

Dielectric properties of $(\text{NH}_4)_2\text{SO}_4$ crystals in the range of electronic excitations

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Spectra of the real and imaginary parts of the pseudo-dielectric permittivity, $\langle \varepsilon_1 \rangle(E)$ and $\langle \varepsilon_2 \rangle(E)$, of ferroelectric ammonium sulfate crystals, $(\text{NH}_4)_2\text{SO}_4$, have been measured in the range of electronic excitations 4.0 to 9.5 eV by ellipsometry using synchrotron radiation. Temperature dependences of the corresponding susceptibilities, $\langle \chi_1 \rangle(T)$ and $\langle \chi_2 \rangle(T)$, obtained for the photon energy $E = 8.5$ eV, related to excitations of oxygen p -electrons, reveal sharp peak-like temperature changes near the Curie point $T_C = 223$ K. The large temperature-dependent increase of the imaginary part of the susceptibility $\chi_2(T)$, together with a simultaneous decrease of the real part of the susceptibility $\chi_1(T)$, take place at the phase transition. These anomalies have been ascribed mainly to the SO_4 group of the crystal structure.

Keywords: ferroelectrics; electronic excitations; dielectric functions.

1. Introduction

Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, is a dielectric crystal with a first-order (discontinuous) ferroelectric phase transition at the temperature $T_C = 223$ K (Matthias & Remeika, 1956; Hoshino *et al.*, 1958; Yamaguchi *et al.*, 1995). The crystal exhibits an unusually large relative change in the dielectric constant at T_C (Hoshino *et al.*, 1958), a very low value (~ 15 K) of the Curie–Weiss constant (Ohshima & Nakamura, 1966; Unruh, 1970) and a very large spontaneous strain (Hoshino *et al.*, 1958). Such observations are not known for common ferroelectric materials. This crystal seems to be a unique example of where ferroelectricity is a secondary effect of an ordinary molecular phase transition (Jain & Bist, 1974).

Ammonium sulfate crystals undergo the ferroelectric phase transition from the high-temperature rhombic phase with symmetry D_{2h}^{16} ($Pnam$) into the low-temperature rhombic phase with C_{2v}^9 ($Pna2$) symmetry at the Curie temperature $T_C = 223$ K (Yamaguchi *et al.*, 1995). This transition is accompanied by the appearance of a spontaneous polarization P_s along the c axis. The P_s changes its sign at a temperature of about 85 K (Unruh, 1970). Some characteristic features (such as a small value of the Curie–Weiss constant, $C_{CW} = 33.8$ K, an anomalous behaviour of the spontaneous polarization in the vicinity of the 85 K temperature *etc.*) allow one to classify $(\text{NH}_4)_2\text{SO}_4$ as a weak ferroelectric (Tagantsev *et al.*, 1987). The mechanism of the ferroelectric phase transition in this crystal is quite complex and is still not completely understood in detail. The $(\text{NH}_4)_2\text{SO}_4$ crystal unit cell contains 60 atoms or four formula units. It is fairly difficult to describe the structural rearrangement of this crystal at T_C . According to the idea

formulated by Dvorak & Ishibashi (1976), two ferroelectric sublattices are formed in $(\text{NH}_4)_2\text{SO}_4$ at the temperature of the ferroelectric phase transition, similar to in some other weak ferroelectrics. These sublattices have oppositely directed spontaneous polarizations P_{s1} and P_{s2} (subscripts 1 and 2 indicate the corresponding ferroelectric sublattices) with different temperature dependences. The spontaneous polarizations P_{s1} and P_{s2} are due to displacements of the tetrahedra $(\text{NH}_4)_1$ and $(\text{NH}_4)_2$ along the c axis. Twisting of these tetrahedra is caused by a rearrangement inside the $(\text{SO}_4)_1$ and $(\text{SO}_4)_2$ groups. It is assumed that the distortion of the $(\text{SO}_4)_1$ and $(\text{SO}_4)_2$ groups and their rotation at some angle take place at the Curie temperature. Their rotation angle depends on the temperature of the sample below the Curie point (Gridnev *et al.*, 2001). Thus, the order parameter coupled with spontaneous polarization seems to have several components including spontaneous strain in the SO_4^{2-} ion as its major contributor. Jain & Bist (1974) claim that this strain appears to arise because of the covalent effects of the SO_4^{2-} ion in the S–O bonds.

