X-ray- and neutron-diffraction measurements on $BaMnF_4$

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X-ray- and neutron-diffraction measurements on powder and single-crystal samples of $BaMnF_4$ have failed to show any evidence for the distortion with wave vector, in reciprocal-lattice units, $\vec{q}=(0.4, 0, 0.5)$ recently reported by Scott, Habbal, and Hidaka. The distorted phase which is observed below 247 K is described by a wave vector $\vec{q}=(\zeta, 0.5, 0.5)$ with ζ incommensurate. There is a small ($\sim 1\%$) increase in the magnitude of ζ as the temperature is lowered to 100 K, and the detailed temperature dependence of ζ is found to be different on heating and on cooling. The low-temperature distortion is characterized by a single wave vector $\vec{q}=(\zeta, 0.5, 0.5)$ rather than by a pair of wave vectors $(\zeta, 0.5, 0.5)$ and $(\zeta, -0.5, 0.5)$.

I. INTRODUCTION

The structural properties of $BaMnF_4$ are unusual and have attracted considerable interest over the past few years, as described in a review by Scott.[1] At about 250 K the material undergoes a phase transition from an orthorhombic structure with space group $A2_1am$ ($a=5.9845$ Å, $b=15.098$ Å, $c=4.2216$ Å at 298 K). The nature of the low-temperature phase was studied in detail by some of the present authors[2] using neutron-diffraction techniques. The results showed that this phase was distorted from the high-temperature phase by a displacement with a wave vector, in reciprocal-lattice units, $\vec{q}=(0.392, 0.5, 0.5)$. This phase was unusual in that it remained incommensurate down to the lowest temperatures and that the wave vector of the distortion did not change with temperature within the resolution of the experiment.

More recently Scott, Habbal, and Hidaka[3] have reported specific-heat measurements, and more briefly some piezoelectric resonance studies, and x-ray-, neutron-, and electron-diffraction measurements on $BaMnF_4$. On the basis of the results from the first two techniques, they conclude that there are two transitions, at 247 and 255 K. The diffraction measurements showed many samples to exhibit a disordered $P2_12_12_1$ structure, which was attributed to a particular type of stacking fault in which the MnF_6 chains are stacked antiparallel along the b axis. Unlike the sample with the usual $A2_1am$ structure, these disordered samples showed no structural phase transition between 77 and 570 K.

Samples with the $A2_1am$ structure were studied by Scott *et al.* below 250 K, and x-ray and electron scattering data showed superlattice reflections at a wave vector $\vec{q}=(0.4, 0, 0.5)$, corresponding to a commensurate unit cell $5a\times b\times 2c$ with respect to the room-temperature cell. However, neutron scattering results showed reflections of the type $\vec{q}=(0.392, 0.5, 0.5)$, in agreement with our earlier work.[2] This led Scott *et al.* to suggest that the neutron scattering arises from magnetic reflections due to short-range spin ordering at 250 K.

This explanation seems unlikely to us in view of our earlier detailed measurements both at the structural transition around 250 K and the magnetic transition at 26 K, but in view of the discrepancy, and the suggestion of Scott *et al.*, that there is another phase between 247 and 255 K which is incommensurate,[4] we have performed further neutron studies and new x-ray-diffraction measurements with improved resolution to elucidate the nature of the structural phase transition in $BaMnF_4$. In Sec. II we describe our results and show that both x-ray- and neutron-diffraction results for our specimens of $BaMnF_4$ are consistent with our earlier measurements and inconsistent with those of Scott *et al.*[3] We then report on measurements of the temperature dependence of the modulation wave vector $\vec{q}$ and on the structure of the incommensurate phase, which is shown to have a form such that in each domain only one of the modes $\vec{q}_1=(0.392, 0.5, 0.5)$ or $q_3=(0.392, -0.5, 0.5)$ describes the wave vector of the modulation (the notation is that of Ref. 2). In Sec. III the results are summarized and discussed.

