Origin of second-harmonic generation in the incommensurate phase of K$_2$SeO$_4$

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We show that a ferroelectric phase transition takes place in the incommensurate phase of the K$_2$SeO$_4$ crystal. The ferroelectric character of the IC phase explains the second-harmonic generation observed in the corresponding temperature range.

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The crystals of the A$_2$BX$_4$ family (about 20 crystals) undergo two successive phase transitions on cooling: an incommensurate (IC) transition at temperature $T_1$ with a modulation vector near the $b/3$ point in the Brillouin zone, and upon further cooling at temperature $T_2$ a commensurate lock-in transition to the triple-period ferroelectric phase with the modulation vector $b/3$. The most striking peculiarity of the K$_2$SeO$_4$ crystal, which belongs to the A$_2$BX$_4$ family, is the second-harmonic generation (SHG) in the IC phase of the same intensity magnitude as that in the $b/3$ phase. Low temperature $b/3$ phases of the A$_2$BX$_4$ type crystals are improper ferroelectrics, and therefore the SHG is a normal manifestation of this feature. However, so far there was never pointed out a plausible reason for the SHG in the IC phase of K$_2$SeO$_4$, nor explained why it takes place not in all the crystals of the A$_2$BX$_4$ family. It is worth noting that the SHG was observed also in the IC phase of quartz by Dolino and Bachheimer (1977) and in the IC phase of the ammonium fluoroberyllate (NH$_4$)$_2$BeF$_4$ by Alexandrov et al. (1978), and both observations also can be explained using the theory developed below. The attempt to explain the SHG in the IC phase of (NH$_4$)$_2$BeF$_4$ was carried out by Golovko and Levanyuk based on the spatial dispersion of the dielectric constant. However, the expected effect appeared to be small, and besides, it is not explained why in such a case the SHG is not observed in all the crystals with the IC phases.

In the present paper we show that within the IC phase of the K$_2$SeO$_4$ crystal, necessarily a transition to the ferroelectric IC phase takes place. We analyze the exact solution in frame of the Landau theory. The physical reason for such a ferroelectric transition is the coupling between the crystal’s polar symmetry vibrational mode $P$ and some displacements of the IC domain walls. We demonstrate that relative displacements of the domain walls in the domainlike IC structure induce polarization along the $z$ direction, and can be viewed as an additional phonon branch of a polar symmetry. This mode is not explicitly introduced in the equations below. It is a component of the IC phase $\phi(x)$ function, and is taken into account implicitly, in the integral form. The coupling of the two modes renormalizes the frequency of the lower mode down to zero within the IC range, which induces a ferroelectric transition.

Structure of the IC modulation of K$_2$SeO$_4$ was defined in the neutron diffraction by Iizumi et al. The thermodynamic potential describing the IC phase of K$_2$SeO$_4$ was detailed studied by Samnikov and Levanyuk. For the two-component order parameter with components $\eta_1 = \eta_0 \cos u$ and $\eta_2 = \eta_0 \sin u$ it can be written as:

$$\Phi = \int dx \left[ \frac{\alpha}{2} \eta_0^2 + \frac{D}{2} \frac{\partial \eta}{\partial x} \frac{\partial \eta}{\partial x} + \frac{\sigma_0}{2} \frac{\partial \eta}{\partial x} + \frac{f}{2} \eta_0^2 \cos 6u + B \eta_0^4 + F \eta_0^6 + \frac{r}{2} P \eta_0^2 \cos 3u + \frac{\lambda_0^{-1}}{2} P^2 + h P^4 - PE \right]$$

where $P$ is polarization vector in the $z$ direction, $E$ is electric field in the $z$ direction. In case of $\sigma = 0$, $D > 0$ this potential would describe a phase transition from the symmetric high-temperature phase to the triple-period commensurate phase at the temperature $\alpha = 0$. For $f < 0$ the equilibrium values of the modulation phase $u = 0, \pi/3, 2\pi/3, \ldots$ (otherwise $\pi/6, 3\pi/6, \ldots$). However, in virtue of the Lifshitz invariant ($\sigma \neq 0$) the phase transition takes place from the high-temperature phase to the IC phase at $\alpha > 0$ with $u = kx + \varphi$ and $k = -\sigma/D$.

