Dielectric dispersion of \((\text{NH}_4)_2\text{SO}_4\) in the near-millimetre and far-infrared range: manifestations of disorder

G V Kozlov†, S P Lebedev†, A A Volkov†, J Petzelt‡, B Wyncke§ and F Bréhat§

† Institute of General Physics, Academy of Sciences of the USSR, 117942 Moscow, Vavilov Street 38, USSR
‡ Institute of Physics, Czechoslovak Academy of Sciences, 18040 Prague 8, Na Slovance 2, Czechoslovakia
§ Laboratoire Infrarouge Lointain, UA 809 CNRS, Université de Nancy I, BP 239, 54506 Vandœuvre les Nancy Cédex, France

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Abstract. Dielectric dispersion of ammonium sulphate in the 4–400 cm\(^{-1}\) range has been investigated in a broad temperature region around the pseudo-proper ferroelectric transition at \(T_c = 223\) K. In the 4–18 cm\(^{-1}\) range the backward-wave-oscillator transmission technique and in the 20–400 cm\(^{-1}\) range polarised reflectivity with a grating spectrometer were used to determine the dielectric response function. All external lattice mode parameters have been evaluated as a function of temperature. Near the phase transition a pronounced increase of damping of all modes has been observed. In addition to phonon mode dispersion, broad relaxation-type dispersions occur in all polarisations with characteristic frequencies 20–60 cm\(^{-1}\) and increasing strength on approaching \(T_c\) from below. In the ferroelectric \(E_{11}\) polarisation, this absorption appears in addition to the critical soft relaxation of lower frequency. The absence of any anomaly in mode frequencies near \(T_c\) indicates that the dynamic origin of the phase transition consists of ordering of \(\text{NH}_4^+\) ions. Higher-frequency relaxations are assigned to anharmonic rotations of partially disordered \(\text{SO}_4^{2-}\) ions. Consequences for thermodynamic theories of the phase transition are discussed.

1. Introduction

Ammonium sulphate, \((\text{NH}_4)_2\text{SO}_4\) (AS), is one of the most investigated ferroelectrics. It represents a classical example of a pseudo-proper ferroelectric (Petzelt et al 1974, Dvořák 1974) with the very small role of dipolar Coulombic interactions indicated by a small Curie–Weiss constant \(C = 40\) K and small spontaneous polarisation \(P_s \approx 0.6\) \(\mu\)C cm\(^{-2}\) with peculiar temperature behaviour. The transition at \(T_c = 223\) K from \(D_{1h}^{16}\) to \(C_{2v}^0\) space groups is strongly first-order, the difference between \(T_c\) and the Curie temperature \(T_0\) being about 10 K (Luther and Unruh 1979, 1980).

The phase transition mechanism is complex and in spite of many investigations it is not yet definitely clear. The main instability originates from the critical slowing down of a soft dielectric relaxation of \(B_{1u}\) symmetry \((E_{11}\parallel e\) polarisation). Its frequency \(\nu_s = 1/2\pi\tau_s\) fulfils the classical law (see e.g. Blinc and Žekš 1974)

\[
\nu_s = \gamma(T - T_0)
\]
with $\gamma = 2 \text{ GHz K}^{-1}$ and $T_0 = 210.4 \text{ K}$ for $T - T_c < 10 \text{ K}$. This represents at $T_c$ the relaxation time $\tau_s(T_c) = 6 \times 10^{-12} \text{ s}$. The microscopic origin of this relaxation is most probably connected with the disorder observed in both types of NH$_4$ groups, (NH$_4$I) and (NH$_4$)$_2$I (O’Reilly and Tsang 1967, 1969, Dahlberg et al 1970, Shibata et al 1976, Nordland et al 1976, Hasebe 1981). More especially, it corresponds essentially to a reorientation (tilting) of NH$_4^+$ ions about the $a$ axis at an angle $\pm20-30^\circ$ from the (001) plane.

However, another slightly weaker instability occurs in the totally symmetric $A_g$-type light scattering spectra. It manifests itself as a softening of the longitudinal acoustic wave along the $a$ axis in the Brillouin spectra and as a narrowing of the central peak in $b(aa)c$ Raman spectra (Unruh and Ayere 1976, Unruh et al 1978). This central mode is very probably due to reorientation of the NH$_4^+$ ions as well, because of the presence of an isotope effect on deuteration.

