research papers

Anharmonicity of potentials of atoms in potassium hydrogensulfide (KDS) determined by neutron single-crystal diffraction

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Potassium hydrogensulfide (KHS) is an ionic compound with an anionic molecular group HS^-. The fast reorientational disorder of the anions was determined for the ambient temperature modification [$R\bar{3}m$; Jeffrey (1974). *Can. J. Phys.* **52**, 2370–2378]. Single crystals are available now as protonated or deuterated specimens. With neutron single-crystal diffraction at room temperature, a considerable anharmonicity of the atom potential of the H or D atoms was observed. Even the thermal motions of K and S atoms show small deviations from an isotropic probability density function, which can be modelled using anharmonic temperature factors. The temperature factors of the atoms were expanded into a Gram–Charlier series [Kuhs (1992). *Acta Cryst.* A**48**, 80–98] in order to evaluate the anharmonicity quantitatively. Parameters up to a fourth-order approximation are relevant for the D atoms. Results from neutron single-crystal diffraction are compared with split-atom models extracted from neutron powder diffraction patterns of fully deuterated samples.

1. Introduction

Hydrogensulfides of the alkali metals (MHS) are salt-like compounds, containing molecular anionic groups HS^-. These substances undergo various phase transitions as a function of temperature from a fully ordered structure at low temperatures to almost free orientational disorder of the anions before melting.

The hydrogensulfides of sodium, potassium and rubidium each exhibit three different modifications, (I), (II) and (III), as a function of temperature, which are isotypic of the different cations (Jacobs *et al.*, 1991). Therefore, the main varying factor is the radius of the cations. Their crystal structures are related to the NaCl type. The anions are antiferroelectrically ordered in the monoclinic low-temperature modification (I). A split position model of the H atoms is established in the rhombohedral modification (II), which is stable for KDS between $T = 426$ and 101 K. The split positions are linearly connected *via* S atoms. The anions align along the c axis of the hexagonal unit cell (see Fig. 1). The probability density function (p.d.f.) of the H atoms is smeared in the cubic high-temperature modification (III). Nevertheless, a split position model is favoured to describe the p.d.f. of the H atoms.

Several studies using IR, Raman and NMR spectroscopy, as well as inelastic neutron scattering, focus on the reorientational disorder of the anions of these compounds (Rush *et al.*, 1973; Beckenkamp & Lutz, 1994; Jeffrey, 1974). Additional investigations in order to study the crystal structure were performed with X-ray and neutron powder diffraction (Schroeder *et al.*, 1973; Jacobs *et al.*, 1991). Our aim was to

study the structure and the dynamics of these compounds crystallizing isotypically as a function of the radius of the cations. Therefore, we have investigated these compounds using elastic and quasielastic neutron scattering and solid-state NMR (Haarman, Jacobs, Asmussen *et al.*, 2000; Haarmann, Jacobs & Kockelmann, 2000; Haarmann, 2000).

Owing to the strong incoherent scattering of neutrons by hydrogen and the limitations of beam time we restricted ourselves to the fully deuterated samples of the sodium and potassium compounds for the neutron powder diffraction experiments. These studies were carried out in the temperature range from T = 4 to 470 K (Haarmann, Jacobs & Kockelmann, 2000). For these substances differences in the mechanism of phase transitions are expected (Beckenkamp & Lutz, 1994). We used the high-resolution time-of-flight diffractometer ROTAX (ISIS, UK) for our investigations. A large anisotropy of the p.d.f. of deuterium was observed in all modifications, caused by the librational motion of the anions. However, diffraction patterns obtained in the rhombohedral modification (II) of MDS show significant deviations from the calculated patterns, even if the anisotropy of the p.d.f. of deuterium is considered (Haarmann, Jacobs & Kockelmann, 2000).