Substituting $u = kx + \varphi(R)$ in potential (1) one obtains for the $\varphi$- and $P$- dependent part of potential (1) the following expression:

$$\tilde{\Phi} = \int dx \left[ \frac{D}{2} \eta_0^2 \left( \frac{\partial \tilde{\varphi}}{\partial x} \right)^2 + \frac{f}{2} \eta_0^2 \cos(6kx + 6\varphi) + \frac{r}{2} P \eta_0^2 \cos(3kx + 3\varphi) + \frac{\lambda_0^{-1}}{2} P^2 + h P^4 - PE \right]$$

Minimization of this expression with respect to $\varphi$ gives the equation:

$$D \frac{\partial^2 \varphi}{\partial x^2} + 3f \eta_0^4 \sin(6kx + 6\varphi) + \frac{3r}{2} P \eta_0 \sin(3kx + 3\varphi) = 0$$

After single integration over $x$ and taking for the integration constant the form $|f| \eta_0^2 (1 + c)$ one obtains:

$$\frac{\partial u}{\partial x} = \sqrt{|f| D \eta_0^2} \sqrt{1 + c - \cos 6u + \frac{r P}{|f| \eta_0^2} \cos 3u}$$

where $u = kx + \varphi$. The integration constant $c$, as well as the polarization vector $P$, can be defined via minimization of the potential with respect to these parameters after substituting the solution of Eq. (3) in the potential (2). Prior to considering the ferroelectric transition in this system let us discuss the solutions of Eq. (3) for
FIG. 1: a) Coordinate dependence of the IC modulation phase for different temperatures. The curves I, II, III represent various stages of evolving of the domainlike modulation on cooling: curve I, \( \varphi_0^2 = 0.21, c = 0.138 \); II, \( \varphi_0^2 = 0.23, c = 0.010095 \); and III, \( \varphi_0^2 = 0.2326288, c = 9 \times 10^{-9} \) (the last is very close in \( \varphi_0 \) to the lock-in phase amplitude \( \eta_0^2 \)). The coordinate \( x \) is given in multiples of the lattice parameter. The height of each step on the curves is equal to \( \pi/3 \). Each domain (plateau) has nonzero polarization vector in the \( z \) direction. However, the neighboring plateaus are polarized in opposite directions, providing crystal’s zero integral polarization. b) Transformation of the curves I, II, III induced by the electric field, applied in the \( z \) direction. The effect of the electric field \( E \) comes to the increasing of the plateaus’ areas if the polarization vector is in the direction of \( E \), and to the reduction of those otherwise. The height of each step remains \( \pi/3 \). Such a transformation should take place spontaneously, without an external field.

the case of \( P = 0 \). The solution to this kind of equations for the IC structures was analyzed in the pioneer work by Dzyaloshinskii (it was also detailed studied by Golovko), and for Eq. (3), it has the form:

\[
\varphi(x) + kx = \frac{1}{3} \text{am}(3\sqrt{|f|/D} \eta_0 \sqrt{c} x, -\frac{2}{c}),
\]

where \( \text{am} \) is the elliptic amplitude function and \( k \) is the IC vector at the temperature of the IC transition.