Besides ordering of NH$_4^+$ ions, below $T_c$ both $B_{1u}$ and $A_g$ types of distortions appear, including a large spontaneous strain (Ikeda et al 1973) and internal distortions of all the ions (Fujimoto et al 1977, Hasebe 1981, Jain et al 1986, Bajpai and Jain 1987a, b). Spontaneous strain and distortion of SO$_4^{2-}$ ions display a large increase at $T_c$ with minor temperature dependences below $T_c$. The NH$_4^+$ ions distort even more but more gradually below $T_c$ (Hasebe 1981, Jain et al 1986). Owing to the rather strong first-order nature (discontinuity) of the transition, it is impossible to decide from temperature dependences below $T_c$ which distortions correspond to freezing of the primary order parameter and which are triggered by it.

The only way to solve this question is to determine more accurately the eigenvector of the relaxational soft mode near $T_c$, i.e. the primary order parameter. It can be evaluated in principle from temperature dependences of the soft mode frequency and all other lattice mode frequencies in a broad temperature range around $T_c$. Here we represent the results of such investigations in the 4–400 cm$^{-1}$ range, i.e. in the range covering the external lattice modes down to the soft mode frequency. We have not observed anomalous changes in any of the mode frequencies which indicates that the soft mode eigenvector is temperature-independent near $T_c$. The essential instability originates from NH$_4^+$ ordering. In addition, we have observed pronounced broadening of all modes near $T_c$ and additional non-critical relaxations in the sub-millimetre range indicating an important role of disorder in this crystal. The origin of these effects will be discussed.

2. Experiment, results and evaluation

The measurements of sub-millimetre spectra have been carried out on a tunable backward-wave-oscillator (BWO) spectrometer ‘Epsilon’ using the technique of complex transmittance measurements of plane parallel plates (Volkov et al 1985). The reflectivity measurements in the 15–400 cm$^{-1}$ range have been performed using a far-infrared (FIR) grating spectrometer. A broad temperature range of 80–400 K was studied.

An example of reflectivity spectra is shown in figure 1. More complete results have been published recently (Wyncke and Brehat 1988). Agreement between the low-frequency reflectivity measured and calculated from more accurate sub-millimetre spectra was within $\pm0.01$. The complete combined reflectivity and permittivity spectra ($R(\nu)$ and $\varepsilon(\nu)$) have been fitted to a model of the sum of classical oscillator and Debye
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Figure 1. Example of the FIR reflectivity spectra of $E \parallel b$ at 300 and 80 K (----) together with the fit (-----) to equation (2).

relaxation contributions:

$$R(\nu) = \left| \frac{[\hat{\varepsilon}(\nu)]^{1/2} - 1}{[\hat{\varepsilon}(\nu)]^{1/2} + 1} \right|^2$$

$$\hat{\varepsilon}(\nu) = \varepsilon_\infty + \sum_{i=1}^{n} \frac{\Delta \varepsilon_i \nu_i^2}{\nu_i^2 - \nu^2 + i\nu \gamma_i} + \sum_{j=1}^{m} \frac{\Delta \varepsilon_R^i \nu_R^j}{\nu_R^j + i\nu}.$$  \hspace{1cm} (2)

Here $\varepsilon_\infty$ is the permittivity at frequencies much higher than all oscillator eigenfrequencies $\nu_i$ and relaxation frequencies $\nu_R^j$, $\gamma_i$ is the damping of the $i$th oscillator, $\Delta \varepsilon_i$ is its contribution to the static permittivity (strength) and $\Delta \varepsilon_R^i$ is the dielectric contribution of the $j$th relaxation. Eight, ten and ten oscillators and one, one and two relaxations were used for the fit of $E \parallel a$, $E \parallel b$ and $E \parallel c$ spectra, respectively. The fitting curves are added in figure 1 as an illustration of the typical quality of our reflectivity fits. In table 1 we list all the parameters of the oscillator fit at 90 and 300 K, but we fitted spectra for several temperatures in between as well.

