Phase transitions in $BaMnF_4$: Specific heat

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Specific-heat measurements are reported for $BaMnF_4$ in the temperature region around its incommensurate phase transition. At $T_I = 255.3$ K a mean-field discontinuity of 0.4 cal/mol K is observed upon which is superimposed a power-law divergence of 6.4 ± 0.5 cal/mol. The shape and magnitude of the divergence are compared with the theoretical predictions of Levanyuk, Osipov, Sigov, and Sobyanin; good agreement is observed. A second, smaller C_P anomaly is observed at 247.1 K of integrated magnitude 0.3 ± 0.1 cal/mol. This is compatible with observations by Levstik, Blinc, Kadaba, and Cizikov that some samples exhibit two phase transitions a few degrees apart, as evidenced by two peaks in the *b*- and *c*-axis dielectric constants. The presence of two transitions at 247 and 255 K is also confirmed by piezoelectric resonance measurements. Further evidence that the phase-transition characteristics in this material are sample dependent is provided by x-ray studies, briefly summarized.

I. INTRODUCTION

The history of specific-heat measurements on ferroelectrics near their Curie temperatures has involved controversy almost from the beginning with regard to the presence or absence of true critical (non-meanfield) phenomena. The discovery of cusplike divergences in C_P for triglycine sulfate (TGS) was first made by Strukov in 1964.¹ More recently efforts by this group have shown² that the C_P divergence near T_C in this material is entirely due to defects; it can be removed by proper annealing procedures, leaving only the steplike discontinuity predicted by meanfield theories; and it can be recreated by irradiation. Similarly, it has been known since 1969 that KH₂PO₄ exhibits a C_P anomaly near T_C which can be fitted best to power-law divergence below T_C (with exponent 0.50) and logarithmic divergence above T_C .³ Very recently Courtens has shown⁴ that, as in TGS, the specific-heat anomaly in KDP can be removed entirely by proper sample preparation and anneal. These studies point to defects as the physical mechanism dominating the thermal characteristics near T_C in these materials. Indeed, interest in defect contributions in phase transition dynamics has been growing over the past five years, following the theoretical study by Varma and Halperin.⁵ In the standard text on ferroelectrics. Lines and Glass withhold judgment on the matter of critical effects manifest as C_P divergences near T_C^6 ; but recent work⁷ by Levanyuk, Osipov, Sigov, and Sobyanin provides detailed predictions from a model based upon defectdominated dynamics, and the generally good agreement of the results on TGS, KDP, and the BaMnF₄ data presented in the present paper suggests that ferroelectrics may in general have their thermal properties near T_C controlled by defects at the 10¹⁸-cm⁻³ level.

BaMnF₄ has been studied extensively since 1974 by a variety of techniques. A review emphasizing the phase transition characteristics was published by one of the present authors,⁸ and more recent light scattering studies are detailed in the accompanying paper by Lyons *et al.* ⁹ BaMnF₄ has an unusual phase transition near 255 K inasmuch as it is an improper ferroelectric phase transition in which the low-temperature phase is incommensurate,¹⁰ and the transition appears to be continuous.

II. SPECIFIC-HEAT MEASUREMENTS

In our measurements single crystals of $BaMnF_4$ were studied by means of a commercial scanning calorimeter (Perkin-Elmer DSC II) modified to permit operation below ambient temperatures. Experimental details are outlined in Ref. 11. Typical samples were of order 50-mg mass, and measurements were made with both increasing and decreasing temperatures at heating or cooling rates of 1.25, 5.0, and 10.0 K/min. The samples studied included both pure BaMnF₄ and BaMn_{0.99}Co_{0.01}F₄. The data for these

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samples were nearly identical. A representative trace is shown in Fig. 1. It can be seen from this trace that there are four separate features of qualitative interest: First, there is a large divergence in C_p with a peak at 255.3 K. We show in the following section that this peak is best characterized as a power-law divergence and fits the theory of Levanyuk et al. quantitatively. Second, there is a much smaller peak at 247.1 K. The origin of this peak is due, we believe to a second transition. Third, there is a change in the background value of C_P above T_I in comparison with the value below; the value below T_I is 0.4 cal/mol K greater. Fourth, there is a small but reproducible "shoulder" on the C_P divergence below T_I which peaks at about 253 K. This shoulder is predicted in the theory of Levanyuk et al.⁷