(In the present paper the notations of the Wolfram Research, “Mathematica” program for the elliptic functions are used.) Substituting solution (4) in the potential (2) and minimizing over the parameter \( c \) one obtains:

\[
2\sqrt{|f|/D} \eta_0 \sqrt{c} E(-\frac{2}{c}) = \pi k;
\]

\( E \) is the complete elliptic integral of the second kind, which has the asymptotic

\[
\sqrt{c} E(-\frac{2}{c}) \sim \sqrt{2}(1 - \frac{c}{4} \ln c) \text{ for } c \to 0.
\]

Eq. (5a) can be numerically solved with respect to \( c \) for given coefficients \( f, D, k, \eta_0 \), and one obtains that the parameter \( c \) monotonously decreases from \( +\infty \) at \( \eta_0 = 0 \) (i.e., at the IC transition \( T_i \)) down to \( c = 0 \) at the continuous lock-in transition \( T_c \). As it follows from Eq. (5a), at the lock-in transition point the IC amplitude is tending to

\[
\eta_0^2 \to \eta_0^* \sim \frac{\sqrt{2}\pi k}{4} \sqrt{D/|f|} \text{ with } c \to 0,
\]

which gives that \( k \sim \eta_0^* \), if the remaining coefficients are of the same order of magnitude.

In Fig. 1(a) the solutions given by Eq. (4) for \( k = 2\pi/30, D/|f| = 1 \) and \( P = 0 \) for the three values of the IC amplitude are plotted. At the IC transition \( T_i \) the corresponding graph must look like a straight line with slope \( k \) (\( \varphi = \text{const}, \) i.e., sinusoidal modulation), and on cooling it acquires the domain-like features. Due to the symmetry, each point \( x \) on the curves of Fig. 1(a) is associated with a nonzero polarization, which is spatially distributed as \( P \sim \eta_0^* \cos(3kx + 3\varphi) \) with zero-integral effect. Meanwhile, each domain there has a nonzero-integral polarization. In the areas of any of two neighboring domains \( \varphi + kx \approx n\pi/3 \) and \( \varphi + kx \approx (n + 1)\pi/3 \) respectively, giving rise to the \( P \)-s of opposite signs.

In Fig. 1(b) the transformation of the curves of Fig. 1(a) under the applied electric field \( E \) is shown. The field \( E \) is taken into account via replacing in Eq. (3) of the polarization vector \( P \) by \( P = \chi E \). An identical transformation of the domains takes place in the presence of nonzero polarization \( P \) in crystal (when \( E = 0 \)). Corresponding solutions were found both analytically and numerically (using the ”Mathematica” software) with the same result. Note that the integral polarization vector contributed by the nonequal domains in Fig. 1(b) is not zero.

Now we show, that the above described transformation of the domain structure from that shown in Fig. 1(a) to Fig. 1(b) takes place spontaneously, i.e., without applying an external electric field. In other words, there takes place a ferroelectric phase transition inside the IC phase. Let us calculate the dielectric susceptibility of the crystal in the IC phase:

\[
\chi = \frac{\partial P}{\partial E} = \left( \frac{\partial^2 \Phi}{\partial P^2} \right)^{-1}{\bigg|}_{P=0}
\]
Differentiation of potential (2) gives:

\[
\left( \frac{\partial^2 \tilde{\Phi}}{\partial P^2} \right)_{P=0} = \chi_0^{-1} - \frac{3 \eta_0^2}{2t} \int_0^t \sin 3u \left( \frac{\partial u}{\partial P} \right)_{P=0} dx, \tag{6}
\]

\( t = 2\pi/q \) is the IC period, given by Eq. (10) below. In order to calculate the derivative \( (\partial u/\partial P)_{P=0} \), we introduce notation

\[
\mathcal{F}(u, P) = \int_0^u \frac{dv}{\sqrt{1 + c - \cos 6v + \frac{P}{f(\eta_0^2)}} \cos 3v}.
\]

Integration of Eq. (3) gives in this notation, \( \mathcal{F}(u, P) - \sqrt{|f|/D\eta_0^2} x = 0 \), from which follows that \( \partial \mathcal{F}/\partial P + (\partial \mathcal{F}/\partial u) \partial u/\partial P = 0 \). The latter allows one to calculate the derivative \( (\partial u/\partial P)_{P=0} \) via calculation of the corresponding derivatives of the function \( \mathcal{F} \) in the integral form (see the Appendix). After substituting of the calculated derivative in Eq. (6), one obtains:

