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Coherent neutron scattering amplitudes of Br and ^{127}I.* By M. ATOJI, *Chemistry Division, Argonne National Laboratory, Argonne, Illinois* 60439, *U.S.A.*

Neutron diffraction data of KBr and KI yielded the thermal neutron coherent scattering amplitudes in 10^{-12} cm, $b(Br) = 0.670 \pm 0.004$, $b(^{127}I) = 0.525 \pm 0.004$, taking $b(K) = 0.370 \pm 0.001$ as standard.

Neutron powder diffraction measurements of KBr and KI yielded the coherent neutron scattering amplitudes in ratios $b(Br)/b(K) = 1.81 \pm 0.01$ and $b(^{127}I)/b(K) = 1.42 \pm 0.01$ respectively. Uncertainties quoted are standard deviations. The pioneer research of Shull & Wollan (1951) gave $b(K) = 0.35$, $b(Br) = 0.67$ and $b(^{127}I) = 0.52$, all in 10^{-12} cm. Recently, Koester & Knopf (1972) obtained $b(K) = 0.371$, $b(Br) = 0.677$ and $b(I) = 0.528$, all with ± 0.002. Brown & Walker (1966) reported $b(K) = 0.370 \pm 0.004$, and Bacon & Plant (1968) obtained $b(K) = 0.369 \pm 0.003$. The agreement among the last three $b(K)$'s is excellent and the weighted average is $b(K) = 0.370 \pm 0.001$. Using this $b(K)$, our data lead to $b(Br) = 0.670 \pm 0.004$ and $b(I) = 0.525 \pm 0.004$. The $b(Br)$ and $b(I)$ values obtained from the Bragg diffraction intensities (Shull & Wollan, and the present work) agree satisfactorily with those deduced from the Christiansen-filter small-angle scattering (Koester & Knopf, 1972). The weighted averages are $b(Br) = 0.676 \pm 0.001$ and $b(I) = 0.527 \pm 0.001$, both of which may now be considered as the firmly established amplitude values.

Our samples are Johnson Matthey's spectrographically certified KI, Fisher certified KI and KBr, and Harshaw Optical KI and KBr crystals. These were ground down to < 200 mesh in particle size and were dried in air at 150°C for several hours. The powder was then packed into a thin-walled null-matrix Ti–Zr holder 1 cm in diameter. The diffraction data were taken with 1.069 Å at 23°C. The higher-order wavelength contamination is less than 0.04%. Some samples gave weak extraneous peaks or abnormal diffuse scattering other than the intrinsic thermal scattering (Chipman & Paskin, 1959; Iveronova, Parogtopa & Zvyagina, 1967; Kashiwase, 1968). These samples were discarded. At least six independent measurements were made on each reflection. The graphical plotting, log F_{obs} *vs.* (sin $\theta/\lambda)^2$, was

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

made on the isolated all-even reflections, 200, 220, 222, 400, 422, 440 and 620. The overlapped peak groups are {331, 420} and {531, 600, 442}. These were resolved using the Gaussian profile analysis. The odd-reflection plotting was then made using 111, 311, 331, 511, 333 and 531. The linear least-squares method was then applied to each set of scanning data with and without appropriate weighting factors. The statistical averages of the resultant parameters were employed in the scattering amplitude determination. The Debye–Waller coefficients in $Å^{-2}$ are $B(K) = 2.6 \pm 0.2$ and $B(Br) = 2.5 \pm 0.2$ for KBr and $B(K) = 3.4 \pm 0.3$ and $B(I) = 2.7 \pm 0.2$ for KI. Wasastjerna (1946) obtained $B(K) = 2.06$ $B(Br) = 1.92$ for KBr and $B(K) = 2.69$ and $B(I) = 2.37$ for KI at 293°K, some of which are significantly different from our values. The following B values are insignificantly different from ours: $B(K) = 2.45$ and $B(Br) = 2.23$ for KBr at 300°K (Meisalo & Inkinen, 1967); $B(K) = 3.66$ and $B(I) = 2.92$ for KI at 296°K (Pearman & Tompson, 1967).