The structure of modification (II) is described by a hexagonal setting in space group $R\bar{3}m$ with one split position of deuterium [D1, Wyckoff site 6(c)]. Presentations of the crystal structure and crystallographic settings are given in Fig. 1 and Table 1, respectively. Fourier sections of the *ab* plane at the *z* position of the D atoms indicate a triangular shaped p.d.f., which can be modelled by introducing a second site for deuterium [D2, Wyckoff site 18(h), see Table 1]. The p.d.f. is given by a superposition of both sites D1 and D2 with a different occupation.
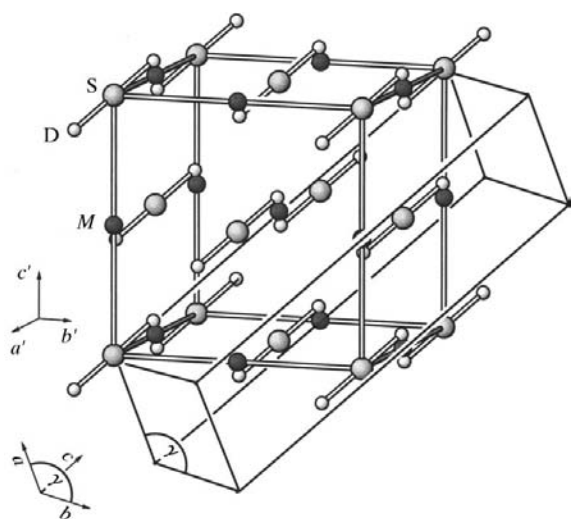

Figure 1
Idealized structure of the rhombohedral modification (II) of MDS with M = Na, K, Rb. Two different orientations of the anions are indicated by a two-site split position of the D atoms (small spheres). The orientation of the rhombohedral unit cell (*a*, *b*, *c*), space group $R\bar{3}m$, with respect to the unit cell of the cubic modification (III) (*a′*, *b′*, *c′*) is indicated.

Table 1
Modified structural model of *M*DS with M = Na, K, Rb in the rhombohedral modification (II).

The standard model includes only the position D1 for deuterium. Space group $R\bar{3}m$.

Atom	Wyckoff position	x	y	z
M	3(a)	0	0	0
S	3(b)	0	0	1/2
D1	6(c)	0	0	z
D2	18(h)	x	$-x$	z

A problem known for such models is a correlation of the parameters of both sites. Therefore, we repeated our measurements several times with different samples and experimental settings. To improve the quality of the data we measured at room temperature without any additional sample environments such as a cryostat or furnace, which would add a considerable amount of background to the diffraction patterns. Nevertheless, determination of the atomic displacement parameters from powder diffraction data is difficult because of correlations between background, displacement and absorption parameters. In addition, the overlap of the reflections in a powder pattern causes a problem since the results of refinement are somewhat dependent on the structural model.

These problems can be overcome by the use of single-crystal diffraction. Moreover, the signal-to-background ratio is very much improved compared with powder diffraction. Apart from split-atom models (Itoh & Nakamura, 1996; Bachmann & Schulz, 1984), anharmonic temperature factors (Kuhs, 1992) are useful to model this type of deformation of a p.d.f. Computer programs for Rietveld refinement of time-of-flight diffraction patterns able to handle these anharmonic temperature factors are not available.

2. Experimental

The hydrogensulfides of all the alkali metals except lithium are available as protonated or deuterated samples. For details see Jacobs *et al.* (1991). They are sensitive against reaction with moist air. Therefore, an inert gas atmosphere is necessary to handle these substances. Single crystals of the potassium and rubidium compound can be synthesized by recrystallization of the samples from liquid ammonia at ambient temperature and 7 bar pressure of the solvent. Carefully handled glass containers were used to grow the crystals by slow evaporation of the solvent. The temperature was controlled by a thermostat during the process. For details see Haarmann (2000). Protonated and deuterated crystals can be obtained by the choice of solvent: NH_3 or ND_3, respectively. Single crystals of NaHS/DS are not available by this method. A reaction of the salt with the solvent gives $NaNH_2$ and NH_4HS as the main products of this reaction.