In figure 2 we give some examples of the sub-millimetre and near-millimetre spectra for $E \parallel c$ together with the fit mentioned above. Notice the softening of the critical ferroelectric relaxation above $T_c$. On the basis of such spectra we can plot the temperature dependencies of $\varepsilon'(T)$ and $\varepsilon''(T)$ for a fixed frequency $\nu$. In figure 3 we show these dependences for all polarisations at $\nu = 17.7 \text{ cm}^{-1}$.

In figure 4 we would like to illustrate the importance of the relaxations for the fit of sub-millimetre data. Here we plot in double logarithmic scale the fitted dielectric losses for $E \parallel b$ at room temperature along with the same fit with relaxation omitted. Clearly, no acceptable fit of sub-millimetre data is possible without introducing the relaxation.

The parameters of relaxations obtained from our fits are plotted as a function of temperature in figure 5. The soft relaxation for $E \parallel c$ fulfils equation (1) in the broad range above $T_c$ with the same parameters as those obtained by Luther and Unruh (1979).
Table 1. Oscillator mode parameters of the fit at 90 and 300 K.

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<th>$\nu_r$ (cm$^{-1}$)</th>
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$\sum \Delta \epsilon_r = 3.25$ $\sum \Delta \epsilon_r = 3.45$ $\sum \Delta \epsilon_r = 3.85$

$\epsilon_i = 3.0$ $\epsilon_i = 2.8$ $\epsilon_i = 3.0$

$\Delta \epsilon_R = 0.2$ $\Delta \epsilon_R = 0.8$ $\Delta \epsilon_R = 0.8$

$\epsilon_0 = 6.5$ $\epsilon_0 = 6.3$ $\epsilon_0 = 6.9$
Figure 2. Example of the sub-millimetre permittivity spectra of AS in the soft mode range ($E \parallel c$). Dots represent the experiment and full curves represent fit using two relaxations and 10 FIR oscillators (for the parameters of relaxations, see figure 5).

Figure 3. Temperature dependences of all complex permittivity tensor components of AS at a fixed frequency $\nu = 17.7 \text{ cm}^{-1}$. 
Figure 4. Dielectric loss spectrum of AS for $E \parallel b$ at 300 K with and without considering the relaxations: (-----) sub-millimetre data; (----) fit; (-- --) fit without relaxation. Notice the double logarithmic scale.

Figure 5. Temperature dependence of the relaxation frequencies and strengths in AS.
Below $T_c$ the critical relaxation disappears in the background of the stronger higher-frequency relaxation, so that its parameters cannot be determined unambiguously. The additional faster relaxations behave in a similar way in all the polarisations: they remain roughly temperature-independent above $T_c$, but soften and weaken upon cooling below $T_c$.

3. Discussion

From factor group analysis (Petzelt et al. 1974) it follows that in each of the $E \parallel a$, $E \parallel b$ and $E \parallel c$ spectra one should expect eight and 17 external lattice modes in the paraelectric and ferroelectric phases, respectively. It is well known (Sawada et al. 1976) that the paraelectric phase $D_{ii}$ is in fact slightly distorted hexagonal phase $D_{6h}$ with the hexagonal axis parallel to the orthorhombic $a$ axis which actually occurs at high temperatures in other isomorphous crystals like $K_2SO_4$ and $K_2SeO_4$ (Shiozaki et al. 1977). In this phase the external modes of $AS$ are classified as follows:

$$3A_g + 3A_{2u}(E \parallel a) + 2B_{1g} + 2B_{1u} + B_{2g} + B_{2u} + 3E_{1g} + 3E_{1u}(E \perp a) + 3E_{2g} + 3E_{2u}$$

which after subtraction of acoustic modes yields only two IR active modes for both $E \parallel a$ and $E \perp a$ polarisations. These modes are assigned to translations of $SO_4^-$ ions against $(NH_4)^+$ and $(NH_2)^+$ groups along the three crystal axes. As the nearest $SO_4^-$–$NH_4^+$ distances do not differ very strongly from each other (3.5–3.8 Å), it is not surprising that at room temperature we see only one broad mode in all polarisations with a very small anisotropy (Petzelt et al. 1974). However, a single-oscillator fit of these spectra is not satisfactory.