Ammonium sulfate crystals are colourless and transparent over a wide photon energy range. This means that the low-energy edge of electronic optical excitations in this crystal is placed in the energy range $E > 3$ eV (El-Korashy *et al.*, 2003; El-Fadl & Bin Anooz, 2006). Only weak optical electronic absorption with the imaginary part of dielectric permittivity $\varepsilon_2 \simeq 10^{-4}$ was found in the range 2–6 eV (El-Fadl & Bin Anooz, 2006). Thus, the fundamental optical absorption of the crystal takes place in the photon energy range $E > 6$ eV. Optical properties in this energy range reflect the electronic excitations of constituent atoms of the crystal. These proper-

ties are of interest to the study of the band structure and the ferroelectric phase transition.

The physical properties of the ammonium sulfate crystal have generally been studied intensively in connection with the ferroelectric phase transition since 1956 (Matthias & Remeika, 1956). However, reference data on the dielectric functions [photon energy dependences of the real and imaginary parts of dielectric permittivity $\varepsilon_1(E)$ and $\varepsilon_2(E)$] or other optical characteristics of these crystals in the range $E > 6$ eV have not been found.

The main aim of the present study is the experimental investigation of the dielectric functions of a $(\text{NH}_4)_2\text{SO}_4$ crystal in the photon energy range of electronic excitations, 4–9.5 eV, and its temperature changes in the range 170–295 K, involving the temperature of the ferroelectric phase transition. The experimental results will be compared with the corresponding results of first-principle calculations in order to obtain a better understanding of peculiarities related to chemical bonding and phase transition in the crystal.

2. Methods of investigation

Measurements of the pseudo-dielectric functions $\langle\varepsilon_1\rangle(E)$ and $\langle\varepsilon_2\rangle(E)$ ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) of $(\text{NH}_4)_2\text{SO}_4$ crystals were performed by spectroscopic ellipsometry (Azzam & Bashara, 1987; Wethkamp *et al.*, 1998) using synchrotron radiation at BESSY II, Berlin, Germany, in the range 4.0–9.5 eV with a resolution of $\delta E < 0.1$ eV. The angle of incidence was $\sim 68^\circ$, while the polarization of the incident beam was chosen to be $\sim 20^\circ$ tilted with respect to the plane of incidence during the measurements. A MgF_2 polarizer and rotating analyzer ensured a degree of polarization of more than 99.998%. The ellipsometric measurements were conducted for three cuts, perpendicular to the a , b and c orthogonal axes of the unit cell, of mechanically polished $(\text{NH}_4)_2\text{SO}_4$ crystals, and the corresponding dielectric functions $\langle\varepsilon_1(E)\rangle$ and $\langle\varepsilon_2(E)\rangle$ were subsequently calculated using an isotropic two-layer model.

3. Results and discussion

From the definition of the dielectric permittivity ε and the susceptibility χ ($\chi = \varepsilon - 1$), it can be seen that the relative changes of susceptibility describe the relative changes of the atomic and electronic properties of low-density material more adequately. Therefore, the presentation of the results is carried out here in terms of the susceptibility.

The susceptibility $\langle\chi_2\rangle(E)$ shows an increasing quasi-monotonously behaviour with a maximum at 9.37 eV (for the temperature 298 K) and at 9.50 eV (for the temperature 175 K) (Fig. 1). This looks very similar to the corresponding theoretical dependences of RbNH_4SO_4 crystals obtained from first-principles calculations using the *CASTEP* code (Andriyevsky *et al.*, 2007). An analysis of the density of electronic states of RbNH_4SO_4 crystals indicates that the large maximum of $\langle\chi_2\rangle(E)$ at 9.37 eV in the case of $(\text{NH}_4)_2\text{SO}_4$ mainly corresponds to the excitation of oxygen p -electrons.

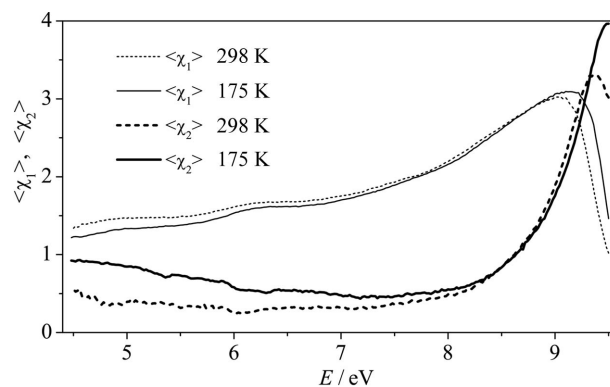


Figure 1
Spectra of the real and imaginary parts of the susceptibility of a $(\text{NH}_4)_2\text{SO}_4$ crystal, $\langle\chi_1\rangle(E)$ and $\langle\chi_2\rangle(E)$, at temperatures 298 and 175 K.

