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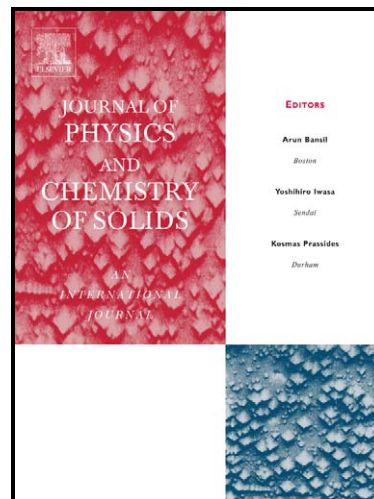
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First principles study of structural stability, electronic and related properties of $(\text{NH}_4)_2\text{SO}_4$

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Abstract

The electronic structure and related physical properties of crystalline ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, have been studied using the first principles code CRYSTAL06 at the B3LYP level of theory. The title compound has been found to possess one stable and three metastable configurations, all within the polar space group $Pna2_1$ (no. 33). Two of the metastable polymorphs are newly predicted and have not yet been observed experimentally. The different configurations show considerably varying magnitudes of the spontaneous polarization P_s . All coefficients of the elastic stiffness tensor, c_{kl} , and elastoelectrical tensor, e_{ki} have been calculated for the first time and have been found to agree satisfactorily with experimental data, as far as available.

Keywords: A. Inorganic compounds; C. Ab initio calculations; D. Elastic properties; D. Electronic structure; D. Ferroelectricity.

1. Introduction

Crystalline ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ undergoes a first-order ferroelectric phase transition at 223 K [1, 2]. Characteristic properties are a relatively small value of the Curie-Weiss constant [3] and a peculiar temperature dependence of the spontaneous polarization, which vanishes by cooling within the ferroelectric phase and changes its sign at 85 - 87 K [4, 5]. Such a complicated temperature dependence of the spontaneous polarization has been assigned to the existence of two nonequivalent ammonium groups $\text{NH}_4^{(1)}$ and $\text{NH}_4^{(2)}$, giving non equal temperature dependent contributions to the spontaneous polarization, which therefore can be regarded as of ferroelectric type [5, 6]. In both phases, four formula units $(\text{NH}_4)_2\text{SO}_4$ are in the unit cell [2, 3, 7, 8]. The transition from the space group $Pnam$ to $Pna2_1$, accompanied with the loss of the mirror plane ab and of the center of symmetry, leads to the occurrence of a spontaneous polarization along the c -axes. Despite many previous investigations, the phase transition mechanism in this crystal is still not well understood. Two different mechanisms have been suggested. The first one [9] considers the changes in the strengths of hydrogen bonds the driving force for the transition, while the second one [10, 11]

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suggests it to be a transition of order-disorder type due to the permanent dipole moments of the NH_4 groups. In [12], a phenomenological theory based on an order parameter was introduced; whereas other explanations were based on a soft mode behavior [13] or a reorientation of the complex group $\text{NH}_4^{(1)}\text{-SO}_4\text{-NH}_4^{(2)}$ [14].

One of the most important properties of ferroelectric materials is the spontaneous polarization. Only a few years ago, a sound theoretical basis for the calculation of the spontaneous polarization was given, by the modern theory of polarization [15]. According to this theory, the polarization is only defined as a difference, and a quantitative description became possible. It is thus one of the aims of this manuscript to compute properties such as the spontaneous polarization, for the title compound. Besides, the influence of elastic distortions is studied, and properties such as the piezoelectric response and elastic constants are computed.

2. Method

In the present investigation, the first-principles LCAO code CRYSTAL'06 [16] was used. A full geometry optimization was performed and the $E(V)$ curves were computed for various configurations. Subsequently, the spontaneous polarization P_s , bulk modulus B , coefficients of the elastic stiffness, c_{kl} , ($k, l = 1, 2, \dots, 6$) and coefficients of the elasto-electrical tensor e_{ik} ($i = 1, 2, 3$) were calculated using the same approach as for the earlier study of triglycine sulfate [17]. P_s , c_{kl} , and e_{ik} have been calculated in the *ab-initio* approach for the first time. These calculations thus complement previous experimental studies of the dielectric properties [18].