From table 1 and our fit at intermediate temperatures it is seen that in fact most of the modes seen below $T_c$ survive above $T_c$ with about the same strength but with much higher damping. The number of modes is in agreement with factor group analysis above $T_c$ (Petzelt et al. 1974). New modes that should appear below $T_c$ are mostly too weak to be observed in reflectivity spectra. Some of them have been observed in previous transmission measurements on thin samples (Bréhat et al. 1974) in the 60–100 cm$^{-1}$ range. Our results are compatible with these transmission measurements as well as with earlier reflectivity measurements (Petzelt et al. 1974), but our low-temperature reflectivities show somewhat sharper peak structure.

Let us now discuss the enormous increase of mode damping. Similar broadening was observed also in Raman scattering (Iqbal and Christoe 1976). The reason for it is obviously the disorder in the lattice, which increases with temperature in a similar way as the damping. The disorder concerns not only $NH_4^+$ ions but also $SO_4^-$ ions as follows from closer examination of thermal vibrations of the latter (Hasebe 1981). It shows that these groups perform thermal rotational motion as large as $\pm 7^\circ$ above $T_c$, which seems to be too much for harmonic librations. According to a comparative study of $A_2BX_4$ compounds by Itoh et al. (1983) and Hogervorst (1984), $AS$ (together with $(NH_4)_2BeF_4$) represents a crossover between harmonic and pseudo-spin-like motion concerning the thermal amplitude of $BX_4^-$ anions. In this way, the disorder in both $NH_4^+$ and $SO_4^-$ ions causes local and temporal fluctuations of all the mode frequencies, which leads to effective broadening of all the modes.

Another manifestation of the strong disorder in the lattice is the sub-millimetre relaxation-type absorption observed for all the polarisations in the 20–60 cm$^{-1}$ range (see figure 5). In the $E \parallel c$ polarisation such relaxation appears in addition to the soft
relaxation with much lower frequency. It reveals no critical anomaly near $T_c$ and its strength decreases continuously with decreasing temperature, disappearing completely below about 100 K where the crystal becomes ordered. Relaxations in other polarisations, $E \parallel a$ and $E \parallel b$, behave similarly, $\Delta \varepsilon_{\parallel}^c$ and $\nu_{\parallel}^c$ exhibiting a step at $T_c$. These steps explain the stepwise increase of $\varepsilon_{\parallel}^c(T)$ at $T_c$ (see figure 3). The stepwise decrease of $\varepsilon_{\parallel}^c(T)$ at $T_c$ is mainly due to a sudden increase of the critical relaxation frequency below $T_c$, but probably also due to some decrease of strength of the non-critical relaxation below $T_c$.

As already mentioned, similar relaxations have been observed also as central peaks in Raman scattering for various geometries (Unruh and Ayere 1976, Unruh et al 1978), having widths of the same order of magnitude as the dielectric relaxation frequencies. Especially anomalous is the $b(aa)c$ scattering geometry ($A_g$ species) where the central peak displays softening down to about 3.5 cm$^{-1}$ which (owing to a linear coupling) causes softening of the corresponding longitudinal acoustic wave along the $a$ axis. In this geometry a broader central peak of width approximately 20 cm$^{-1}$ is also present, which rapidly disappears below $T_c$. This peak interacts strongly with the SO$_2^-$ translational mode at about 40 cm$^{-1}$, causing its increase of strength above $T_c$. Therefore the broader central peak can be assigned to hindered rotational motion of SO$_2^-$ ions, as will be discussed later.

We see that there is an analogy between the dielectric relaxation behaviour and the appearance and behaviour of central modes in light scattering, especially between the critical behaviour in $B_{1u}$ and $A_g$ symmetry spectra. Concerning the degree of softening, $B_{1u}$ relaxation (ferroelectric soft mode) softens only slightly more (the critical temperature is about 2 K higher) than the acoustic wave in $A_g$ spectra (Unruh et al 1978).