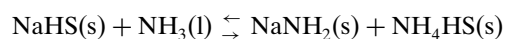$$NaHS(s) + NH_3(l) \underset{\rightarrow}{\leftharpoondown} NaNH_2(s) + NH_4HS(s)$$

Table 2
Experimental settings for neutron single-crystal diffraction on KDS at room temperature.

The E5 diffractometer at BENSC HMI, Germany, was used.

λ (Å)	0.912
Sample range (°)	$6 \leq \theta \leq 52$
h, k, l	$-8/7, -7/8, -17/9$
Number of reflections	659
with $I > 3\sigma(I)$	368
Number of symmetry-inequivalent reflections	161
with $I > 3\sigma(I)$	100
R_{int}(all/obs)	0.067/0.045
Crystal size (mm³)	$3.2 \times 2.6 \times 1.5$
μ (cm^{-1})	0.1887
Correction for absorption	Gaussian
Transmission (min/max)	0.946/0.968
Crystal colour	Colourless, transparent
a (Å)	4.988 (3)
c (Å)	9.997 (7)
V (Å³)	215.4 (3)
Number of parameters	12
R_{F_o}(all/obs)	0.122/0.058
R_{wF_o}(all/obs)	0.031/0.029

Table 3
Quality of the refinements for different models of the D atom distribution in KDS at room temperature.

Model	No. of parameters	R_{wF_o}(all)	g.o.f.
Standard model, isotropic	4	0.102	5.75
Standard model, anisotropic	6	0.076	4.27
Expanded model, Wyckoff 6(c) and 18(h)	9	0.032	1.84
Anharmonic third order	9	0.036	2.02
Anharmonic fourth order	12	0.031	1.75
Anharmonic fifth order	15	0.030	1.72

Two data sets were collected on the E5 four-circle single-crystal diffractometer (Robertson, 1996) at the Hahn–Meitner Institut in Berlin, Germany, using a wavelength of λ = 0.912 Å. The data of the protonated sample suffer from bad counting statistics and will not be discussed here in detail. A fully deuterated crystal of approximately $3.2 \times 2.6 \times 1.5$ mm³ was measured with adequate counting statistics. The experimental details are summarized in Table 2.[1]

The crystal was fixed with dry high-vacuum grease in a quartz capillary and mounted on a goniometer head.

The data were analyzed and refined with the computer program package *JANA*98 (Petricek & Dusek, 1998). The scattering lengths used are b(K) = 3.71, b(S) = 2.84 and b(D) = 6.674 fm (Sears, 1992). A numerical correction for absorption was applied. For extinction correction an isotropic Zachariasen model with Gaussian mosaic spread was applied. Refinement of the g value of extinction resulted in a value close to zero not significantly larger than its standard deviation. Therefore, this correction has been dropped. Thermal diffuse scattering (TDS) corrections were not taken into account.

3. Results and discussion

Several models were applied. Hamilton's test (Hamilton, 1974) with a 0.5% significance level was used to validate improvements of the models. As a start model we used the results of Jacobs *et al.* (1991). In agreement with observations from neutron powder diffraction (Haarmann, Jacobs & Kockelmann, 2000), an improvement was achieved by intro-

ducing an anisotropic thermal motion of D atoms (see Table 3). Nevertheless, the results were not satisfactory. Difference Fourier patterns show positive difference density for D atoms at the corners of a triangle and negative difference density on the corners of a triangle rotated by 60° with respect to the first. The negative differences occur on a line between K and D atoms (see Fig. 2). A test of the model extracted from the neutron powder diffraction data yields an acceptable result (see Table 3). Apart from the lattice parameters the results agree within estimated errors to the mean value of the parameters from four diffraction experiments of powdered samples. The difference in lattice parameters is caused by the fact that an individual single crystal can differ from the average of a powder sample. A simultaneous Rietveld refinement of all the powder diffraction patterns, obtained from different KDS powder samples with different experimental settings, did not significantly improve the quality of individual fits (see Table 4).