\[
\left( \frac{\partial^2 \tilde{\Phi}}{\partial P^2} \right)_{P=0} = \chi_0^{-1} - \frac{3 \sqrt{|f|} r^2}{4t|f|^2 \eta_0^2 c} \int_0^{2r/3} \frac{\sin 3u du}{\sqrt{1 + c - \cos 6u}} = \\
\chi_0^{-1} - \frac{\pi \sqrt{|f|} r^2}{4t \eta_0^2 |f|^2 c^2} \text{F}_2(\frac{1}{2}, \frac{3}{2}, 2, -\frac{2}{c}) \tag{7}
\]

where \( \text{F}_2(1/2, 3/2, 2, -2/c) \) is a hypergeometric function. This hypergeometric function has the asymptotic

\[
\text{F}_2\left(\frac{1}{2}, \frac{3}{2}, 2, -\frac{2}{c}\right) \approx \frac{\sqrt{8c}}{\pi} \text{ for } c \to 0,
\]

which well fits the function in all the range \( 0 < c < 1 \), i.e., not only at \( c \to 0 \). As one can see from Eq. (10), the IC period has an asymptotic: \( c \to 0, \quad t \sim |\ln c|/\eta_0^2 \) (as shown below, on approaching the lock-in temperature \( T_e \) the coefficient \( c \) is tending to zero as \( c|\ln c| \sim |T - T_e| \).

So, for the susceptibility \( \chi \) one obtains:

\[
\chi^{-1} = \chi_0^{-1} - \frac{\pi r^2}{16 |f| c K} \approx \chi_0^{-1} - \frac{r^2}{|f| c |\ln c|} \tag{8}
\]

and the stability coefficient \( \chi^{-1} \) necessarily vanishes (since the \( c \)-dependent term in Eq. (8) is negative and diverging with \( c \to 0 \), inducing ferroelectric phase transition at the temperature \( \chi^{-1} = 0 \)). A loss of stability necessarily takes place even for the case of large \( \chi_0^{-1} \) (i.e., even for a not soft polar mode of the high temperature phase), and it is expected in the medium temperature range of the IC phase (\( c \lesssim 0.1 \)).

However, some alternative situations are possible near the loss of stability \( \chi^{-1} = 0 \). As it follows from Eq. (3), the polarization \( P \) which appears below the transition should be sufficiently small:

\[
P \approx c \eta_0^3 |f|/r \tag{9}
\]

Otherwise, the expression under the root in Eq. (3) takes negative values for some \( u \), what means that the crystal does not fall within the IC phase, but within the commensurate lock-in phase instead, skipping the ferroelectric IC phase. In terms of Fig. 1(b), it is equivalent to the infinite increasing of the one domain’s size, which covers all of the crystal area. The right hand side of Eq. (9) is very small, since \( \eta_0^3 \) in Eq. (9) is a small parameter, and \( c \) tends to zero in the low-temperature range of the IC phase (see also below). In the case of a first-order ferroelectric phase transition giving rise to a large \( P \) (in Landau theory, it means a negative fourth-order term in the potential’s \( P \)- expansion), inequality (9) does not hold, and the transition transfers the crystal directly to the lock-in phase, skipping the ferroelectric IC phase. Even for some order-disorder transitions, which are very close to the second-order type (the polarization vector \( P \) below the order-disorder transitions is larger, due to the small Curie constant compared to that for the displacement type) the expected ferroelectric transition is more likely to turn into the transition to the lock-in phase, skipping the ferroelectric IC phase. Note that among the crystals of the \( A_2BX_4 \) family only \( K_2SeO_4 \) is of a displacement type, and therefore this crystal the ferroelectric phase transition (from the IC to the ferroelectric IC phase) can be considered as a most likely. In other words, the IC structure of \( K_2SeO_4 \) becomes ferroelectric with the modulation, spatially distributed like that in Fig. 1(b). One should expect that the ferroelectric transition takes place in the beginning of the domainlike modulation formation, i.e., at temperatures near the curve I in Fig. 1(a), when the \( c \) coefficient falls below unity.