The calculations were done within the framework of the hybrid functional B3LYP for the exchange and correlation part of the Hamiltonian. The basis sets were chosen as follows: for sulfur a $[4s3p1d]$ basis set (the inner $[3s2p]$ shells as in [19], one more sp -shell with exponent 0.2413, and one more d -shell with exponent 0.383), for oxygen a $[4s3p]$ basis set (the inner $[2s1p]$ shell as in [20], and two more sp -shells with exponents 0.4520495 and 0.167888); for nitrogen a $[3s2p]$ basis set (as in [21], but without d -shell); for carbon a $[3s2p]$ basis set (as in [21], but without d -shell); and for hydrogen a $[2s]$ basis set (as in [21], but without p -shell). The H, C and N basis sets used correspond to the original 6-31G basis set, whereas the oxygen and sulfur basis sets are somewhat larger. A k -point sampling net of the size $4 \times 4 \times 4$ was used.

3. Results and discussion

The main part of the present study was the optimization (relaxation) of the crystal structure. The starting point was the ammonium sulfate structure in space group $Pnam$ (sequential notation 62, labeled as as62 in the following) [8] and two crystal structures in the space group $Pna2_1$ (sequential notation is 33, labeled as as33_1 and as33_2 in the following) [7]. The latter two structures in space group $Pna2_1$ correspond to the ferroelectric phase [6].

The calculation of the potential curves of the atomic configurations as62 (space group $Pnam$) and as33_2 (space group $Pna2_1$) was straightforward. The potential curve of configuration as33_1 (space group $Pna2_1$) could only be computed up to a minimum volume. When a volume reduction $\Delta V = V - V_0$ of more than $\Delta V/V_0 = -0.03$ was reached (where V_0 is the volume at the minimum in energy), the total energy E of the structure as33_1 dropped by $\Delta E \approx -0.2$ eV (red arrow in Fig. 1), and a new structure was obtained. When compressing further and again expanding, a new potential curve was obtained, labeled as as33_3.

While computing the potential curve of configuration as33_3, another discontinuity in the potential curve was found, associated with another structure, labeled as as33_4. The corresponding equation of state $E(V)$ for this fourth configuration is shown in figure 1 (magenta curve). The total energy of this configuration at the equilibrium is very close to the analogous energy for the structure as33_2 (Fig. 1). In figure 1, all $E(V)$ curves were fitted with the Murnaghan equation of state [22],

$$E(V) = E_0 + \frac{9V_0B}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B' + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}. \quad (1)$$

A view of the b -planes of the different structures is shown in figure 2. Configurations as33_1, as33_2 and as33_3 are obviously different. Although configuration as33_3 looks similar to as33_4, however, it has clearly different unit cell dimensions and is therefore different. Also, when computing the powder diffraction diagram (with the code Diamond, (<http://www.crystalimpact.com>)), then the 4 structures have a different powder diffraction diagram for the main peaks and their intensities, for angles around $2\theta = 20^\circ$. A method to test the stability of the newly predicted phases would be to compute phonon frequencies and search for imaginary frequencies. This is however not possible for general k with the present CRYSTAL'06 release, and would also be very demanding due to the unit cell size.

Within space group $Pnam$, the structure possesses an additional ab -plane of symmetry, which is perpendicular to the horizontal direction of figure 2, and, in this case, the sulfur and nitrogen atoms lie in this ab -plane of symmetry.

As it is shown in figure 1, a common tangent of $E_2(V)$ and $E_3(V)$ can be fitted (green line); or equivalently, the enthalpies $H_2(P) = H_3(P)$ are equal for the corresponding pressure (inset in figure 1) which is computed to be $P = 1.36$ GPa. This demonstrates that there is a pressure induced transition between the configurations $as33_2$ and $as33_3$.

Thus, as a first result, two new configurations of $(NH_4)_2SO_4$ in space group $Pna2_1$ have been found. The existence of these new configurations seems plausible due to the existence of three different symmetry independent molecular groups: $NH_4^{(1)}$, $NH_4^{(2)}$, and SO_4 . If we assume a fixed number of building units per unit cell, then the larger number of independent building units in space group $Pna2_1$ supplies more degrees of freedom to create more than one variant of atomic configurations, compared to the case of the space group $Pnam$ with only two symmetry independent molecular groups NH_4 , and SO_4 .

