complicated sequence of spatially modulated structures, with parameters such as temperature and pressure, has been observed for a wide variety of materials; examples are CeSb [1], $Ti_{1+x}Al_{3-x}$ [2], and various ferroelectrics [3]. Despite the great diversity of their physical nature, theoretical studies on simple discrete site models have shown that a number of modulated structures are stabilized as a consequence of the competition between interactions that favour different spatial periodicities [4]. Furthermore, theories predict many peculiar properties of the competing-interaction model system: the phase diagram consists of an infinity of commensurate phases [5, 6], the 'Devil's staircase' [5] of the variation curve of the wave vector of the modulation, and the phase transition associated with the formation of phase defects or solitons [6, 7]. Of particular interest is how far the calculated results can describe the structure and behaviour of the real system. So far only a few systems have been experimentally investigated with the purpose of testing these theoretical predictions. In this letter we present an x-ray scattering study of the lock-in transition in tetramethylammonium tetrachloromanganate (TMATC-Mn) under pressure.

TMATC-Mn is a member of the TMATC compounds group having the chemical formula $[N(CH_3)_4]_2XCl_4$ (TMATC-X where X = Mn, Fe, Co, Ni, Zn). They have the same β-K_2SO_4 structure with space group *Pmcn* in their normal (N) phases at high temperatures [8], and exhibit a similar phase transition sequence of the modulated structures characterized by the wave vector of the modulation along the c axis, ζc^*, as a function of temperature and pressure [3]. So far the commensurate (C) phases with $\zeta = \frac{1}{2}, \frac{3}{7}, \frac{2}{5}$ and $\frac{1}{3}$ have been observed, respectively, in TMATC-Mn and -Ni, in -Mn and -Fe, in -Co and -Zn, and in all salts, as well as the incommensurate phases with $\frac{1}{3} < \zeta < \frac{1}{2}$. An interesting feature of the TMATC system is that the interrelation of various phases of different salts can be summarized in a universal P–T phase diagram [9]. A good interpretation of this

§ Present address, to which any correspondence should be sent.

0953-8984/91/193387 + 05 $03.50

universal phase diagram has been provided by theories based on an extended version of the axial next-nearest-neighbour Ising (ANNNI) model [10], the Janssen–Tjon model [11], and the Chen–Walker model [12]. Stimulated by the success of these theories, we decided to begin a detailed experimental study of the transition behaviour of the TMATC system. In this study we primarily concentrate upon the search for higher-order C phases, which are theoretically predicted to exist but have not been observed yet. We chose the Mn salt as a sample because in this salt we can make systematic measurements of ξ over the wide range of $\frac{1}{3} < \zeta < \frac{1}{2}$ [13].

Single crystals, $\sim 1\ \mathrm{mm}^3$ in size, were cleaved from crystals grown from aqueous solution. A sample was mounted in a berylium pressure cell of a type previously described [14] with a mixture of methanol and caster oil as the pressure-transmitting medium. The pressure was varied with an accuracy of ± 0.4 MPa. The sample temperature was controlled with long-term stability of ± 0.05 degree. The x-ray diffraction experiments were performed on a double-axis diffractometer equipped with a one-dimensional position-sensitive detector. The Mo Kα radiation from a rotating anode source operated at 50 kV and 40 mA was monochromatized with a Ge(111) crystal. The transverse resolution measured for the TMATC-Mn 400 reflection was about $0.001\ \mathrm{\AA}^{-1}$ in full width at half maximum (FWHM). To determine the wave vector of the modulation, we used the 400 and 402 fundamental reflections and the satellite reflection at $(4, 0, \zeta)$. Isothermal scans were carried out at various temperatures between 19.0 °C and 24.0 °C. Care was taken to use a virgin crystal for each run so as to minimize distortion of the transition behaviour due to the radiation-damage effect, which we encountered in our previous synchrotron x-ray scattering study [14]; such effect was recognized throughout this study. The a and c lattice parameters were determined at each pressure; for ambient conditions $a = 9.064$ Å, $b = 15.63$ Å and $c = 12.30$ Å.

