Existence of a Lifshitz Point in Incommensurate $RbH_3(SeO_3)_2$

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The temperature variation of the dielectric constant has been measured in $RbH_3(SeO_3)_2$ at various bias electric fields. The results show a nonlinear variation of the transition temperature between the incommensurate and the commensurate phase with the applied electric field; this is consistent with the existence of a Lifshitz point at the critical field $E_L \approx 49$ kV/cm.

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In incommensurate (I) systems the Lifshitz point (LP) represents a multicritical point in the phase diagram where three phases merge: the high-temperature para (P) phase, the modulated-incommensurate (I) phase, and the commensurate (C) phase.[1,2] So far the LP has been experimentally found in helicoidal magnetic structures[3] and nearly reached in ferroelectric liquid crystals.[4] Recently, it has been shown[5] that such a point could be observed by application of a bias electric field E on those I ferroelectrics which are characterized by a degeneracy parameter $n=4$. This parameter denotes the power of the umklapp term in the free-energy functional[5] and predicts for $n=4$ the doubling of the unit cell at the I-C transition. The reason for the existence of the Lifshitz point in this class of I ferroelectrics is that here the electric field couples to the square of the order parameter[2,6] as in chiral liquid crystals in a magnetic field.[2] The well-known representative of the $n=4$ class is $(NH_4)_2BeF_4$[6,7] where the temperature interval of the I phase has indeed been reduced by a factor of 3 in the highest external field.

$RbH_3(SeO_3)_2$ belongs to the same $n=4$ class. The temperature interval of the I phase is, however, only 1.8 K.[8-10] Connected with the smaller width of the I phase is also the weaker ϵ anomaly near the transition temperature to the C phase. So far the I phase in $RbH_3(SeO_3)_2$ has been studied with dielectric,[11] ultrasonic,[10,12] NMR,[13] EPR,[14] and macroscopic quadrupole-moment measurements.[8] The modulation wave vector $q_I = q_c(1-\nu)$ for $RbD_2(SeO_3)_2$ has been found[15] to vary between $\nu = 0.003$ at T_I and $\nu = 0.0015$ at $T_c = 146$ K for $E=0$.

The Landau free-energy density in the presence of an external electric field E can be, for $RbH_3(SeO_3)_2$, expressed in terms of a complex one-dimensionally modulated order parameter $Q(x)$ and the polarization $P(x)$ along the b axis:

$$f(x) = \frac{\alpha}{2}|Q|^2 + \frac{\beta}{4}|Q|^4 - i\frac{\delta}{2}\left(Q\frac{dQ^*}{dx} - Q^*\frac{dQ}{dx}\right) - \frac{\gamma}{2}(Q^4 + Q^{*4}) + \frac{\kappa}{2}\left|\frac{dQ}{dx}\right|^2 + \zeta P(Q^2 + Q^{*2}) + \frac{P^2}{2\chi_0} - PE. \quad (1)$$

Here, $\alpha = \alpha_0(T - T_0)$ whereas the other parameters are assumed to be temperature independent and positive. By analyzing the functional (1) it has been shown that the P-I transition temperature T_I changes with E as[6]

$$T_I - T_0 = (T_I^0 - T_0)(1 + E^2/E_L^2), \quad (2)$$

where $T_I^0 = T_I(E=0)$ and E_L denotes the critical Lifshitz field which can be expressed in terms of the free-energy parameters $E_L = \delta^2/2\kappa\zeta\chi_0$. As a result of the small width of the I phase it is plausible that the modulation remains always of the plane-wave type so that the I-C transition is of first order[2] for all applied electric fields. In this case the width $T_I - T_c$ exhibits a quadratic dependence on $E_L - E$:

$$T_I - T_c = \frac{T_I^0 - T_0}{1-\eta}\left(1 - \frac{E}{E_L}\right)^2, \quad (3)$$

where $\eta^2 = (2 - 8\bar{\gamma}/\bar{\beta})/3$ and $\bar{\gamma} = \gamma + \zeta^2\chi_0$, $\beta = \beta - 4\zeta^2\chi_0$. In the plane-wave regime we can also calculate the dielectric susceptibility which is given by

$$\epsilon - 1 = \frac{2\zeta\chi_0\alpha_0}{3\bar{\beta}E_L}\left(T_I - T + 3(T_I^0 - T_0)\frac{E^2}{E_L^2}\right). \quad (4)$$