As it follows from Eqs. (5a, 5b), for estimates of inequality (9), the asymptotic of the parameter \( c \to 0 \) can be used:

\[
c \ln c \approx 8 \eta_0^2 \eta_0^2 \approx 16 a(T_e - T) \tag{9}
\]

near the lock-in point we presented \( \eta_0 - \eta_0^2 \approx a(T_e - T) \), where \( a \) is some constant. So, Eq. (9) can be presented as \( P \leq 16a(T_e - T) \eta_0^2 |f|/r \), when \( T \to T_e \) (we neglected a logarithmically diverging term \( \ln c \), which does not change order of magnitude of the estimated values, since, as discussed below, \( |T_e - T| \) can not be sufficiently small for it).

For obtaining of the inharmonic fourth order term in the \( P \) expansion of the potential one should calculate the derivative \( \left( \frac{\partial^4 \tilde{\Phi}}{\partial P^4} \right)_{P=0} \). We shall introduce here only the result of this calculation. In addition to the \( hP^4 \) term in Eq. (2), one obtains a negative, strongly diverging as \( c^{-3} \) with \( c \to 0 \) term. If the sum of the inharmonic \( P^4 \) terms becomes negative earlier than \( \chi^{-1} = 0 \), then takes place a first-order transition. The latter makes more probable the first order transition, even if the coefficient \( h > 0 \) is not small.

Now we shall discuss some features of the IC phase for \( P = 0 \) case in order to compare it with behavior
of the ferroelectric IC phase. To study the temperature evolving of the ferroelectric IC structure upon cooling one should minimize potential (2) also over the IC amplitude \( \eta_0 \). However, we imply in the present paper only increasing of the IC amplitude \( \eta_0 \) upon cooling, and do not discuss the character of the lock-in transition.

First we discuss some structure peculiarities of the non-ferroelectric IC phase of K\(_2\)SeO\(_4\). The length of each plateau in Fig. 1(a) is six times shorter than the IC wavelength \( 2\pi/q \), where \( q \) is the IC wavevector [\( q \) is equal to the average slope of the given curve in Fig. 1(a)]. From this geometrical fact it follows, that the IC modulation argument \( u = kx + \varphi \) can be presented as \( u = qx + \theta(x) \), where \( \theta(x) \) is a periodic function with period \( 2\pi/6q \). As it follows from Eq. (4), roughly \( \theta(x) \) can be approximated by \( \sin 6qx \). The IC satellite reflections observed in the X-ray diffraction are induced by the Fourier-components by \( \sin \frac{1}{3} \theta \) in the points \( b \). Points \( b \) are increasing of the IC amplitude \( \eta_0 \) upon cooling, and one should minimize potential (2) also over the IC amplitude \( \eta_0 \).

The IC period increases on cooling towards the lock-in temperature \( T_c \). To study the temperature \( T \) can approach the lock-in temperature \( T_c \) not closer than the temperature fluctuation \( \sqrt{\langle (\Delta T)^2 \rangle} \), i.e.,

\[
|T - T_c| > \sqrt{\langle (\Delta T)^2 \rangle} \quad \text{and} \quad \langle (\Delta T)^2 \rangle = \frac{T^2}{Vc_v},
\]

where \( V \) is the crystal volume and \( c_v \) is the heat capacity. So, for any crystal of a finite size (\( V \sim 10^3 a^3 \)), the period \( t \) can increase only about 10 times compared to \( 2\pi/k \), in virtue of the logarithmical character of the divergence (it is also confirmed by our numerical simulations). Besides, in the real experiment the temperature \( T \) can not approach the lock-in temperature \( T_c \), even closer than the instrumental temperature resolution \( \Delta T \sim 10^{-3} - 10^{-4} K \), which does not allow to observe any diverging IC period, and the lock-in transition always should be observed as a discontinuous phase transition with jump in the wavevector \( q \) down to \( q = 0 \).