In figure 1, we show three curves depicting the variation of ζ with increasing pressure at 24.0, 22.0 and 20.0 °C. An important feature of these data is the staircase behaviour of the ζ-curve, which becomes obvious with decreasing temperature. At 24.0 °C (figure 1(a)), as the pressure is raised, the crystal first transforms from the N phase to the IC phase at 36.0 MPa, outside of the range of this figure. The wave vector appears to change smoothly in the IC area. When ζ reaches 0.4317 at 118.9 MPa, it locks discontinuously onto the rational value $\frac{3}{7}$. Above 122.8 MPa, ζ again takes incommensurate values and, finally, two successive lock-in transitions to $\zeta = \frac{2}{5}$ and $\zeta = \frac{1}{3}$ occur. Those three lock-in transitions are accompanied by both the splitting of fundamental Bragg reflections and a pressure hysteresis of about 2 MPa, indicating their being of first order.

At lower temperatures, we observe several steps on the ζ-curves (figures 1(b) and 1(c)). Among these, the steps at $\zeta = \frac{5}{11}, \frac{4}{9}, \frac{7}{16}$ and $\frac{5}{12}$ are indicative of the existence of new high-order C phases with periods $11c$, $9c$, $16c$ and $12c$, respectively. Figure 2(a) shows the pressure dependence of scans of the satellite reflection near the lock-in to $\zeta = \frac{5}{12}$. Comparing the profile for 120.2 MPa with that for 121.2 MPa, we note that the peak located at $\zeta = \frac{5}{12}$ grows at the expense of another peak at the incommensurate position, $\zeta = 0.4200$. It is clear that the lock-in transition to the $\frac{5}{12}$ phase is also of first order. Figure 2(b) shows the diffraction profiles measured at 23.0 °C. In this figure, we observe pronounced peak broadening of the satellite reflection, apparently consisting of two peaks, when it passes across the rational values of $\zeta = \frac{8}{19}$ at 127.7 MPa and $\zeta = \frac{7}{17}$ at 136.3 MPa. The peak broadening at these ζ-values has also been observed at 22.0 °C and 24.0 °C. Although the lock-in behaviour is not evident in these cases, such peak broadening has led us to find the very narrow $\frac{8}{19}$ and $\frac{7}{17}$ C phases. Note in figure 2(b)

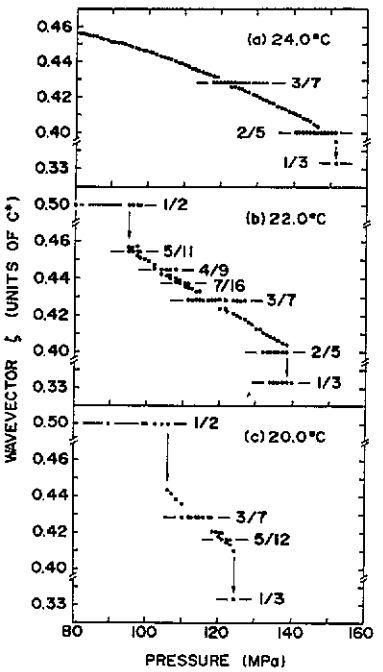

Figure 1. Pressure dependence of the modulation wave vector ζ along the c axis measured at (a) 24.0 °C, (b) 22.0 °C, and (c) 20.0 °C. The variation curve forms an incomplete Devil's staircase.