Using the experimental data of the temperature dependence of the molar specific heat $c_p = E/mol/\Delta T$ in the range from 50 to 290 K [2, 23], we have approximated the change of the internal energy by integration (inset in figure 3). The discontinuity near the Curie temperature T_C is of the order of 0.042 – 0.075 eV, per 4 formula units. This discontinuity at T_C due to the ferroelectric transition can be compared with the theoretical difference of the electronic energies $\Delta E = 0.0547$ eV of the crystal unit cell (again per 4 formula units) between the minima of the volume dependences $E(V)$ of $as62$ and $as33_2$ (figure 3) and is in the same range.

From the computed crystal structures, which were fully optimized for various fixed volumes, the volume dependences of the unit cell parameters $a(V)$, $b(V)$, and $c(V)$ were obtained. They are displayed in figure 4 together with corresponding experimental temperature dependences $a(T)$, $b(T)$, and $c(T)$ [2], extrapolated to $T = 0$ K (inset of figure 4). As the calculated lattice constants refer to $T = 0$ K, they should be compared with the corresponding experimental values at the same temperature $T = 0$ K for both structures. If we take into account that the volumes above and below the phase transition are similar [2], then we can see that c becomes larger above the phase transition (i.e. in the $as62$ structure), compared to the value of c below the phase transition, (i.e. in any of the ferroelectric phases $as33_1$, $as33_2$, $as33_3$, $as33_4$). This is in reasonable agreement with the experimental result (see the inset in figure 4). Similarly, a becomes smaller above the phase transition in the

experiment, and in the present simulation. A reasonable agreement between experiment and theory is also found for b , when the extrapolation to $T = 0$ K using a quadratic polynomial approximation is taken into account. The unit cell dimensions a , b , and c of the structures as33_3 and as33_4 are clearly different, as can be seen in figure 4. This, together with the corresponding difference of the total energies (Fig. 1), illustrates clearly that the structures as33_3 and as33_4 are two different structures.

The spontaneous polarization P_s has been calculated for the four structures in space group $Pna2_1$ on the basis of the modern Berry phase approach [15, 24-25]. According to this approach, the spontaneous polarization P_s of a crystal is the sum of the electronic P_{el} and ionic P_{ion} components [26],

$$\vec{P}_s = \int dt \frac{1}{V_{cell}} \int_{cell} d\vec{r} \vec{j}(\vec{r}, t) = \vec{P}_{el} + \vec{P}_{ion} . \quad (2)$$

The results are displayed in table 1 and figures 5–8. The magnitudes of the polarization are different which confirms that these are really four different structures.

The results on the calculated spontaneous polarization in table 1 show that the absolute magnitudes of the spontaneous polarization P_s obtained are 2-5 times greater than the maximum experimental value $P_s^{(exp)} \approx 0.006$ C/m². [4, 5, 30]. This is a very large deviation, and the spontaneous polarization in ferroelectrics using the Berry phase approach is usually relatively close to the experimental one; for instance, in the molecular crystal triglycine sulfate, the computed value of the spontaneous polarization $P_s = 0.035$ C/m² [17], is within the range of the experimental value, 0.029–0.042 C/m² [31, 32], so that the corresponding deviation is 20%; or in the case of NaNO₂ [33], the deviation of calculated and experimental values of P_s is within a few percent. An uncertainty of the experimental value of P_s is usually caused by the absence of the corresponding experimental data at the temperature $T = 0$ K. One however should take into account two points, which may reduce the difference of the calculated and experimental absolute values of P_s . Firstly, the signs of P_s is positive for two configurations and negative for the two other configurations: with the unit cell arranged as in figure 2, the sign of P_s is positive for as33_2 and as33_4, but negative for as33_1 and as33_3. As it was already mentioned, two polar atomic configurations, as33_1 and as33_2, were found experimentally [7]. Because of the opposite signs of spontaneous polarization calculated for these configurations (Fig. 5, 6) when arranged as in figure 2 and of because of the change of the sign of $P_s(T)$ as a function of temperature [4, 5], we suggest that the low temperature phase of (NH₄)₂SO₄ ($T < T_C = 223$ K) could be a mixture of the 4 polar

configurations as33_1, as33_2, as33_3 and as33_4. Therefore, the total spontaneous polarization of the crystal can be smaller than the individual magnitudes of the spontaneous polarization of the configurations as33_1, as33_2, as33_3 and as33_4. Secondly, the relative part of a certain configuration, among the four mentioned above, changes with temperature. At relatively low temperatures this part must be the greatest for the atomic configuration as33_2 possessing the lowest total energy E . As a result of this consideration and the data in figure 1 and table 1, one can expect that at a certain temperature T below the Curie temperature $T_C = 223$ K, the resultant spontaneous polarization P_s of the real crystal structure of $(\text{NH}_4)_2\text{SO}_4$ may be equal to zero, which agrees qualitatively with experiment [4, 5, 27].