Some components of the tensor, describing the anharmonic temperature factor, do not differ significantly from their estimated standard deviations. They were set to zero for the final refinement (see Table 3). Refinement of third-order coeffi-
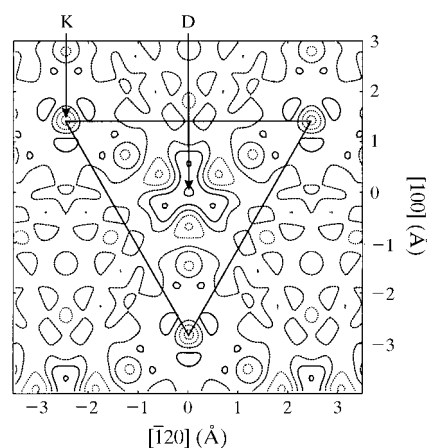
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[1] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD411446, the name of the author(s), and the citation of the paper. Supplementary data for this paper are available from the IUCr electronic archives (Reference: SN0007). Services for accessing these data are described at the back of the journal.

Figure 2
Difference Fourier expansion of the structure factors for KDS (II) after refinement considering the anisotropic motion of D atoms. Scattering densities less than or equal to zero are indicated by dotted lines. Solid lines indicate the positive scattering density. The levels are scaled to the maximum difference scattering by $-2/4$, $-1/4$, 0, 1/4, 2/4. The three positions of the K atoms are linked with full lines.

Table 4
Comparison of the results obtained with powder and single-crystal diffraction on KDS at room temperature.

Sample	1	2	3	4	Simultaneous refinement	Mean value	Single crystal
a (Å)	4.9559 (1)	4.9561 (1)	4.9563 (1)	4.9564 (1)	4.95608 (4)	4.9561 (2)	4.988 (3)
c (Å)	9.9220 (2)	9.9240 (2)	9.9266 (2)	9.9281 (2)	9.9257 (1)	9.925 (2)	9.997 (7)
$\langle u_{iso}^2(M)\rangle$ (Å^2)	0.0407 (7)	0.0436 (7)	0.0408 (7)	0.0447 (8)	0.0439 (3)	0.043 (2)	0.0402 (2)
$\langle u_{iso}^2(S)\rangle$ (Å^2)	0.0377 (7)	0.0379 (6)	0.0354 (7)	0.0328 (4)	0.03443 (6)	0.036 (2)	0.0327 (2)
z(D1)	0.3654 (5)	0.3634 (8)	0.3659 (4)	0.3666 (4)	0.3650 (4)	0.365 (1)	0.3643 (3)
Occupancy (D1)	0.78 (2)	0.62 (3)	0.76 (2)	0.82 (9)	0.74 (2)	0.74 (8)	0.68 (2)
$\langle u^2(D1)\rangle$ (Å^2)	0.0678†	0.0530†	0.0600†	0.0727†	0.0659†	0.064(8)	0.063†
$\langle u_{11}^2(D1)\rangle$ (Å^2)	0.081 (1)	0.066 (5)	0.076 (2)	0.085 (2)	0.079 (2)	0.077 (7)	0.078 (1)
$\langle u_{33}^2(D1)\rangle$ (Å^2)	0.041 (2)	0.027 (4)	0.027 (2)	0.048 (1)	0.041 (1)	0.037 (9)	0.0325 (8)
d(D1−S) (Å)	1.335 (5)	1.356 (8)	1.331 (4)	1.324 (4)	1.340 (4)	1.34 (1)	1.355 (3)
x(D2)	0.082 (5)	0.067 (8)	0.085 (5)	0.083 (3)	0.074 (7)	0.078 (8)	0.067 (1)
z(D2)	0.392 (7)	0.387 (2)	0.392 (3)	0.397 (3)	0.393 (1)	0.392 (4)	0.3909 (9)
$\langle u_{iso}^2(D2)\rangle$ (Å^2)	0.062 (7)	0.068 (4)	0.082 (6)	0.025 (5)	0.045 (6)	0.07 (2)	0.058 (2)
d(D2−S) (Å)	1.29 (2)	1.26 (1)	1.30 (2)	1.24 (1)	1.233 (6)	1.26 (3)	1.233 (8)