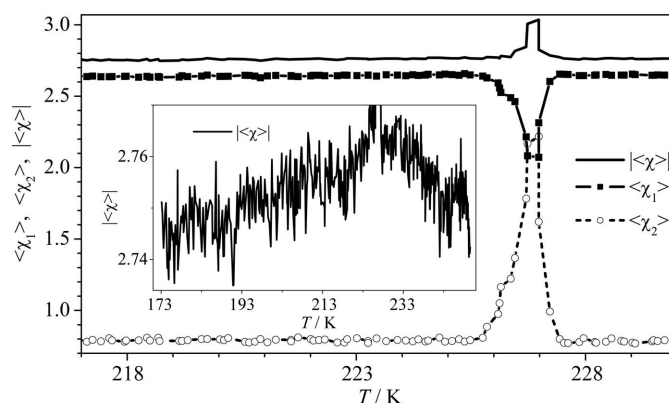


Figure 2
Temperature dependences of the real part ($\langle\chi_1\rangle$), imaginary part ($\langle\chi_2\rangle$) and modulus ($|\langle\chi\rangle|$) of the susceptibility $\langle\chi\rangle$ of $(\text{NH}_4)_2\text{SO}_4$ crystals during heating at $E = 8.5$ eV. The insert shows the temperature dependence of the modulus of the susceptibility $|\langle\chi\rangle|(T)$ over a larger temperature range.

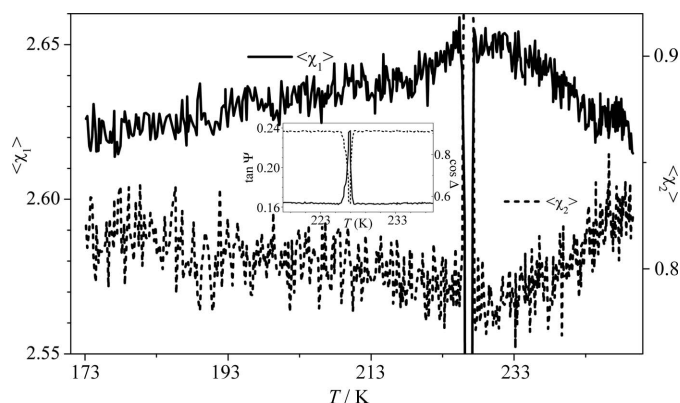


Figure 3
Temperature dependences of the real $\langle\chi_1\rangle(T)$ and imaginary $\langle\chi_2\rangle(T)$ parts of the susceptibility of $(\text{NH}_4)_2\text{SO}_4$ crystals during heating at $E = 8.5$ eV on a finer vertical scale than in Fig. 2. The insert shows the temperature dependences of the standard ellipsometric parameters $\tan\Psi(T)$ and $\cos\Delta(T)$.

Distinct and large anomalies of the temperature dependences of pseudo-susceptibilities $\langle\chi_1\rangle(T)$ and $\langle\chi_2\rangle(T)$, and reflectance intensity $I_R(T)$, have been obtained at the temperature of the discontinuous ferroelectric phase transition for the c -cut sample of the crystal studied (Figs. 2 and 3). Much smaller anomalies were seen for the a - and b -cut

samples. One can distinguish here two types of anomalies: (i) broad band with broad and small extremum in $\langle\chi_1\rangle(T)$ and $\langle\chi_2\rangle(T)$ near T_C , and (ii) narrow peak-like dependences of $\langle\chi_1\rangle(T)$ and $\langle\chi_2\rangle(T)$ with extremum position 5 K lower than the corresponding position of the broad extremum. The maximum of the broad anomaly in $\langle\chi_1\rangle(T)$ corresponds to the minimum of the narrow and large anomaly in $\langle\chi_1\rangle(T)$, and *vice versa*, the minimum of the broad anomaly in $\langle\chi_2\rangle(T)$ corresponds to the maximum of the narrow and large anomaly in $\langle\chi_2\rangle(T)$ (Figs. 2 and 3). Therefore, two different temperature-dependent processes can be suggested for $(\text{NH}_4)_2\text{SO}_4$ crystals. The first process is a discontinuous phase transition at $T_C^{(1)}$ taking place over the narrow temperature range of approximately 1–2 K. The sharp maximum of $\langle\chi_2\rangle$ and the minimum of $\langle\chi_1\rangle$ are associated with this process (Fig. 2). The second, continuous, process is associated with the slower variation in $\langle\chi_1\rangle(T)$ and $\langle\chi_2\rangle(T)$ which creates a maximum in $\langle\chi_1\rangle$ and a minimum in $\langle\chi_2\rangle$ at temperature $T_C^{(2)}$, approximately 5 K higher than $T_C^{(1)}$ (Fig. 3).