Concerning the origin of $B_{1u}$ and $A_g$ critical relaxations (a central peak in scattering experiments is practically equivalent to the appearance of a relaxation in IR spectra), both are very probably connected with reorientations (tilting) of NH$_4^+$ ions (Petzelt et al 1974, Shibata et al 1976, Unruh et al 1978, Fujimoto et al 1977, Abe and Shibata 1977, Hasebe 1981). Partial substitution of NH$_4^+$ groups by Rb atoms reduces the $A_g$ instability with respect to the $B_{1u}$ instability, i.e. the difference between both critical temperatures increases (Unruh et al 1978). As the Rb atoms preferentially substitute (NH$_4$)$_m$ groups it seems that $B_{1u}$ ordering, which represents the primary order parameter, consists prevalingly of (NH$_4$)$_m$ ordering whereas the $A_g$ ordering, which concerns prevalingly (NH$_4$)$_l$ groups, represents a secondary parameter that can be triggered by the first one (for triggered phase transitions, see e.g. Holakovský (1973)). Such a mechanism could explain the discontinuity of the transition and different ordering of both groups below $T_c$ (Kydont et al 1967).

Concerning the order of magnitude of the critical relaxation time of NH$_4^+$ tilting ($\tau_s = 10^{-12}$ s), it should be noticed that it is in sharp disagreement with the value deduced from H nuclear magnetic resonance (NMR) measurements (Nordland et al 1976) which is three orders of magnitude greater ($\tau_s(298 K) = 6.7 \times 10^{-9}$ s, $\tau_s(236 K) = 8.3 \times 10^{-9}$ s). As there has been no further lower-frequency dispersion observed in the permittivity, i.e. $\varepsilon'(T)$ in the gigahertz range agrees with the static data (Luther and Unruh 1979, 1980), it is obvious that the dynamic process observed in NMR is not connected with any dipole moment and is not due to the critical ferroelectric mode.

Let us now discuss the origin of non-critical relaxations that appear in all polarisations. One possible mechanism, suggested already by Petzelt et al (1974), could be the disorder-induced absorption proportional to the one-phonon density of states (see e.g. Barker and Sievers 1975). However, it seems improbable that the phonon
Dielectric dispersion of (NH$_4$)$_2$SO$_4$

density of states could have critical points at such low frequencies ($\approx 50$ cm$^{-1}$) and that this mechanism could explain the stepwise changes at $T_c$. Also, the magnitude of the absorption is at least comparable to amorphous glasses or even greater (Barker and Sievers 1975) (absorption coefficient $\alpha$ (18 cm$^{-1}$) $\geq 20$ cm$^{-1}$) which seems to be too high for a small translational disorder in AS as compared to glasses.

Hence it seems to be more probable to assign the relaxations directly to large anharmonic rotations of SO$_4^{2-}$ ions. This should not be mixed up with normal harmonic librations which appear at higher frequencies $\nu > 80$ cm$^{-1}$ (Carter 1976, Torgashev 1988). The relaxations show several features that are not usual for relaxations in dynamically disordered systems. First of all their frequencies are at least one order of magnitude higher than usual and fall just below the range of normal external vibrations. Secondly, they show nearly no anisotropy, in contrast to the usual relaxations which as a rule appear only in one symmetry type of spectra (i.e. for a single IR polarisation). Thirdly, their rates do not follow the classical Eyring's law for thermally activated processes—hopping over a potential barrier $\Delta U$ ($\nu_\phi \propto \exp\left(-\Delta U/kT\right)$). All these features show that disordered atoms (in our case O atoms of SO$_4^{2-}$ ions) move in a shallow potential well with small barriers between local minima ($\Delta U \ll kT$ rather than $\Delta U \gg kT$) so that the Eyring formula and pseudo-spin approach do not hold. This is in agreement with structural considerations already mentioned (Itoh et al 1983, Hogervorst 1984).