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The magnitude of the integrated area under the C_P anomaly at 255 K is 6.4 ±0.5 cal/mol. This is comparable to the value observed in systems now known to be defect dominated; in TGS the value of the latent heat is typically² 2 cal/mol. The magnitude of the step discontinuity in background value of C_P is smaller in comparison with that measured in other incommensurate transitions; our value of 0.4 cal/mol K is to be compared with 2.3 cal/mol K in K₂SeO₄.¹²

The value of the integrated area under the small peak at 247 K is approximately 0.3 ± 0.1 cal/mol (average of several runs). This value is close to that at T_C (not T_I) in K₂SeO₄, where Aiki *et al.* estimate 0.5 cal/mol. We will return to this point of comparison in the discussion.



FIG. 1. $\Delta C_P(T)$ in BaMnF₄ for increasing temperature. Absolute background value of C_P is not accurately determined. The incommensurate phase transition at 255 K is labeled T_I . The origin of the weaker feature at 247 K is unknown; its label as T_C is only speculative and is discussed in the text. From integration of these data we find $\Delta Q(T_I) = 6.4 \pm 0.6$ cal/mol; $\Delta S(T_I) = 25 \pm 2$ m cal/mol K; $\Delta Q(T_C) = 0.5 \pm 0.2$ cal/mol; $\Delta S(T_C) = 2.0 \pm 0.7$ m cal/mol K.

In Fig. 2. we present a least-squares fit to a powerlaw dependence for C_P below $T_I = 255.3$ K. The philosophy of this choice of fit is that suggested by Levanyuk *et al.*⁷ In their theory the presence of point defects renders first order a ferroelectric phase transition which would intrinsically be continuous. In addition to predicting a power-law dependence, their theory therefore predicts a specific dependence of the form given in Eq. (1), with $T' \neq T_C$:

$$\Delta C_P(T) = A \left(\frac{T' - T}{T'} \right)^{-\tilde{\alpha}} , \qquad (1)$$

where the exponent $\tilde{\alpha}$ is assumed to be nonintrinsic and different from the intrinsic thermodynamic α ; it is of order unity ($\tilde{\alpha} = 2 - \nu$ or $\tilde{\alpha} = 2 - 2\beta$, depending⁷ upon microscopic properties of the defect; here ν and β have their usual meanings). For $T > T_C$ an expression analogous to Eq. (1) is used with T'' replacing T'.

The best least-squares fit shown in Fig. 2 has T' = 281 K and yields a χ^2 value of 38. Note that the difference $T' - T_C = 26$ K is reasonable for weakly first-order phase transistions; for example,¹³ in $Ag_{26}I_{18}W_4O_{16}$ where $T_C = 199$ K, T' = 200.5 K but T'' = 160 K, despite a small (4.1 K) thermal hysteresis. This goodness of fit parameter is better than that obtained using other functional forms, including logarithmic dependences, having the same number of parameters. The agreement could be improved somewhat were it not for the small shoulder at 253 K mentioned above. Such a shoulder has been observed on the low-temperature side of many specificheat studies, but not explained; even in fluids it appears to be characteristic and a source of fitting difficulties in the determination of critical exponent α . See for example the work of Morrison and



FIG. 2. $\Delta C_P(T)$ in BaMnF₄ fitted to Eq. (1). Error bars indicate reproducibility of several runs. Least-squares fit by Handschy. Data for $T < T_I$.

Knobler^{14(a)} or Scheibner *et al.*^{14(b)} We note that such a shoulder is predicted explicitly in the theory of Levanyuk *et al.*⁷ for cases in which the coupling of defect to intrinsic lattice order parameter is of intermediate strength. Unfortunately, however, their theory presents no published formulas to which we can fit our data which incorporate explicitly this nonmonotonic feature; only the asymptotic power-law dependences are given.