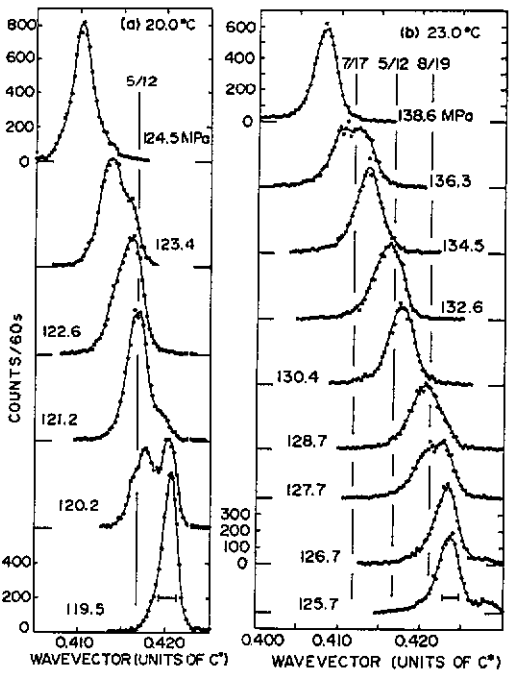

Figure 2. The sequence of scans of the 40ζ satellite reflection with increasing pressure near $\zeta = \frac{5}{12}$: (a) at 20.0 °C, ζ locks discontinuously onto $\frac{5}{12}$; (b) at 23.0 °C, the pronounced peak broadening occurs at $\zeta = \frac{8}{19}$ and $\frac{7}{17}$. Full curves are drawn to guide the eye. A horizontal bar represents the instrumental resolution width.

that the satellite peak near $\zeta = \frac{5}{12}$ shows only subtle broadening, in contrast to the clear lock-in behaviour observed at 20.0 °C (figure 2(a)). This manifests a crucial role of the temperature in determining the stability of the modulated structure of TMATC-Mn.

The results described above were checked on some crystals of different origin. We found, as a result, that the quantity showing sample dependence was only the extent of the C phase coexisting with the IC phase upon the lock-in and lock-out transitions. This seems to be due to the effects of impurities and defects in a crystal. The IC phase, on the other hand, behaves identically within experimental error. Those observations indicate that the stability of the C phase is intrinsic only over the pressure range where it exists as a single phase. As seen in figure 1 the intrinsic widths of the short-period C phases can be easily determined. For the $\frac{5}{12}$ phase, we may estimate its width as being ~1 MPa at 20 °C (see figure 2(a)). However, we were not able to resolve the single-phase pressure ranges of other higher-order C phases with the pressure resolution of ±0.4 MPa at any temperatures studied.

The principal results of the present measurements are summarized in the P–T phase diagram shown in figure 3, where the higher-order C phases are illustrated in a somewhat exaggerated mannner. The following features are noted in this phase diagram:

(i) the long-period phases lie in a region bounded by the short-period $\frac{1}{2}$ and $\frac{1}{3}$ phases (and the N phase);

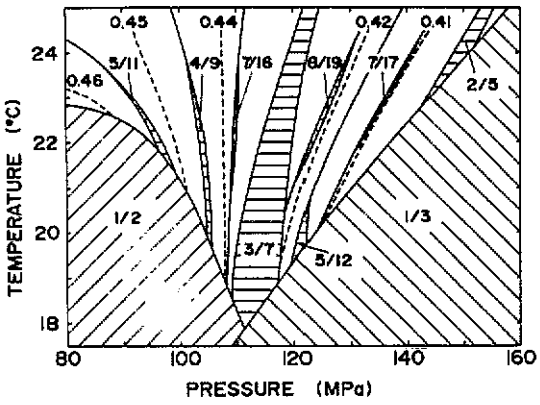

Figure 3. A part of the P–T phase diagram of TMATC-Mn determined in this study; hatched areas: commensurate phases; blank areas: incommensurate phases. Broken curves in the incommensurate area denote the contour of equal wave vector. The higher-order phases are illustrated in a somewhat exaggerated manner. The stability field of the $\frac{3}{7}$ phase reaches the normal phase at $P_i = 164.0$ MPa and $T_i = 37.5$ °C.

(ii) the $\frac{3}{7}$ phase dominating the modulated region becomes progressively narrower with increasing temperature; this phase was found to reach the N phase at $P_i = 164.0$ MPa and $T_i = 37.5$ °C—its width along the P axis, Δ, decreases as $\Delta \propto (T_i - T)^{1.7 \pm 0.1}$;

(iii) the stability field of the modulated phases decreases rapidly with their increasing period;

(iv) the contours of equal wave vector in the IC area appear in a very characteristic pattern, as if they were springing from a certain (P, T) point that is actually hidden by the $\frac{1}{2}$ and $\frac{1}{3}$ phases.