As the configurations as33_1, as33_2, as33_3 and as33_4 in the ferroelectric phase have the same space group $Pna2_1$, it is possible that these four crystalline structures could exist simultaneously. Then, if taking into account different values and signs of spontaneous polarization of these structures (Fig. 5-8), and a different "population" of the various structures as a function of temperature, one could expect a complicated temperature dependence of the total spontaneous polarization. A superposition of different isomorphic crystalline structures with a temperature dependent "population" within the ferroelectric phase would imply a displacement type of phase transition rather than an order-disorder one. However, a simulation of the temperature dependence is beyond the scope of this article.

The computed Mulliken charges of SO_4 , $\text{NH}_4^{(1)}$, $\text{NH}_4^{(2)}$ for the configurations as33_1 and as33_2 (space group 33, $Pna2_1$) are presented in tables 2 and 3. The Mulliken charges are similar for both cases and confirm essentially an ionic picture, with SO_4 being close to a formal charge of -2, and similarly NH_4 being close to +1.

For the optimized crystal structure of $(\text{NH}_4)_2\text{SO}_4$ the coefficients of the elastic stiffness tensor c_{ij} ($i, j = 1, 2, \dots, 6$),

$$\sigma_i = \sum_j c_{ij} \varepsilon_j, \quad (3)$$

and the bulk modulus B ,

$$B = -V \frac{\partial P}{\partial V} = V \frac{\partial^2 E}{\partial V^2}, \quad (4)$$

have been calculated using the approach presented in [26]. For the calculation of one coefficient of the elastic stiffness tensor c_{ij} or bulk modulus B , seven distortions in the range from -3% to 3% were applied. All the coefficients of the elastic stiffness c_{ij} and elastic

compliance tensors s_{ij} of $(\text{NH}_4)_2\text{SO}_4$ have been calculated for the structure with space group $Pnam$ and two structures with space group $Pna2_1$, respectively (see tables 4 - 7).

For the crystal configurations as33_3 and as33_4 of ammonium sulphate, the corresponding bulk modulus have been found from the definition $B = V(d^2E/dV^2)$ to be 14.4 and 15.4 GPa, respectively, close to the magnitudes 12.1 and 13.7 GPa corresponding to as33_1 and as33_2 configurations (see table 6).

The computed and experimental values of the bulk modulus of the crystal in space group $Pnam$ agree excellently. The tensors of elastic stiffness c_{ij} and elastic compliance s_{ij} also agree well. It is also a affirmative, that the bulk moduli B_v (5) and B_r (6) obtained on the basis of the tensors c_{ij} and s_{ij} [34] also agree very well with the experimental data.

$$B_v = [(c_{11} + c_{22} + c_{33}) + 2 \cdot (c_{12} + c_{13} + c_{23})]/9 . \quad (5)$$

$$1/B_r = (s_{11} + s_{22} + s_{33}) + 2 \cdot (s_{12} + s_{13} + s_{23}) . \quad (6)$$

The same sets of the quantities B , c_{ij} , and s_{ij} have been calculated for ammonium sulfate in the space group $Pna2_1$ (see tables 6 and 7). The agreement with the corresponding experimental data is also good.

The coefficients of the elasto-electrical tensor e_{ki} of ammonium sulfate were calculated using the approach described in [16, 26],

$$e_{ki} = \frac{|e|}{2\pi V} \sum_l a_{kl} \frac{d\varphi_l}{d\varepsilon_i}, \quad k, l = 1, 2, 3; \quad i = 1, 2, \dots, 6 , \quad (7)$$

where V and a_{kl} are the undistorted unit cell volume and component along the cartesian axis k of the direct lattice vector \mathbf{a}_l , respectively. According to equation (6), the elasto-electric constants can be obtained by evaluating the phase φ as a function of the deformation of the unit cell parameters.