Figure 3 presents a power-law fit to the C_P data for BaMnF₄ above T_1 . The χ^2 value is 25, which is acceptable for the number of data points and degrees of freedom; and T'' was found to be ~ 230 K, in analogy with the fitting results below T_I . The value of $\tilde{\alpha}$ for $T > T_I$ was found to be 0.54. However, this value is correlated with the value T'' in the fitting procedure and may therefore be inconsequential. These results may be compared with those of Reese of KDP³: He found a power-law divergence below T_C with critical exponent $\tilde{\alpha} = 0.50$ and a logarithmic divergence above T_C . Of course, intrinsic statistical mechanical theory yields values of α as large as 0.5 only at tricritical points. The idea that BaMnF4 has a slightly first-order transition with hysteresis ~ 0.5 K has been very recently proposed.¹⁵ Whether this first-order character is due to intrinsic fluctuations¹⁶ or to defects is unknown.

Levanyuk *et al.* have made estimates¹⁷ which show that 10^{18} -cm⁻³ defect concentrations may lead to C_P anomalies with integrated latent heat of order 1 cal/mol, as observed here. Since BaMnF₄ is known to be an ionic conductor with absolute conductivities, anisotropies, and activation energies of magnitudes comparable with those known for fluorine vacancy hopping in other systems, it seems reasonable to hypothesize fluorine vacancies as a cause of the latent



FIG. 3. $\Delta C_P(T)$ in BaMnF₄ fitted to power law. Error bars indicate reproducibility of several runs. Data for $T > T_I$. Exponent found to be 0.54.

heat measured here. In the attempt to confirm or disprove this hypothesis we have subjected BaMnF₄ samples to extended heat treatment (24-72 h at 800 K in a sealed furnace containing dry nitrogen). These results¹⁷ showed that T_I could be lowered about 3 K for each 24 h at 800 K, from an initial value of about 251 K for the virgin sample used, to T_C (measured via dielectric techniques) as low as 241 K. We believe that at 800 K, a temperature chosen as well above the onset for isotropic ionic conduction but well below the melting point, fluorines boil off the sample surface; if prolonged, this procedure leads to surface darkening. We note that in samples sealed in He-filled glass vials no discoloration occurred¹⁸; however, in the He-filled system the sample was at a considerable overpressure (≥ 2 atm), which may impede the loss of fluorines from the surface.

If the defect-dominated dynamics described by Levanyuk et al.⁷ are correct as descriptions of the phase transition characteristics in BaMnF₄, two additional independent checks can be made: Specific predictions for the temperature dependences of ultrasonic attenuation exponent and of soft mode linewidth are provided. As shown in Table I, these predictions agree semiquantitatively with experimental results. The soft mode linewidth has been known to exhibit a power-law divergence,¹⁹ as does that in KMnF₃ and SrTiO₃.²⁰⁻²² However, anharmonic lattice dynamics predicts no divergence at all (linewidth approximately proportional to absolute temperature). Levanyuk et al.⁷ have suggested that these divergences, which are sometimes extremely large,^{23, 24} arise from defects. The predicted exponent for the soft mode linewidth from the defect dominated dynamics theory⁷ is 3/2 and does not agree with that observed in BaMnF₄ (0.37) or SrTiO₃(0.20); however, the numerical value of 3/2 quoted from the theory is perhaps inappropriate for the cell-doubling transitions in SrTiO₃ or BaMnF₄ and certainly does not consider the incommensurate characteristics of the latter crystal. In the case of the ultrasonic attenuation, Fritz reported²⁵ usually large and unexplained values of critical exponent. These varied from 2.2 for the longitudinal mode to 3.9 (5.7) for the transverse mode above (below) T_{I} . The prediction from Ref. 7 for ultrasonic attenuation exponent is $2(\gamma - 1) - 5\nu$; for mean-field systems this is 3.3, and for more realistic statistical mechanical models it is 2.7. Thus, the predictions of Ref. 7 are in better agreement with experiment than are other published theories. Fritz suggested that these large (2.2 to 5.7) exponents might arise from the two-dimensional character of intrinsic fluctuations near T_I . The good agreement discussed above suggests an extrinsic (defect) origin; this view has also been expressed by Rehwald.²⁶ Note that the simplest scaling theory predicts an ultrasonic attenuation exponent of unity.²⁷

In summarizing this section, then, we see that the

Quantity	Predicted ^a form	Observed form	Predicted ^a exponent	Intrinsic theories ^b	Observed exponent	Ref.
Specfic heat	Power law ^c	Power law	1/3 to 1	~0.1 ^d	$0.54 \ (T > T_I)$ $\ge 1 \ (T < T_I)$	This work ^e
Ultrasonic attenuation	Power law	Power law	2.7 to 3.3	1.0	2.2 $LA (T < T_I)$ 3.9 $TA (T > T_I)$ 5.7 $TA (T < T_I)$	23
Soft-mode linewidth ^f	Power law	Power law	3/2		0.37	17

TABLE I. Comparison of the phase transition characteristics observed for $BaMnF_4$ with the predictions of the defect dominated dynamical theory of Levanyuk, Osipov, Sigov, and Sobyanin (Ref. 7).