These features are, at least at the qualitative level, consistent with those found in the phase diagrams of the competing-interaction models.

The systematics of the C phases seen in figure 3 is quite simple. We note that the observed rational ζ-values constitute the Farey-tree series [15]. Generating the Farey mediants successively between $\frac{0}{1}$ and $\frac{1}{1}$, we obtain $\frac{1}{2}$ at the first level, $\frac{1}{3}$ at the second, $\frac{2}{5}$ at the third, $\frac{3}{7}$ at the fourth, $\frac{4}{9}$ and $\frac{5}{12}$ at the fifth, and $\frac{5}{11}$, $\frac{7}{16}$, $\frac{8}{19}$ and $\frac{7}{17}$ at the sixth. From this self-similar hierarchy and the interrelations of the C phases in the phase diagram in figure 3, we can derive a simple rule that the first higher-order phase to appear between two neighbouring lower-order phases with $\zeta = n/m$ and n'/m' always has $\zeta = (n + n')/(m + m')$. This is in good agreement with the systematics resulting from structural branching process found by Duxbury and Selke [16] within the mean-field treatment of the ANNNI model. Since the lock-in transitions in TMATC-Mn take place at quite high temperatures, thermal fluctuations must suppress the C phase into the IC phase. Thereby, the branching points are smeared out and the variation curve of ζ necessarily forms an incomplete, instead of complete, Devil's staircase.

In summary, we have presented x-ray scattering results that strongly suggest the existence of higher-order C phases of TMATC-Mn. The systematics of the C phases can be understood in terms of the structural branching process based on the ANNNI model.

References

[1] Rossat-Mignod J, Burlet P, Villain J, Batholin H, Wang-Tcheng-Si, Florence D and Vogt O 1977 *Phys. Rev.* B **16** 440

[2] Loiseau A, van Tendeloo G, Portier R and Ducastelle F 1985 *J. Physique* **46** 595

[3] Cummins H Z 1990 *Phys. Rep.* **185** 211 and references therein
[4] For a review, see
Bak P 1982 *Rep. Prog. Phys.* **45** 587
[5] Aubry S 1978 *Solitons and Condensed Matter Physics* ed A R Bishop and T Schneider (New York: Springer) p 264
[6] Bak P and von Boehm J 1980 *Phys. Rev.* B **21** 5297
[7] Jensen M H and Bak P 1983 *Phys. Rev.* B **27** 6853; 1984 *Phys. Rev.* B **29** 6280
[8] Wiesner J R, Srivastava R C, Kennard C H L, DiVaria M and Lingafelter E C 1967 *Acta Crystallogr.* **23** 565
[9] Shimizu H, Abe H, Kokubo N, Yasuda N, Fujimoto S, Yamaguchi T and Sawada S 1980 *Solid State Commun.* **34** 363
[10] Yamada Y and Hamaya N 1983 *J. Phys. Soc. Japan* **52** 3466
[11] Janssen T 1986 *Ferroelectrics* **66** 203
[12] Chen Z Y and Walker M B 1990 *Phys. Rev. Lett.* **65** 1223
[13] Gesi K and Ozawa K 1984 *J. Phys. Soc. Japan* **53** 627
Hamaya N, Fujii Y, Shimomura S, Kuroiwa Y, Sasaki S and Matsushita T 1988 *Solid State Commun.* **67** 329
[14] Hamaya N, Kuroiwa Y and Fujii Y 1987 *Nucl. Instrum. Methods* B **29** 537
[15] Hardy G H and Wright E M 1954 *An Introduction to the Theory of Numbers* 4th edn (Oxford: Clarendon) p 23
[16] Duxbury P M amd Selke W 1983 *J. Phys. A: Math. Gen.* **16** L741
Selke W and Duxbury P M 1984 *Z. Phys.* B **57** 49