The presence of these two processes agrees with results of dielectric constant measurements on $(\text{NH}_4)_2\text{SO}_4$ for frequencies 10–10² kHz (Yoshihara *et al.*, 1976). In this study a small anomaly in the dielectric constant ε was found between 6 and 12 K below the well known ferroelectric transition at 223.5 K. It is proposed that this new anomaly is due to the appearance of a spontaneous polarization, which is produced by the secondary order parameter and is in an anti-parallel direction to the spontaneous polarization owing to the primary order parameter, which produces the well known ferroelectric transition. According to this model, ammonium sulfate is ferroelectric just below the transition at 223.5 K, but it gradually changes into a weak ferroelectric material below this new anomaly temperature.

An interesting result has been obtained when analyzing the temperature dependence of the light intensity $I_R(T)$ reflected from the sample and the temperature dependence of the normal-incidence reflection coefficient $R(T)$ (Fig. 4). The normal-incidence reflection coefficient R has been calculated

according to the known relationship (Philipp & Ehrenreich, 1963)

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \tag{1}$$

$$n = \left[\frac{(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1}{2} \right]^{1/2}, \quad k = \left[\frac{(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1}{2} \right]^{1/2}.$$

For *a*- and *b*-cuts of the $(\text{NH}_4)_2\text{SO}_4$ crystal, similar temperature anomalies of the total reflected radiation $I_R(T)$ and susceptibilities $\langle\chi_1\rangle(T)$ and $\langle\chi_2\rangle(T)$ were almost absent.

To suggest a proper explanation for the $I_R(T)$ dependence one has to mention that the change in birefringence at T_C occurs mainly due to the elasto-optical effect rather than electro-optical effect caused by the appearance of spontaneous polarization (Anistratov & Martinov, 1970). Evidently the crystal exhibits an ordinary molecular phase transition and the resulting ferroelectricity is a secondary effect. Hence, it was defined as an improper ferroelectric (Ikeda *et al.*, 1973). Jain & Bist (1974) have concluded that spontaneous strain rather than spontaneous polarization acts as an order parameter to be used for describing the transition. Such spontaneous strain should arise due to covalent effects in directed bonds (Kanzig, 1957; Megaw, 1957). Taking into account the great spontaneous deformations in the crystal and the piezo(elasto)optical effect mentioned, the large and abrupt decrease of the reflectance intensity $I_R(T)$ observed for the *c*-cut (Fig. 4) can be explained as a result of light scattering on a domain-like structure grid. This structure is generated by the non-homogeneity of the refractive index caused by the abrupt increase of spontaneous deformation.

Because the ellipsometric method for determination of the dielectric permittivities $\langle\varepsilon_1\rangle$ and $\langle\varepsilon_2\rangle$ is not sensitive to the overall magnitude of light intensity, results of the normal-incidence reflectivity $R(T)$ (Fig. 4), derived from $\langle\varepsilon_1\rangle$ and $\langle\varepsilon_2\rangle$, can be analyzed independently from the measured $I_R(T)$ dependence. Therefore, independent information on the change of the crystal properties of $(\text{NH}_4)_2\text{SO}_4$ (dielectric permittivity) at phase transition is provided. However, one can see the same broad maximum-like band in $I_R(T)$ as takes place for the dependences of $|\langle\chi\rangle|(T)$ (Fig. 2) and $\langle\chi_1\rangle(T)$ (Fig. 3) and a sharp minimum-like band in $I_R(T)$ as takes place for the dependence $\langle\chi_1\rangle(T)$ (Fig. 3). Again the extremum of the continuous-like process is placed by temperature 5 K higher than the extremum of the first-order phase transition. Unfortunately the accuracy of determination of the absolute sample temperature was not appropriate owing to the limited thermal conductivity between thermocouple, sample holder and $(\text{NH}_4)_2\text{SO}_4$ crystal. The real temperature of the crystal during cooling was 5–6 K greater than the thermocouple temperature and 5–6 K smaller during sample heating. Therefore, at the moment it is difficult to state the correct absolute temperature values where the extrema are observed.