^a Reference 7. ^b Reference 25.

^c Analogous results are predicted by B. M. McCoy and Tai Tsun Wu, Phys. Rev. 176, 631 (1968).

^d Note, however, that effective exponents as large as 0.65 are found at tricritical points: H. T. Sheng and M. B. Salamon, Phys. Rev. B 22, 4401 (1980).

^e We note that in addition to the value $\tilde{\alpha} = 0.50$ measured in KDP by Reese (Ref. 3), Lopez Echarri *et al.* report $\tilde{\alpha} = 0.4$ both above and below T_1 in K₂SeO₄ [A. Lopez Echarri, M. J. Tello, and P. Gili, Solid State Commun. <u>36</u>, 1021 (1980)]. We suggest that their results may also be due to defects.

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specific-heat data on BaMnF₄ are analogous to those in K₂SeO₄, and that they appear to satisfy the defect dominated dynamical theory of Ref. 7, like TGS and KDP. In particular, the phase transition is found to be very slightly first order. This result has recently been obtained independently from birefringence studies²⁸ and is compatible with theoretical predictions.²⁹ However, the primary result, $\tilde{\alpha} \approx 0.5$ is also expected near or at tricritical points even in defect-free materials.

III. ANOMALY AT 247 K

The presence of a small but reproducible anomaly in the specific heat of some BaMnF₄ samples (as shown in Fig. 1) suggest the possibility of a second phase transition about 8 K below T_I . Reports of BaMnF₄ specimens with two transitions have been made before.³⁰ In Ref. 30 Levstik et al. found, via dielectric measurements on the b and c axes, two divergences indicative of phase transitions approximately 4 K apart. However, measurements in the temperature region between the two anomalies were not entirely reproducible; this "middle phase" appeared to be ferroelastic and exhibited fielddependent effects and a hysteresis loop which did not close. A subsequent report³¹ by the same group deleted data for this anomalous sample; and the peculiar effects mentioned above, including the existence of a middle phase, were not pursued elsewhere.



FIG. 4. Piezoelectric resonance frequencies near 1.6 MHz in a sample of $BaMnF_4$ as functions of temperature from 200 to 300 K, showing frequency anomalies near 247 and 255 K; from Ref. 34.



FIG. 5. Piezoelectric resonance frequencies near 8 MHz in a sample of $BaMnF_4$, showing two anomalies near 245 and 257 K; from Ref. 34.

We have independently confirmed³⁴ the presence of a middle phase via piezoelectric resonance techniques, however, with results shown in Figs. 4 and 5. Two samples were employed. That in Fig. 4 yielded indications of phase transitions at 247 and 255 K, in agreement with the specific-heat data of Fig. 1, whereas the second sample (Fig. 5) indicates a slightly wider middle phase, from \sim 245 to \sim 257 K.

IV. X-RAY STUDIES

Extensive x-ray, neutron, and electron scattering data to be reported elsewhere³⁴ have confirmed the sample dependence of the phase transitions in BaMnF₄. Many samples are found to exhibit a particular kind of stacking fault in which the MnF₆ chains are stacked antiparallel along the *b* axis, yielding a disordered D_2^3 space group symmetry rather than the usual ordered C_{2v}^2 structure. These disordered samples exhibit *no* phase transition between 77 and 570 K. This dramatic effect of fluorine octahedron disorder upon the phase transition(s) in BaMnF₄ is not surprising, since fluorine octahedron rotation is considered to be the primary order parameter.