Support for our assignment also comes from Raman measurements (Unruh et al 1978) where central modes of comparable width have been observed. In AS spectra a strong coupling is observed between the central mode and the SO$_4$ translational mode at about 40 cm$^{-1}$, as already mentioned. Further support is given by some other crystals of the A$_2$BX$_4$ family ($\beta$-K$_2$SO$_4$ structural type) like Rb$_2$ZnCl$_4$, Rb$_2$CoCl$_4$ and Rb$_2$ZnBr$_4$ where no protons are available but nevertheless broad IR peaks similar to those observed in AS appear in the disordered phase (Goncharov et al 1988). However, in these crystals the broad features overlap with external lattice modes which have lower frequency than in AS because of higher atomic masses. Earlier, we saw a similar broad absorption also in (NH$_4$)$_2$BeF$_4$ (Petzelt et al 1980) where the situation is very similar to AS (at that time we assigned it to the disorder-induced absorption proportional to the one-phonon density of states).

Summarising, we have enough evidence to assume that the higher-frequency non-critical relaxations are mainly due to a partial disorder in heavy SO$_4$ groups and the lower-frequency critical relaxations are mainly due to proton disorder in NH$_4$ groups. The sub-millimetre relaxations due to dynamical lattice disorder represent a new phenomenon not yet practically studied quantitatively.

Finally, let us come back to the question about the nature of the phase transition in AS. Jain et al (1986) and Bajpai and Jain (1987a, b) have recently stressed the role of internal SO$_4^{2-}$ distortion which appears suddenly below $T_c$ with only minor temperature dependence below $T_c$ following roughly that of the order parameter (Ikeda et al 1973). To explain this, they suggest that the soft mode should consist of SO$_4^{2-}$ librations mixed with SO$_4^{2-}$ internal vibrations mostly of $\nu_3$ type (asymmetric stretching in the 1100 cm$^{-1}$ range). In the light of our previous discussion we see no support for such a picture. The soft mode is purely relaxational and consists predominantly of NH$_4^+$ reorientation. The higher-frequency B$_{1u}$ relaxation assigned to hindered rotations of SO$_4^{2-}$ reveals no sign of coupling with the soft mode. Neither does any mode observable up to 400 cm$^{-1}$. However, we have to note that SO$_4^{2-}$ librations are not explicitly visible in IR spectra above $T_c$; they probably correspond to the weak mode at 114 cm$^{-1}$ (see table 1) which develops into a sharp mode at 132 cm$^{-1}$ at 90 K. Also, detailed information on the
$\nu_3$($SO_4$) mode is missing, but large softening is improbable. So, even if we cannot exclude a small admixture of $SO_4$ librations and distortions in the order parameter, we see no support for it from the IR spectra. The dynamical origin of the phase transition is merely reorientation of the NH$_4$ groups.

The SO$_3^-$ internal distortions can appear mainly as a secondary effect of hard mode condensation (Aizu 1974). This is allowed for $A_s$ modes through the lowest-order coupling $\eta_3 Q$ ($\eta$ is the order parameter, $Q$ the normal coordinate of the hard mode) and for $B_{1u}$ modes through the coupling $\eta_3 Q$. This leads to proportionality for the spontaneous values $Q_s(A_g) \propto \eta_3(T)$ and $Q_s(B_{1u}) \propto \eta_3(T)$. The admixture of $B_{1u}$ hard mode coordinates directly in the order parameter leads of course to direct proportionality $Q_s(B_{1u}) \propto \eta_3(T)$. As all these dependences are expected to hold only relatively close to a continuous phase transition and as $\eta_3(T)$ shows only small temperature dependence in the case of AS, it is practically impossible to make a definite conclusion from the temperature dependence of the structure below $T_c$. For a strongly discontinuous transition even the magnitude of the secondary frozen coordinates can be comparable to that of the frozen order parameter. Moreover, in an order–disorder system like AS it is difficult to compare the magnitude of the statistical coordinate (describing here the mean NH$_4^+$ tilt) with that of the displacive coordinates describing the distortions of individual groups.

Finally, let us comment briefly on various thermodynamic theories of AS (Ikeda et al 1973, Petzelt et al 1974, Dvořák and Ishibashi 1976, Kopsky 1976, Bajpai and Jain 1987a, b). All of them have the common feature that the order parameter is not identical with the total polarisation $P \parallel c$ even if both variables transform according to the same irreducible representation $B_{1u}$. This represents the definition of pseudo-proper ferroelectricity (Petzelt et al 1974, Dvořák 1974). The first basic question is the nature of the soft mode polarisation, which manifests itself as the critical dielectric relaxation and determines the value of the Curie–Weiss constant. Its small value indicates that the admixture of a polar coordinate to the soft mode eigenvector is very small ($\leq 10\%$). Such a small value can result from a weak coupling of pseudo-spin (NH$_4^+$) reorientation with several polar modes including internal ones. Therefore it is very difficult to specify this coupling more accurately and to elucidate the nature of the weak soft mode polarisation. Probably even the internal NH$_4^+$ ion distortions can be sufficient to explain it.