† Determined from the anisotropic thermal displacement of deuterium.

cients is nearly as good as the split-atom model, but including fourth-order approximation improves the fit. Fifth-order parameters are not significant (see Table 3).

Fourier sections of the *ab* plane orthogonal to the DS bond of the anions with $z = z_D$ and the *ac* plane with $y = 0$, showing a section through the anion, are presented in Fig. 3. The triangular shape of the p.d.f. of the D atoms is clearly visible in Fig. 3(a). This can be interpreted considering a librational motion of the anion restricted by the neighbouring atoms. The asymmetry of the p.d.f. of the D atoms along the [100] direction indicates the same situation. The extension is small in the direction of the nearest cation (negative x value) and large in the opposite direction. The curvature of the p.d.f. is caused by the librational motion of the anion.

The p.d.f. of the S atoms is slightly expanded along the [001] direction. This can be explained by a translational motion of
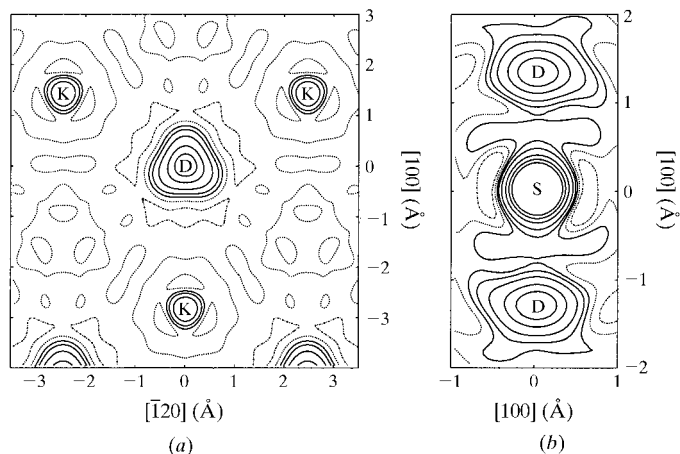
the whole ion into that direction. Another explanation may be a coupling of rotational and translational motion. That means that the centre of sulfur is shifted along the [001] direction with the orientation of the hydrogen and into the opposite direction. The observed p.d.f. is a superposition of both orientations.

Even the p.d.f. of the K atoms is not isotropic (see Fig. 3a). The anisotropy of the p.d.f. for K and S atoms are due to fourth-order anharmonic contributions to the temperature factors. However, refining these parameters did not improve the results of the fit significantly. The ratio of symmetry-independent reflections to parameters is 7.3 and the system tends to be underdetermined. Therefore, only a qualitative description of the observations can be given.

For the final refinement a model with isotropic thermal motion for S and K atoms was used. The results from this refinement are summarized in Table 5. Fig. 4 shows the p.d.f.s of the atoms for a coordination polyhedron of the anions.

The p.d.f.(u) of an atom shifted by u is linked to the so-called isolated atom potential (IAP) by (Kuhs, 1992)

$$V(u) = -k_B T [\ln p.d.f.(u) - \ln p.d.f.(u = 0)].$$

Here k_B is Boltzmann's constant and T is the absolute temperature. The isolated atom potential (IAP) obtained from the anharmonic temperature factor of deuterium differs much from the harmonic potential obtained from the anisotropic
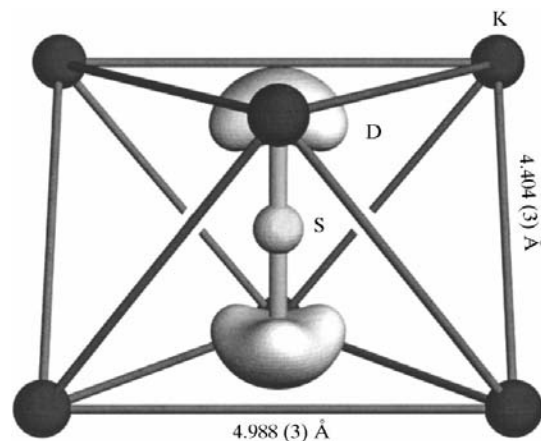