Using the dependences of the calculated Berry phases φ_1 , φ_2 , and φ_3 on the strains ε_i ($i = 1, 2, 3, 4, 5$), all elasto-electrical coefficients e_{2i} were obtained (Table 8).

The corresponding piezo-electric constants d_{ik} (Table 9) were calculated using equation (7) and the components of elastic compliance s_{ik} calculated before,

$$d_{ik} = \sum_l e_{il} s_{lk}, \quad i = 1, 2, 3 \quad k, l = 1, 2, \dots, 6 . \quad (8)$$

Taking into account the different polar atomic configurations of the crystal, the agreement of the data obtained and the existing experimental data for the constants d_{ik} is good.

4. Conclusions

The first principles code CRYSTAL'06 has been applied successfully to the study of the equation of state $E(V)$ of the ferroelectric crystal $(\text{NH}_4)_2\text{SO}_4$.

Four isomorphs of $(\text{NH}_4)_2\text{SO}_4$ have been found in space group $Pna2_1$, in which the crystal is ferroelectric. Only two of these configurations are known experimentally so far, and it would be very interesting to experimentally investigate the existence of the two new predicted configurations. The spontaneous polarization for these different atomic configurations has a very different magnitude. This agrees qualitatively with the corresponding experimental data on the characteristic temperature dependence of the spontaneous polarization of the crystal, which changes sign as a function of temperature.

The spontaneous polarization, and all components of the elastic and elasto-electric tensors of the crystal have been calculated from first principles for the first time, and a good agreement with the existing experimental data was found.

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Figure captions

of the paper “First principles study of structural stability, electronic and related properties of $(\text{NH}_4)_2\text{SO}_4$ ” by B. Andriyevsky, K. Doll, and M. Jansen

Figure 1. Total energy E as a function of the unit cell volume V for the polymorphs as33_1, as33_2, as33_3, and as33_4 (all within space group $Pna2_1$). The unit cell contains 4 formula units, and the energy is thus for 4 formula units. In the inset, the pressure dependence of the enthalpy difference $H_3(P) - H_2(P)$, for the polymorphs as33_2 and as33_3 is displayed.

Figure 2. Irreducible parts of the b -plane of the unit cell for four configurations, as33_1 (a), as33_2 (b), as33_3 (c), and as33_4 (d). The cell dimensions are given for the optimized crystal structure. Sulfur – blue, oxygen – cyan, nitrogen – olive, hydrogen – black.

Figure 3. Total energy E as a function of the unit cell volume V for the structures as62 ($Pnam$) and as33_2 ($Pna2_1$).

Figure 4. Calculated unit cell parameters a , b , and c as a function of the volume. Inset: experimental values of the unit cell parameters a , b , and c , as a function of the temperature [2].

Figure 5. Total energy E and double spontaneous polarization $2P_s$ vs unit cell volume V for configuration as33_1.

Figure 6. Total energy E and double spontaneous polarization $2P_s$ vs unit cell volume V for configuration as33_2.

Figure 7. Total energy E and double spontaneous polarization $2P_s$ vs unit cell volume V for configuration as33_3.

Figure 8. Total energy E and double spontaneous polarization $2P_s$ vs unit cell volume V for configuration as33_4.

Table 1. Spontaneous polarization P_s of the polar structures at the computed equilibrium volume V_e and for volumes $V_e \pm 10 \text{ \AA}^3$.

Atomic configuration of space group $Pna2_1$	P_s at $V_e - 10 \text{ \AA}^3$ C/m ²	P_s at V_e C/m ²	P_s at $V_e + 10 \text{ \AA}^3$ C/m ²
as33_1	-0.022	-0.025	-0.026
as33_2	0.012	0.012	0.011
as33_3	-0.025	-0.035	-0.044
as33_4 [*])	-0.017	0.018	0.052

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Table 2. Mulliken charges of the molecular groups SO_4 , $\text{NH}_4^{(1)}$, $\text{NH}_4^{(2)}$ for the configuration as33_1 in space group 33 ($Pna2_1$) ($a = 7.8961 \text{ \AA}$, $b = 11.0998 \text{ \AA}$, $c = 6.6144 \text{ \AA}$)

Group	SO_4	$\text{NH}_4^{(1)}$	$\text{NH}_4^{(2)}$
Parameter			
q_{tot}/e	-1.52	0.78	0.75
$q_{\text{S(N)}}/e$	0.29	-0.95	-0.93
$q_{4\text{O(4H)}}/e$	-1.81	1.73	1.68

Table 3. Mulliken charges of the molecular groups SO_4 , $\text{NH}_4^{(1)}$, $\text{NH}_4^{(2)}$ for the configuration as33_2 in space group 33 ($Pna2_1$) ($a = 8.3057 \text{ \AA}$, $b = 11.1990 \text{ \AA}$, $c = 6.1476 \text{ \AA}$).