According to the Landau theory the dielectric constant ϵ should thus show a linear variation with temperature in the I phase, with a maximum at T_c. The height $\Delta\epsilon_{max} = \epsilon(T_c) - \epsilon(T >> T_c)$ at T_c is, from expression (4), proportional to $T_I - T_c$ and from Eq. (3) we get $\Delta\epsilon_{max} \propto (E_L - E)^2$. It should be, however, stressed that the above results are only qualitatively correct and that the corrections to the Landau theory would yield nonclassical critical exponents[1] in the vicinity of the LP.

We have measured the dielectric constant ϵ in a $\mathrm{RbH_3(SeO_3)_2}$ crystal along the b axis at the frequency 1 kHz. The presented results were obtained on cooling. The temperature has been stabilized to 0.003 K. In Fig. 1 we present the results for the temperature variation of ϵ at different bias electric fields. In the plot we have determined the I-C transition temperature T_c from the position of the peak or the step in ϵ. In $\mathrm{(NH_4)_2BeF_4}$ T_I was determined from the anomaly of the first derivative at the dielectric constant $d\epsilon/dT$. In view of the rather small value of the dielectric constant no anomaly in the first derivative of the dielectric constant could be observed in $\mathrm{RbH_3(SeO_3)_2}$ at T_I. T_I was, however, determined by ultrasonic[10, 12] and macroscopic electric quadrupole-moment measurements[8] on crystals of the same origin. Ultrasonic measurements show that up to the field 22 kV/cm, T_I is nearly field independent. The experimental data are consistent with the fact that the P-I and P-C transitions are continuous whereas the I-C transition is discontinuous.

Our results for T_c and the results for T_I, as presented in Fig. 2, can be well described with the expressions (2) and (3) by assuming $T_\mathrm{I}^0 - T_0 \approx 0.2$ K, $\eta \approx 0.9$, and $E_\mathrm{L} = 49 \pm 2$ kV/cm. The agreement between the theoretical and experimental E-T phase diagrams is rather good and demonstrates the presence of a Lifshitz point. The fact that the P-I and I-C transition lines merge tangentially in particular excludes the possibility of an interpretation in terms of a triple point.

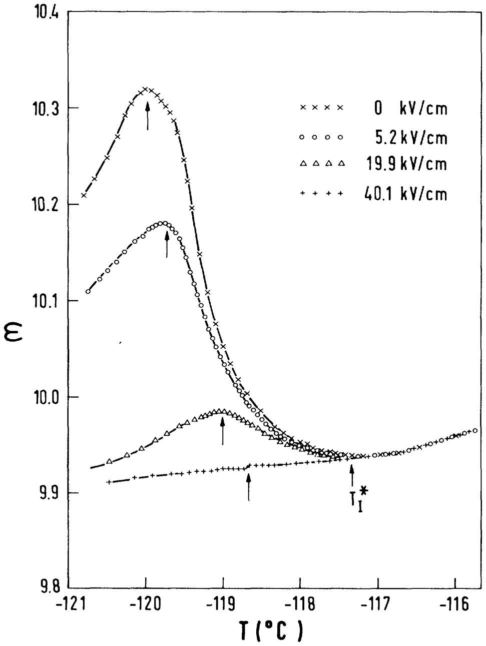

FIG. 1. Dielectric constant of $\mathrm{RbH_3(SeO_3)_2}$ as a function of temperature at various bias electric fields.