Taking into account that the photon energy $E = 8.5$ eV corresponds to the excitation of *p*-electrons of oxygen in

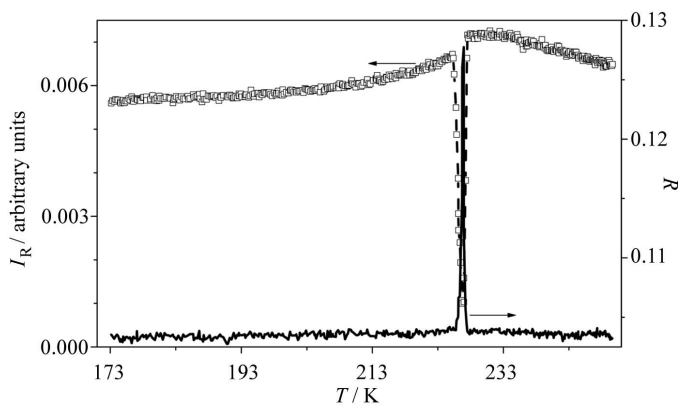


Figure 4 Temperature dependences of the intensity of reflected light $I_R(T)$ and normal-incidence reflectance $R(T)$ calculated from the dielectric functions $\langle\varepsilon_1\rangle(T)$ and $\langle\varepsilon_2\rangle(T)$ of $(\text{NH}_4)_2\text{SO}_4$ crystals measured at $E = 8.5$ eV during heating.

(NH₄)₂SO₄ crystals, the temperature changes described above can be attributed mainly to the SO₄ group. Finally, one can state that the absolute value of the complex susceptibility $|\langle\chi\rangle|$ of (NH₄)₂SO₄ crystal in the range of oxygen *p*-electrons excitation displays a maximum at the temperature $T \simeq 223$ K of the ferroelectric phase transition. For the narrow temperature range $\Delta T \simeq 1\text{--}2$ K near the main maximum of $|\langle\chi\rangle|(T)$, the large relative increase $\Delta\chi_2/\chi_2 \simeq 1.8$ of the imaginary part of the susceptibility $\langle\chi_2\rangle$ takes place together with a simultaneous relative decrease $\Delta\chi_1/\chi_1 \simeq -0.25$ of the real part of the susceptibility $\langle\chi_1\rangle$ (see Fig. 2). This result agrees qualitatively with the conclusion of Jain & Bist (1974) that a considerable part of the spontaneous polarization of (NH₄)₂SO₄ crystals arises from the SO₄ groups. According to Jain & Bist (1974), the main driving interaction of the phase transition has its origin in the S—O bonds of the SO₄²⁻ ion which triggers the transition by gaining a more distorted structure of lower symmetry; the NH₄⁺ ions simply follow an appropriate change. This is probably the reason that the studies related only to NH₄⁺ ions indicate that the phase transition has second-order characteristics (O'Reilly & Tsang, 1967*a,b*; Torrie *et al.*, 1972).

Taking into account the sharp spontaneous deformations at the phase transition of (NH₄)₂SO₄, destroying the crystal, it would be interesting to perform first-principal calculations of the complex susceptibility for different unit-cell dimensions and arrangements of constituent atoms and to compare results obtained using the present experiment.

4. Conclusions

On the basis of the present study of the ferroelectric crystal (NH₄)₂SO₄ by the method of spectroscopic ellipsometry one can conclude the following.

Measurements of the dielectric properties of (NH₄)₂SO₄ crystals in the range of electronic excitations 4 eV to 9.5 eV display a large increase in the pseudo-susceptibility $\langle\chi_2\rangle(E)$ for energy $E > 8$ eV with a maximum at 9.3–9.5 eV (depending on the sample temperature). This spectral band of $\langle\chi_2\rangle(E)$ corresponds to the excitation of oxygen *p*-electrons of sulfate groups.

The temperature dependences of the dielectric properties of the *c*-cut (NH₄)₂SO₄ crystal for the photon energy $E = 8.5$ eV reveal two types of anomalies in the range comprising the ferroelectric phase-transition point $T_C = 223$ K: (i) a broad extremum in the $\langle\chi_1\rangle(T)$ and $\langle\chi_2\rangle(T)$ dependences near T_C , and (ii) narrow and sharp peak-like dependences of $\langle\chi_1\rangle(T)$ and $\langle\chi_2\rangle(T)$ with an extremum position approximately 5 K smaller than for the corresponding position of the broad extremum. These two anomalies can be associated with two separate temperature and structure processes accompanying the ferroelectric phase transitions in the (NH₄)₂SO₄ crystal.

A large relative increase $\Delta\chi_2/\chi_2 \simeq 1.8$ of the imaginary part of the susceptibility $\langle\chi_2\rangle$ of (NH₄)₂SO₄ crystals for the excitation energy $E = 8.5$ eV in the narrow temperature range $\Delta T = 1\text{--}2$ K near T_C testifies for the essential participation of the oxygen *p*-electrons in the rebuilding of crystal structure at the ferroelectric phase transition.

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