II. EXPERIMENTAL

The measurements were performed mostly on the same powder and single-crystal specimens used in our earlier study. The single crystals were grown at Bell Laboratories from zone melted materials and several different specimens were studied. One crystal was also grown by similar techniques at the Clarendon Laboratory, Oxford. In our studies no difference was observed in the results obtained from these various specimens.

The experiments were performed using neutron-diffraction techniques at the Brookhaven National Laboratory High-Flux Beam Reactor (HFBR), x-ray powder measurement at Brookhaven, and x-ray single-crystal measurements at Edinburgh University. These latter measurements were performed partly with an Enraf-Nonius CAD-4 four-circle diffractometer and partly with a high-resolution two-circle x-ray spectrometer with an Elliott 15-kW rotating anode generator as the x-ray source and a Si monochromator to provide a very well-collimated incident beam.

Initially a search was made for a modulation wave vector $\vec{q} = (0.4,\ 0,\ 0.5)$ using neutron-diffraction techniques and the x-ray four-circle diffractometer. No evidence was found for any intensity at the corresponding wave-vector transfers using x-ray-diffraction techniques. Initially some scattering was observed in the neutron-diffraction experiment for a wave vector $\vec{Q} = (2.39,\ 0,\ 0.5)$ (Ref. 5) but this was found to arise from a small second crystal in the sample misoriented by about 4° with respect to the main crystal and is not characteristic of a true single crystal.

X-ray-powder-diffraction measurements were made on an an automated General Electric XRD5 diffractometer with Cu $K\alpha$ radiation at a number of temperatures between 20 – 295 K. Below 250 K, several small satellite reflections characteristic of the modulation $\vec{q} = (0.39,\ 0.5,\ 0.5)$ were observed in the low angle region of the pattern in the range $2\theta = 20° - 40°$, with intensities typically of the order of 1% of those of the fundamental peaks. A careful search was made for superlattice peaks characteristic of the (0.4, 0, 0.5) modulation reported by Scott *et al.*, but none could be detected in this region within the experimental sensitivity, which was about 0.02% of the intensity of the fundamental reflections.

The intensity of the x-ray scattering from the strongest incommensurate peak (which actually consists of two overlapping reflections) from the power sample is shown in Fig. 1. This is clearly very similar to the neutron-diffraction results shown in Fig. 12 of Ref. 2, and we therefore conclude that the incommensurate structure with $\vec{q} = (0.392,\ 0.5,\ 0.5)$ scatters both neutrons and x rays in a similar way, and hence that the scattering cannot be of magnetic origin.

A detailed study of the temperature dependence of the satellite wave vector was performed on single crystals with both neutron- and x-ray-diffraction techniques. In both cases measurements were made of two satellite reflections corresponding to $\vec{q} = (\zeta,\ 0.5,\ 0.5)$ and $(-\zeta,\ 0.5,\ 0.5)$ so as to obtain the wave vector ζ as accurately as possible by taking the difference in the reciprocal-lattice positions. The results of typical scans are shown in Figs. 2 and 3. The results for the temperature dependence of the wave vector are summarized in Fig. 4.

It is quite clear from Figs. 3 and 4 that slightly different wave vectors ζ were obtained in the x-ray-diffraction measurements on heating and cooling. On cooling, the wave vector ζ slowly but steadily increases from about 0.390 to 0.394, but on heating ζ remains largely independent of temperature until the temperature is close to T_c. Although the lower-resolution neutron scattering measurements were not performed in such systematic detail, they are broadly consistent with the x-ray results. The width of the incommensurate reflections along ζ (Fig. 3) is also somewhat larger than the experimental resolution as shown by the results for