In Fig. 2 we plot also the positions of the minima in ϵ, denoted as T_I^*. Our studies of the E-T phase diagram in $\mathrm{(NH_4)_2BeF_4}$ demonstrated that the minimum of $\epsilon(T)$ occurs above T_I at a temperature T_I^* and that the distance $T_\mathrm{I}^* - T_\mathrm{I}$ does not depend on the electric field for $E \ll E_\mathrm{L}$. Nearly constant values of T_I^* at various fields, as shown in Fig. 2, can thus serve as another indication of the weak dependence of T_I on the field E.

The Lifshitz field E_L can be as well determined from the behavior of the maxima of dielectric constant at the I-C transition. In Fig. 3 we plot the field dependence of the dielectric anomaly $\Delta\epsilon_\mathrm{max}$ calculated as a difference between the value $\epsilon(T_c)$ and the background ϵ curve as determined in strong fields at which the dielectric anomaly at T_c vanishes. The variation $\Delta\epsilon_\mathrm{max}(E)$ seems to be consistent with the equation (4). From the dependence $\Delta\epsilon_\mathrm{max} \propto (E - E_\mathrm{L})^2$ we then get $E_\mathrm{L} = 46 \pm 4$ kV/cm which agrees with the previous value within the experimental uncertainty.

The presented experimental results suggest that the LP has indeed been reached in $\mathrm{RbH_3(SeO_3)_2}$, which is thus the first incommensurate crystal having this property in the accessible experimental range. It should be pointed out that the narrow I phase and the rather small Lifshitz field $E_\mathrm{L} \approx 49$ kV/cm are both closely connected with the value of the I part of the modulation wave vector,[12] which is here an order of magnitude smaller than in other incommensurate crystals. Further investigation of $\mathrm{RbH_3(SeO_3)_2}$ thus offers the possibility for the experimental determination of the nonclassical critical behavior in the I systems in the vicinity of the Lifshitz point which has not been studied so far.

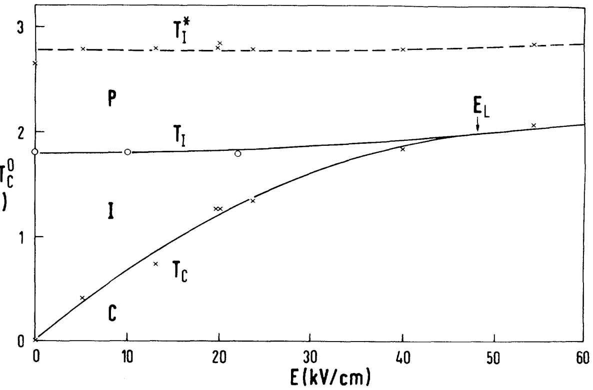

FIG. 2. The E-T phase diagram of a $\mathrm{RbH_3(SeO_3)_2}$ crystal. Crosses represent our dielectric results for T_c and T_I^*. The data for T_I are the ultrasonic results (Refs. 10 and 12). The solid curves represent the theoretical E-T phase diagram according to Eqs. (2) and (3). The P-I and P-C transitions are continuous while the I-C transitions are discontinuous. The three transition lines merge at the Lifshitz point. The dashed curve $T_\mathrm{I}^* = T_\mathrm{I}^*(E)$ serves as a guide to the eye.

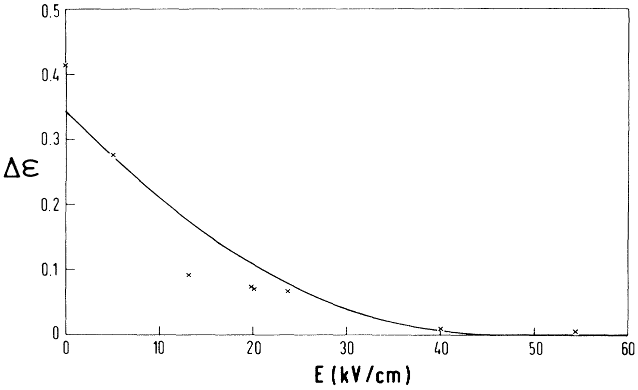

FIG. 3. The magnitude of the peak of dielectric constant $\Delta\epsilon$ at the I-C transition as a function of the bias electric field.

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