Samples having the $C_{2\nu}^{12}$ space group symmetry at room temperature were studied below T = 250 K in order to determine the space group symmetry of the low-temperature phase. Superlattice reflections were observed at $(0.4, 0, \frac{1}{2})$ in these specimens, corresponding to a C_{2v}^2 space group symmetry and a unit cell $5a \times b \times 2c$ with respect to the $a \times b \times c$ ambient primitive cell. Since these results disagreed with the $(0.392, \frac{1}{2}, \frac{1}{2})$ reflections reported from neutron scattering in Refs. 32 and 33, neutron scattering measurements were made on our samples at both Grenoble Institute Laue-Langevin and the Kyoto Reactor facility. The results agreed with earlier studies at Brookhaven, ^{32, 33} showing that different reflections were observable in the sample with x rays and with neutrons, and thus ruling out the possibility of axis mislabeling. Finally, to double check the results, electron scattering was also performed. The results were in agreement with the x-ray data and suggest to us that the neutron scattering arises from mangetic reflections due to short-range spin ordering at 250 K. Such spin ordering at near ambient temperatures has been independently confirmed by birefringence studies²⁸ and by magnetoelectric effects.

Although these studies are summarized in detail elsewhere,³⁴ we believe that it is important to point out their connection here to the specific-heat results: We have found in the C_P measurements that the structural transition in BaMnF₄ is first order, with $\tilde{\alpha} \approx 0.5$. As discussed above, this result could obtain from intrinsic causes; in particular, if the system at zero pressure and applied electric field is at or very near a tricritical point, as suggested by calculations for high order-parameter dimensionality, $\alpha = 0.5$ is expected in the mean-field approximation. On the other hand, defect theories also predict $\tilde{\alpha} \approx 0.5$. Consequently, it is the independent evidence, through x-ray and electron or neutron scattering, of strong differences among samples, together with the dependence of T_C upon samples' thermal history,¹⁷ leads us to favor the defect interpretation.

The further suggestion of the existence of two phase transitions, at 247 and 255 K, in Figs. 1, 4, and 5 permits a possible explanation of the light scattering results. First we note that distinct anomalies occur in the birefringence data¹⁵ at 241 and 247 K, in addition to the one emphasized¹⁵ at about 251 K. As discussed in the accompanying paper,⁹ there are three distinct temperatures in the BaMnF₄ light scattering data at which something qualitative occurs: At 241 K there is an onset of dynamical "central mode" scattering interpreted as due to phasons,³⁵ as well as peaks in pyroelectric constant and elastic scattering intensity; note that there is a sharp inflection point in the linear dichroism at 241 K as well.¹⁵ At 247 K the intensity of the "central mode" scattering peaks; there is a small anomaly in C_P at this temperature, and a second inflection in linear dichroism.¹⁵ At 255 K the central mode scattering intensity vanishes,⁹ there is a large C_P anomaly, and there is a third inflection in the linear dichroism.¹⁵ All of these effects are therefore consistent, and it is a primary aim of the present manuscript to emphasize that consistency.

We believe that there are still two viable interpretations of the central mode scattering in $BaMnF_4$ between 247 and 255 K. As initially proposed,³⁶ the explanations of relaxation modes of characteristic time 1 ns include phasons or mobile relaxing defects (presumably fluorine vacancies). Similar times have been inferred from infrared, Raman, and dielectric measurements in the incommensurate phases of K_2SeO_4 and $RbH_3(SeO_3)_2$.³⁷⁻³⁹ In the latter case the measurement of dielectric constant as a function of frequency allowed its dispersion to be characterized as satisfying a Debye relaxation with characteristic time 2.0 ns at 0.5 K above the lock-in transition temperature T_C . These times are all comparable with the reciprocal central mode linewidth reported for BaMnF₄ by Bechtle et al. ³⁶ and Lyons et al. ^{40,41} There has been some controversy concerning the Raman activity of phasons in crystals; in this regard it should be noted that BaMnF₄ is ferroelectric both above and below T_I , in contrast to systems such as NaNO₂ or K₂SeO₄.

No comprehensive analysis of the light scattering

data on BaMnF₄ near T_1 has yet emerged, despite the elegant experiments of Lyons *et al.* In contrast to the early model of acoustic phonon-phason coupling assumed in Ref. 27, it appears now that the dominant coupling responsible for the light scattering "central mode" spectra is optic phonon-phason interaction.