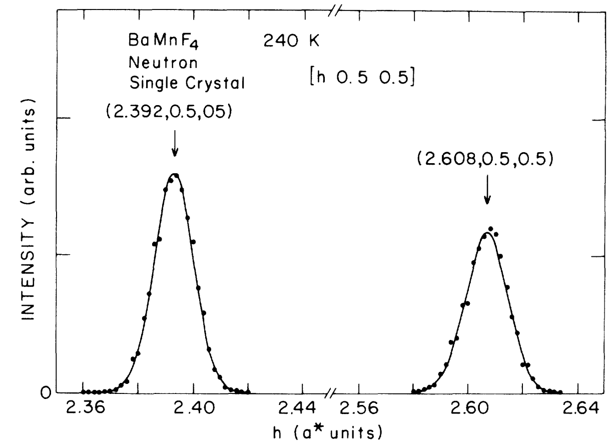

FIG. 2. Neutron scattering from a single crystal of $BaMnF_4$ at 240 K at two satellite positions.

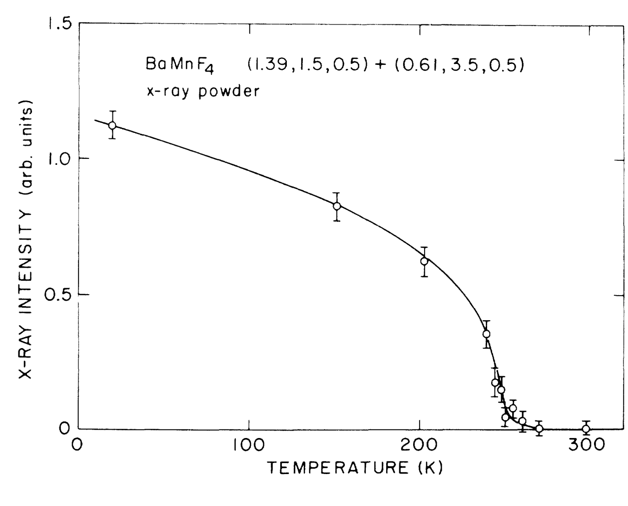

FIG. 1. Temperature dependence of the x-ray intensity of an incommensurate peak consisting of two overlapping satellites in a polycrystalline sample of $BaMnF_4$. The behavior is similar to that shown by neutron diffraction in Fig. 12 of Ref. 2.

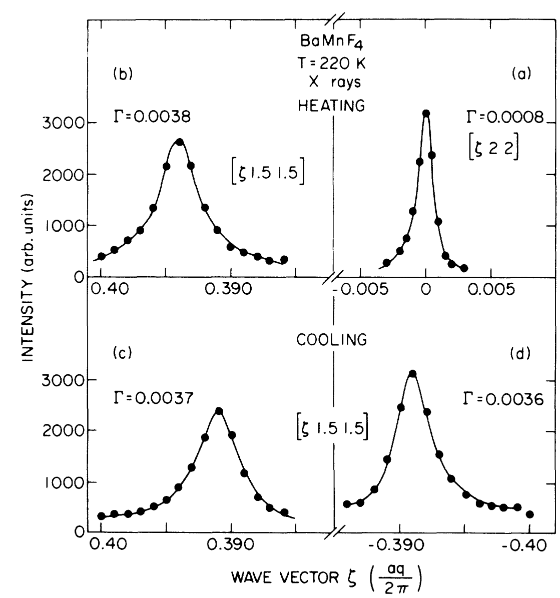

FIG. 3. X-ray scattering from $BaMnF_4$ at $T = 220$ K. (a) Bragg peak showing resolution. (b) Satellite measured on heating. (c) and (d) Satellite measured on cooling. Γ is the full width at half maximum and the vertical scales of parts (a) and (b) are different.

