Generation of the optical second harmonic in noncommensurate phases of crystals

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Experimental investigations of the generation of the second harmonic have revealed an asymmetry in the nonlinear-susceptibility tensor of the noncommensurate phase of the $(NH_4)_2BeF_4$ crystal. This effect is attributed to spatial modulation along the *a* axis.

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The method of second-harmonic generation (SHG) makes it possible to ascertain with great accuracy the presence or absence of a symmetry center in a crystal, and is therefore extensively used in the study of ferroelectric phase transitions.[1]

Recently, so-called noncommensurate phases have been observed in a number of crystals between the ferroelectric and paraelectric phases. We report here a study of SHG in the noncommensurate phase of single crystals of ammonium flouoroberylate $(NH_4)_2BeF_4$). The SHG exists in the temperature interval from $T_c = 175$ K to $T_i = 185$ K. The modulation of the structure is parallel to the *a* axis of the crystal. It was suggested in[2] that the space groups of the noncommensurate and ferroelectric phases coincide, and that there is no macroscopic polarization because it is cancelled out over a wavelength that is a multiple of the modulation wave.

The experiment was performed on oriented single crystals, by procedure described in[3]. It was observed that when the exciting laser radiation ($\lambda = 1.06$ μm) propagates along the *b* and *c* axes in the noncommensurate phase all those (and only those) components of nonlinear dielectric susceptibility of second order d_{ijl} which corresponds to the symmetry of the ferroelectric phase have nonzero values. Their appearance in the noncommensurate phase is due to the fact that the local value of the polarization differs from zero in any section dx perpendicular to the modulation axis *a*.

In the commensurate phases the tensor d_{ijl} is symmetric with respect to permutations of j and l, and the same component d_{ijl} can be measured in two different experimental geometries.[4] When the radiation propagated along the *a* axis of the noncommensurate phase of $(NH_4)_2BeF_4$, however, new nonzero d_{ijl} components were observed. Figure 1 shows the temperature dependence of the SHG intensity in the d_{322} component, which appears only in the noncommensurate phase if the first-harmonic radiation propagates along the *a* axis. To compare the relative intensities, Fig. 1 shows the temperature dependence of the d_{222} component, which is allowed by the symmetry of the ferroelectric phase.

The observed effect can be explained if account is taken of the influence of the structure modulation on the nonlinear polarization of the medium, $\mathbf{P}^{(2)}(\mathbf{R},t)$, which determines the SHG intensity $[I(2\omega)]$. According to[4] we have

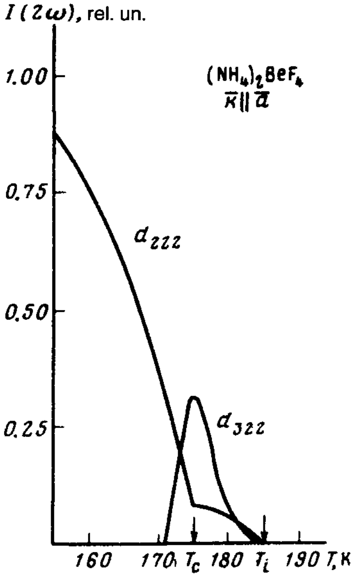

FIG. 1. Temperature dependence of the SHG intensity for single-crystal $(NH_4)_2\ BeF_4$.

$$P_i^{(2)}(\mathbf{R},t) = 4 d_{ijl} E_j(\mathbf{R}) E_l(\mathbf{R}) e^{-i(2\omega t - 2\mathbf{k}\mathbf{R})}, \qquad (1)$$

where $E_j(\mathbf{R})$ is the amplitude, ω the frequency, and $\mathbf{k}$ the wave vector of the first-harmonic field. In the simplest case the structure modulation can be taken into account by replacing $\mathbf{R}$ by $\mathbf{R}+\mathbf{r}$, where

$$\mathbf{r} = \mathbf{r}^{(0)} \sin \delta \mathbf{R} a^*. \qquad (2)$$

Here $\mathbf{r}$ stands for the modulated displacements, $\mathbf{r}^{(0)}$ is the depth of modulation, δ is the noncommensurability parameter, and a^* is the reciprocal-lattice vector, with $(\mathbf{r}\cdot\mathbf{a}) = 0$.[2] Recognizing that $|\mathbf{r}| \ll |\mathbf{R}|$, we can express $P_i^{(2)}(\mathbf{R}+\mathbf{r},t)$ in first order approximation in the form of a sum of $P_i^2(\mathbf{R},t)$ and terms containing the quantities $D_{ijlm} \equiv (\partial d_{ijl}/\partial r_m)_{\mathbf{r}=0}$. Then we have at $\mathbf{k}\|\mathbf{a}$

$$I(2\omega) \sim |E_i^{(2)}(\mathbf{R}_L)|^2 = d_{ijl}^2 \left| \frac{32\omega^2 E_j(\mathbf{R}) E_l(\mathbf{R}) \sin p}{k_2 c^2 \Delta k} \right| + \left| \frac{32\omega^2 E_j(\mathbf{R}) E_l(\mathbf{R})}{L k_2 c^2 (p^2 - q^2)} \right|^2 \left\{ d_{ijl} D_{ijl} \left[\frac{q}{p} (1 + \cos q) \sin p + (1 - \cos p) \sin q \right] + D_{ijl}^2 q^2 \left[\left(\frac{p}{q} \sin q + \sin p \right) + (\cos p + \cos q)^2 \right] \right\}, \qquad (3)$$

where

$$D_{ijl} = r_m^{(0)} D_{ijlm}, \quad \Delta k = k_2 - 2k, \quad p = \Delta kL, q = \frac{\delta}{a} L, k_2$$

is the wave vector of the second-harmonic radiation, $E_i^{(2)}(\mathbf{R}_L)$ is the second-harmonic field amplitude at the exit from the crystal, and L is the length of the sample. As seen from (3), in this case components $I(2\omega)$ can appear even if $d_{ijl} \equiv 0$. At $\mathbf{k} \perp \mathbf{a}$ all the terms containing D_{ijlm} average out to zero over the crystal volume.

It follows from the foregoing analysis that the effective tensor d_{ijl} is not symmetric and from its form we can determine the direction of the structure modulation. The values of the new components of this tensor are determined by the modulation depth $r^{(0)}$ and by the values of D_{ijlm}. Thus, SHG can become one of the methods of investigating in detail noncommensurate structures in ferroelectrics.

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