Group	SO_4	$\text{NH}_4^{(1)}$	$\text{NH}_4^{(2)}$
Parameter			
q_{tot}/e	-1.52	0.74	0.78
$q_{\text{S(N)}}/e$	0.30	-0.96	-0.93
$q_{4\text{O(4H)}}/e$	-1.82	1.70	1.71

Table 4. Bulk modulus B , elastic stiffness constants c_{ij} and bulk modulus B_v of ammonium sulfate with the symmetry of space group $Pnam$ (in 10^9 N/m²)

	B	B_v	c_{11}	c_{22}	c_{33}	c_{12}	c_{13}	c_{23}	c_{44}	c_{55}	c_{66}
Present calculations	21.5	23.5	43.9	50.8	28.0	18.4	11.1	15.1	2.7	3.4	7.4
Experiment [27]	21.5	21.7	35.2	29.7	36.0	14.1	15.7	17.3	9.5	7.0	10.3
Experiment [28]	21.5	21.7	36.1	29.8	35.3	16.5	15.8	14.6	10.3	7.2	9.7
Experiment [29]	-	-	35.6	28.1	36.3	-	-	-	9.3	7.5	9.9

Table 5. Elastic compliance constants s_{ij} (in 10^{-12} m²/N) and bulk modulus B_r (in 10^9 N/m²) of ammonium sulfate in space group $Pnam$

B_r	s_{11}	s_{22}	s_{33}	s_{12}	s_{13}	s_{23}	s_{44}	s_{55}	s_{66}
21.3	27.9	44.2	25.8	-6.7	-8.1	-10.7	365	135	296

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Table 6. Bulk modulus B , B_v and elastic stiffness constants c_{ij} of ammonium sulfate for two configurations in space group $Pna2_1$ (in 10^9 N/m²)

	B	B_v	c_{11}	c_{22}	c_{33}	c_{12}	c_{13}	c_{23}	c_{44}	c_{55}	c_{66}
Configuration as33_1	12.1	15.3	38.7	38.5	22.6	12.6	3.8	2.7	8.1	4.8	10.8
Configuration as33_2	13.7	14.2	23.3	23.4	26.9	6.3	7.8	13.0	6.5	5.8	5.9

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Table 7. Elastic compliance constants s_{ij} (in 10^{-12} m²/N) and bulk modulus B_r (in 10^9 N/m²) of ammonium sulfate for two configurations in space group $Pna2_1$

	B_r	s_{11}	s_{22}	s_{33}	s_{12}	s_{13}	s_{23}	s_{44}	s_{55}	s_{66}
Configuration as33_1	13.5	29.2	29.1	45.8	-9.2	-3.9	-1.9	124	206	92.1
Configuration as33_2	13.81	48.3	59.3	53.0	-7.0	-10.6	-26.5	155	174	170
Experim. (130 K) [12]		46	50	36						

Table 8. Elastic-and-electric constants e_{ik} of ammonium sulfate for two configurations in space group $Pna2_1$ (in 10^{-3} C/m^2)

	e_{31}	e_{32}	e_{33}	e_{24}	e_{15}
Configuration as33_1	-113	-130	-153	-91.3	139
Configuration as33_2	76.9	13.3	-226	505	0.02

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Table 9. Piezo-electric constants d_{ik} of ammonium sulfate for two configurations in space group $Pna2_1$ (in 10^{-12} C/N)

	d_{31}	d_{32}	d_{33}	d_{24}	d_{15}
Configuration as33_1	-1.51	-2.44	-6.32	-11.3	28.7
Configuration as33_2	5.96	6.08	-12.8	78.0	0.004
Experiment [26]	~ 0	5.0	-4.0		

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