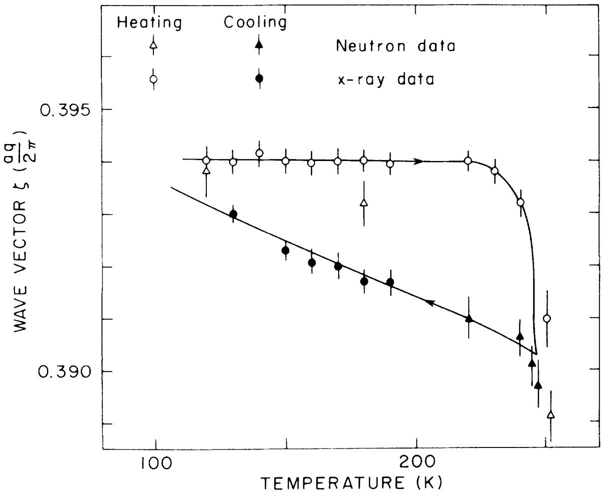

FIG. 4. Temperature dependence of ζ of the incommensurate wave vector (ζ, 0.5, 0.5) in $BaMnF_4$.

a Bragg reflection suggesting that the incommensurate phase is possible pinned by defects.

The nature of the scattering was found to change abruptly at 247 K as revealed by the width of the satellite reflection shown in Fig. 5. No evidence was found for a second phase transition at 255 K.

In our earlier work[2] we showed that the low-temperature phase of $BaMnF_4$ might be either of type (i) in which the displacement ϕ_1 associated with wave vector $\vec{q}_1 = (0.39, 0.5, 0.5)$ was the same as ϕ_2, the displacement associated with $\vec{q}_3 = (0.39, -0.5, 0.5)$, or of type (ii) in which either ϕ_1 or ϕ_2 is zero. These two structures have different types of second-order satellite reflections because domains of type (i) will show reflections for $\vec{q}_1 + \vec{q}_3 = \vec{q}_7 = (0.78, 0, 1)$ as well as for $2\vec{q}_1$ and $2\vec{q}_3$, whereas for type (ii) single scattering processes cannot give rise to scattering for the wave vectors with $\vec{q} = \vec{q}_7$ and only scattering from $2\vec{q}_1$ and $2\vec{q}_3$ would be present.

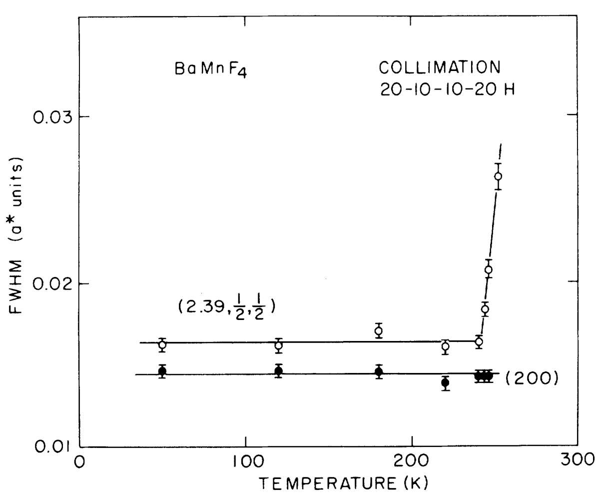

FIG. 5. Neutron scattering measurement of the widths of an incommensurate reflection and a nearby fundamental reflection as a function of temperature.

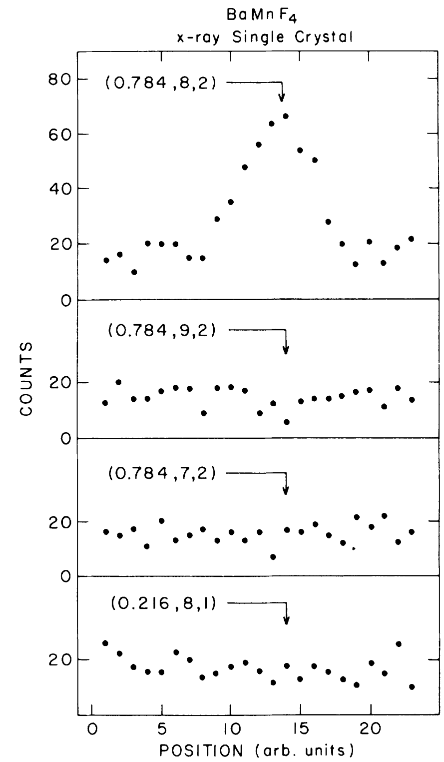

FIG. 6. X-ray scans through possible second-order satellite reflections in $BaMnF_4$.