For calculation of the ferroelectric IC modulation's period [the \( x \)-length of the six neighboring domains in Fig. 1(b)], one should integrate Eq. (3) from \( u = 0 \) through \( u = 2\pi \), which gives:

\[
t = 3 \sqrt{\frac{D}{|f|}} \int_0^{\pi/6} \frac{du}{\eta_0^2 \sqrt{1 + c - \cos 6u + \frac{2P}{|f| \eta_0^3} \cos 3u}} \approx \int_0^{\pi/6} \frac{du}{\eta_0^2 \sqrt{1 + c - \cos 6u}} \quad (11)
\]

\[
-\frac{8i\sqrt{D}}{\eta_0^2 \sqrt{|f|c}} \ln \left[ F \left( \frac{i\sqrt{c}}{2}, \frac{32}{c\Delta c} \right) + F \left( \frac{i\sqrt{\Delta c}}{\sqrt{8}} - \frac{32}{c\Delta c} \right) \right] \quad (12)
\]

where \( F \) is the elliptic integral, and \( \Delta c = c - rP/(|f|\eta_0^3) \), i.e., the condition \( \Delta c > 0 \) coincides with Eq. (9), and therefore it always holds in the IC phase. The parameter \( \Delta c \) decreases down to zero with increasing of the polarization vector \( P \) on cooling. Integral (11) was calculated exactly, and after being simplified to the form of Eq. (12) for \( \Delta c \ll c < 1 \). The first term in Eq. (12), which gives the size of the larger domains in Fig. 1(b), is diverging with \( \Delta c \to 0 \) as \( \sim |\ln \Delta c| \). Meanwhile, the size of the smaller domains is given by the second term in Eq. (12), and it is always finite, though it also increases with cooling.

Summarizing, we showed that in the IC phase of the K\(_2\)SeO\(_4\) crystal takes place ferroelectric phase transition, which explains the SHG in the IC phase of this crystal. Formation of the ferroelectric IC phase is most likely near the displacement-type phase transitions, though it can occur also in those of the order-disorder type. The IC period increases on cooling towards the lock-in temperature \( T_c \) as \( |\ln(T - T_c)| \), though the size of the domains, polarized opposite to the prevailing polarization, remains finite.

**APPENDIX: CALCULATION OF \( \partial u/\partial P \) \(_{P=0}\)**

In order to calculate the derivative \( \partial u/\partial P \) \(_{P=0}\) one should calculate the corresponding derivatives of the
function $F(u, P)$. So one obtains

$$\left(\frac{\partial F}{\partial u}\right)_{P=0} = \frac{1}{\sqrt{1 + c - \cos 6u}}$$

and

$$\left(\frac{\partial F}{\partial P}\right)_{P=0} = -\frac{r}{2|f|\eta_0^3} \int_0^u \frac{\cos 3v \, dv}{(1 + c - \cos 6v)^{3/2}} = \frac{r}{6c|f|\eta_0^3} \frac{\sin 3u}{\sqrt{1 + c - \cos 6u}}.$$

We took into account that for the equilibrium value of $c$, the condition $c(P) = c(-P)$ holds, from which follows that $(\partial c/\partial P)_{P=0} = 0$. Similarly $(\partial \eta_0/\partial P)_{P=0}$ is also equal to zero. So, one obtains:

$$\left(\frac{\partial u}{\partial P}\right)_{P=0} = -\frac{\left(\frac{\partial F}{\partial P}\right)_{P=0}}{\left(\frac{\partial F}{\partial u}\right)_{P=0}} = \frac{r}{6c|f|\eta_0^3} \sin 3u.$$

For integration over $x$ in Eq. (6), the following relations are also used:

$$\int_0^t dx = \int_0^{2\pi} \left(\frac{\partial u}{\partial x}\right)^{-1} du = \frac{3\sqrt{D}}{\sqrt{|f|\eta_0^2}} \int_0^{2\pi/3} \frac{du}{\sqrt{1 + c - \cos 6u}}.$$

where we used the right hand side of Eq. (3) for $(\partial u/\partial x)$ at $P = 0$.

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