Figure 3
Fourier expansion of the structure factors for KDS (II). Scattering density less than or equal to zero are indicated by dotted lines. Full lines indicate the positive scattering density. The levels are scaled to the maximum of scattering, which is found at the center of sulfur, by −1/40, 0, 1/40, 2/40, 4/40, 6/40, 8/40, 16/40. The positions of the atoms are marked. (a) *ab* plane with $z = z_D = 0.3736$; (b) *ac* plane with $y = 0$.

Figure 4
Probability density of KDS at room temperature, modification (II), obtained from single-crystal diffraction. The p.d.f. of the D atom is scaled to ∼75% nuclear density. The nuclear density of the S and K atoms is reduced to ∼50% to focus on the p.d.f. of deuterium. The figure is based on the final results: fourth-order Gram–Charlier expansion for the temperature factor of deuterium and isotropic thermal displacement for S and K atoms.

Table 5
Parameters of the atoms for KDS at room temperature.

Results obtained by least-squares refinement of single-crystal data. The temperature factor of deuterium was expanded into a fourth-order Gram–Charlier series.

$\langle u^2_{iso}(K)\rangle$ (Å^2)	0.0403 (2)	$\langle C_{111}(D)\rangle \times 10^3$ (Å^3)	−0.226 (5)
$\langle u^2_{iso}(S)\rangle$ (Å^2)	0.0322 (2)	$\langle C_{113}(D)\rangle \times 10^3$ (Å^3)	0.059 (2)
$z(D)$	0.3736 (2)	$\langle C_{123}(D)\rangle \times 10^3$ (Å^3)	0.0295 (8)
$\langle u^2_{iso}(D)\rangle$ (Å^2)	0.1024 (7)	$\langle C_{333}(D)\rangle \times 10^3$ (Å^3)	0.0088 (8)
$\langle u^2_{11}(D)\rangle$ (Å^2)	0.1196 (7)	$\langle D_{1111}(D)\rangle \times 10^4$ (Å^4)	0†
$\langle u^2_{33}(D)\rangle$ (Å^2)	0.068 (2)	$\langle D_{1113}(D)\rangle \times 10^4$ (Å^4)	−0.037 (3)
		$\langle D_{1133}(D)\rangle \times 10^4$ (Å^4)	0.011 (1)
		$\langle D_{3333}(D)\rangle \times 10^4$ (Å^4)	0.067 (9)

† Value fixed to zero.

temperature factor of deuterium. It is hard along the direction of the cations and soft along the bisection of the coordinating cations. To check the physical relevance of the IAP of the atoms neutron single-crystal diffraction data must be collected at different temperatures.

4. Conclusions

Single-crystal neutron diffraction has clearly shown that the potential of the D atoms in the hydrogensulfide of potassium is strongly anharmonic. This is due to the repulsive forces between cations and D atoms which influence the librational motion of the anions. A deviation from an isotropic p.d.f. of S and K atoms is visible in Fourier sections, but cannot be quantified by the data.

Qualitative information on the anharmonic motion of D atoms in KDS was already obtained by powder diffraction data. Reflection profile decomposition using the Rietveld method is required to extract more quantitative information from powder data, but current computer programs do not include the Gram–Chalier series expansion.

Rather than powder diffraction, which suffers from peak overlap, single-crystal diffraction yields unambiguous quantitative information about the density distribution.

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