The scattering at a large number of second-order satellite reflection positions has been measured using the CAD-4 x-ray-diffraction instrument. Some typical scans are illustrated in Fig. 6 and the measured intensities along two lines in reciprocal space are given in Table I. Clearly, there is no intensity for $\vec{Q} = \vec{\tau} + \vec{q}_7$ but there is substantial intensity at the positions $\vec{Q} = \vec{\tau} + 2\vec{q}_1$. ($\tau$ is a reciprocal-lattice vector.) We conclude that the low-temperature structure is of type (ii) in which the distortion is characterized by only a single pair of wave vectors $\pm\vec{q}_1$ in each domain.

III. DISCUSSION AND CONCLUSIONS

Firstly, we have found no evidence of distortions characterized by a wave vector $\vec{q} = (0.4, 0, 0.5)$ as reported by Scott *et al.*[3] The distorted phase observed in our samples is characterized by a wave vector $\vec{q} = (0.39, 0.5, 0.5)$ in both neutron- and x-ray-diffraction measurements, and so this scattering cannot be of magnetic origin as suggested by Scott *et al.*[3] We are unable to account for the discrepancy between the x-ray and neutron results reported by these authors. In addition, we find no evidence of two transitions in our diffraction measurements, in contradiction to the results of Scott *et al.*[3] Of course, there is always the possibility of a distortion with a very different wave vector and amplitude too small to be observed by powder-diffraction techniques, but we consider this to be unlikely.

Secondly, we have measured the temperature dependence

TABLE I. Intensities (arbitrary units) of second-order satellite reflections along the lines (0.216, *k*, *l*) and (0.784, *k*, *l*).

h	*k*	*l*	*I*	*h*	*k*	*l*	*I*
0.216	7	1	625 ± 50	0.216	6	1	32 ± 44
0.216	9	1	215 ± 40	0.216	8	1	−36 ± 40
0.216	11	1	247 ± 42	0.216	10	1	10 ± 38
0.216	13	1	161 ± 36	0.216	12	1	−13 ± 36
0.784	2	2	65 ± 45	0.784	3	2	−32 ± 43
0.784	4	2	137 ± 43	0.784	5	2	−9 ± 41
0.784	6	2	170 ± 42	0.784	7	2	−4 ± 39
0.784	8	2	585 ± 47	0.784	9	2	−85 ± 38
0.784	10	2	61 ± 39	0.784	11	2	−45 ± 34
0.784	12	2	259 ± 38				

of the incommensurate wave vector in $BaMnF_4$. Slightly different results are obtained on heating and cooling as also found[6] in other insulating incommensurate systems.[7] Furthermore, the linewidth of the scattering is larger than the resolution width, showing that the incommensurate phase is not properly periodic. This behavior suggests that the incommensurate phase in $BaMnF_4$ may be pinned by defects. However, the affect of defects in phase transitions is not clearly understood, especially so in incommensurate systems where there is some evidence that they play a more significant role.[7,8] We plan to investigate their role in more detail by studying samples where defects are admitted in a controlled manner.

Thirdly, we have determined the structure of the low-temperature phase to be of type (ii) in which the distortion is described by a single wave vector, either $\vec{q} = (0.39, 0.5, 0.5)$ or $(0.39, -0.5, 0.5)$. As pointed out by Golovko and Levanyuk,[9] the structure of the low-temperature phase is then monoclinic with an *xy* strain. No evidence of this distortion was found in the measurements so its amplitude must be small and is of opposite sign in the different domains, which presumably make up the sample at low temperatures.

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