The second question concerns the nature of the spontaneous polarisation. From its peculiar temperature dependence, which differs from that of the order parameter, it is clear that it does not consist of the frozen-in soft mode polarisation only, but results as the sum of the soft and all frozen-in hard mode polarisations of $B_{1u}$ symmetry. The point charge model calculations (Jain and Bist 1974) actually showed that all three types of ions contribute comparably to $P_s$, $\langle NH_4^+ \rangle$ and $\langle NH_4^+ \rangle$ dipole moments having opposite directions. This last fact represents a natural basis for the phenomenological ferrielectric models of AS (Dvořák and Ishibashi 1976, Onodera et al 1978) which, however, do not solve the question about the soft model polarisation and its relation to $P_s$.

Our last comment concerns the temperature dependence of static permittivity in AS. It is given by the soft mode (Curie–Weiss) contribution to $\varepsilon_s(T)$ and appreciable decrease of $\varepsilon_s(T)$ and $\varepsilon_s(T)$ with decreasing temperature. Except for the soft mode contribution, our sub-millimetre values and temperature dependences (figure 3) agree with the static ones (Ikeda et al 1973). Table 1 and figure 5 show that the decrease is caused mainly by the disappearance of sub-millimetre relaxations from the dielectric spectra and partially also by reduction of the strongest lattice-mode strengths on cooling. The latter feature is probably also connected with the disorder. Both these contributions, which make
The background permittivity temperature-dependent, are usually not considered in thermodynamic theories (for a general thermodynamic theory which considers mode parameter changes induced by structural phase transitions, see Petzelt and Dvofáč (1976)) and should be subtracted from the static permittivity data before comparing the theoretical predictions with experiment. This has not been taken into account in existing thermodynamic theories of \( \text{AS} \) so far.

4. Conclusions

From combined measurements of the complete dielectric response function of \( \text{AS} \) in the 4–400 cm\(^{-1}\) range together with earlier structural and Raman data, the following conclusions can be drawn:

(i) The soft ferroelectric relaxation obeys the simple critical slowing-down law (equation (1)) with the same parameters as in the gigahertz range. Its microscopic assignment is predominantly \( B_{1u} \)-hindered rotation of \( \text{(NH}_3_2\text{SO}_4 \) groups about the \( a \) axis between two orientations which can be described in the framework of the simple pseudo-spin formalism.

(ii) No other sign of softening was detected in the higher-frequency range of \( B_{1u} \) spectra or for other polarisations (\( B_{2u} \) and \( B_{3u} \) spectra). This means that the eigenvector of the soft relaxation is not appreciably temperature-dependent in the paraelectric phase. In other words, the above assignment for the eigenvector holds in a broader temperature interval above \( T_c \).

(iii) Non-critical broad absorption was observed in the sub-millimetre range for all polarisations in correlation with the lattice disorder. It can be described by additional hard relaxations in the 20–60 cm\(^{-1}\) range and assigned to anharmonic rotations of \( \text{SO}_4^{2-}\) ions. The potential barrier for the rotation is low, \( U \leq kT \), and the rotational motion represents a crossover between quasi-harmonic and pseudo-spin behaviour.

(iv) All the lattice modes show strong broadening in correlation with increasing disorder. In agreement with group-theoretical expectation, the lattice mode response consists of several modes even if only one broad band is observed for all polarisations above \( T_c \).

(v) In the present state of knowledge it is still impossible to come to any conclusions about the accurate microscopic assignment of the weak soft mode polarisation. Therefore, it is not possible to decide between several existing thermodynamic theories. However, a complete thermodynamic theory should take into account also softening of the \( A_{1g} \) relaxation observed in Raman scattering.

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References