Initially the Brillouin spectra of Bechtle and Scott⁴² were explained by a model in which phasons, assumed diffusive,⁴³ played an important role. The transverse acoustic phonons which soften near T = 247 K were assumed to decay into phasons, and the strong dispersion of the transverse acoustic phonons with characteristic relaxation time of order 1 ns was thereby explained. There was no necessary connection between the dynamic central mode reported in these studies and the 1-ns relaxation time, but it was assumed that both arose from phasons. Subsequently, Lyons et al. showed^{40,41} that the dynamical central mode in BaMnF₄ had a width of about 3 GHz and α_{aa} polarization. These facts in themselves require that the approximations used by Bechtle et al. be altered in order to describe the spectra: All of these observations may still be described in the usual formalism, with the spectral distribution function given by

$$S(\omega, T) = \operatorname{Im} G_{ii}^{-1}(\omega) P_i P_i \overline{n}(\omega, T)$$
⁽²⁾

and the Green's function for the response of the system given by



Here the optic mode has frequency ω_0 and damping Γ ; the acoustic mode, ω_A and γ ; and the phason is assumed diffusive with characteristic Debye time $\tau(T)$. However, in the earlier analysis of Bechtle *et al.* it was assumed that $B \ll \alpha$ was a good approximation. This would give off-diagonal scattering polarizability for the central mode and at T_I a width of 0.73 GHz, in contrast with experiment. The actual experimental data require $\alpha \leq B$ in the above formalism; this enables the explanation of the fact that $\alpha_{aa} \gg \alpha_{bb}$, α_{cc} as well, since that is already known⁴⁴ to be true for the soft optic mode [of frequency ω_0 in Eq. (3)].

The observation of a q^2 dependence of central mode linewidth by Lyons *et al.* is *required* by any analysis which assumes that the phasons are diffusive.

Recently Lavrencic and Scott have presented¹⁷ a theory of phasons in BaMnF₄ based upon a Landau-Khalatnikov approach. Their analysis is more specifi-

cally suited to BaMnF₄ than was the earlier phasondiffusion theory of Bhatt and McMillan.⁴³ However, they not only preserve the q^2 dependence of the phason linewidth in their theory (measured experimentally by Lyons *et al.*^{40,41}), they generate a relationship between the temperature dependence of diffusion parameters and the temperature width of stability for the incommensurate phase. Their result for BaMnF₄, using experimental relaxation parameters,³⁶ is that the width of the incommensurate phase should be of order 3 K. This also bears upon the possibility of two transitions a few degrees apart in various specimens.

To summarize this section: Dielectric and specific-heat data for some $BaMnF_4$ samples indicate the presence of two transitions 4 to 8 K apart. If the lower transition is a lock-in transition to a commensurate phase, the central mode light scattering data of Lyons *et al.* would have a simple explanation. The presence of two transitions in the sample studied at

Brookhaven^{32,33} is, however, completely ruled out.³³ X-ray and neutron data show two different sets of instabilities, at $(0.4,0,\frac{1}{2})$ and $(0.392,\frac{1}{2},\frac{1}{2})$, respectively, which may relate to the possibility of two transitions. No x-ray studies have yet shown the presence of a middle phase, however.

V. CONCLUSIONS

The specific heat of single crystals of BaMnF₄ has been measured and shown to exhibit a mean-field discontinuity at $T_I = 255$ K (Ref. 45) plus additional structure, including a power-law divergence with latent heat 6.4 cal/mol, a small shoulder about 2 K below T_I , and a distinct but small anomaly (0.3 cal/mol) at 247 K. The specific-heat data satisfy the predictions of a defect-dominated dynamical theory of Levanyuk *et al.*, which is further confirmed by

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comparison of ultrasonic attenuation and soft-mode linewidth divergences with its predictions. For some specimens dielectric data, specific-heat measurements, light scattering, and x-ray studies suggest that two separate lattice instabilities (and two phase transitions) may be present.⁴⁶ The light scattering data may be explained by a model in which phasons in the incommensurate phase are diffusive and receive their light scattering cross sections via coupling with the soft optic phonons. The lack of temperature dependence of the incommensurate wave vector^{32,33} is still poorly understood, despite a recent theoretical analysis,⁴⁷ and may involve fluorine vacancies.

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