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Anomalous neutron scattering and the question of ferroelectricity in $^6Li(N_2H_5)SO_4$. By M. R. ANDERSON and I. D. BROWN, *Department of Physics, McMaster University, Hamilton, Ontario, Canada*

The mechanism of the supposed ferroelectric switching in crystals of $Li(N_2H_5)SO_4$ was examined by studying the effect of the anomalous scattering of neutrons from ^6Li on the structure factors of Bijvoet pairs both before and after ferroelectric switching. The absence of any observable change confirms the results of Schmidt, Drumheller & Howell [*Phys. Rev.* (1971). B**12**, 4582] that $Li(N_2H_5)SO_4$ is not ferroelectric.

Introduction

The apparent ferroelectric nature of lithium hydrazinium sulphate, $Li(N_2H_5)SO_4$, was reported by Pepinsky, Vedam, Okaya & Hoshino (1958). They observed good hysteresis

loops from about -15 to 80°C, although they could find neither a dielectric peak between -196 and 140°C nor a specific heat anomaly between -120 and 205°C.

The crystal structure has been investigated by X-ray diffraction (Niizeki & Koizumi, 1964; Brown, 1964; and

Van den Hende & Boutin, 1964) and by neutron diffraction for both a normal (Padmanabhan & Balasubramanian, 1967) and a deuterated sample (Ross, 1970). The crystals are orthorhombic, space group $Pna2_1$, with lattice parameters $a = 9.94$, $b = 8.99$, $c = 5.18$ Å and four molecules in the unit cell. The permanent dipole moment lies along the c direction. The structure is composed of a $LiSO_4^-$ framework of corner-sharing oxygen tetrahedra with channels which run along the c direction and contain the hydrazinium ions. The NH_3^+ group of the hydrazinium ion forms three hydrogen bonds to the framework and the NH_2 group forms one hydrogen bond to the framework and one to the NH_2 group related by the c screw axis to give an ordered N–H$\cdots$N–H chain directed along the negative c direction.

Vanderkooy, Cuthbert & Petch (1964) showed that proton conduction along this chain gives rise to large conductivity in the c direction, an effect which prevents the hysterisis loops being observed above 80°C. Cuthbert & Petch (1963) have also studied the proton magnetic resonance signals and concluded that at room temperature the NH_3^+ group rotates about the N–N axis, whereas the onset of rotation of the NH_2 group occurs between 50 and 150°C.

The supposed ferroelectric switching in $Li(N_2H_5)SO_4$ was thought to result from one of two mechanisms. The first involves only the reorientation of the hydrogen bonds from the negative to the positive c direction. Such a realignment would produce a change in polarization of the right order of magnitude. As the $LiSO_4^-$ framework is non-centrosymmetric, oppositely switched domains would have crystallographically distinct structures. In the second mechanism the hydrogen bonds reorient and in addition the framework changes from a right-handed to a left-handed form. The resulting structure is the enantiomorph of the original structure but the two are otherwise crystallographically equivalent. By examining the changes which occur in the neutron structure factors of Bijvoet pairs during ferroelectric switching we hoped to distinguish between these two mechanism.

In this experiment we made use of the anomolous scattering of neutrons by ^6Li by comparing the ratio $I_{hkl}/I_{\bar{h}\bar{k}\bar{l}}$ ($= x/y$) of a set of reflexions with the ratio for these reflexions when the crystal had been poled* in the opposite

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* We use the verb 'pole' to indicate the process by which the crystal is placed for a short period in an electric field of 630 V/cm. Such a field should be sufficient to produce a single domain in the crystal if it is ferroelectric since it is greatly in excess of the coercive field of 320 V/cm reported by Pepinsky et al. (1958).

sense. After poling, the ratio would be y/x if the structure inverts. If the poling only reorients the hydrogen bond then a different structure results and the individual intensities will change to give a ratio in general different from either y/x or x/y.

Although the predicted effect is small and would normally be masked by experimental errors arising from absorption and extinction, it is possible to measure the ratio by making the measurements on a single reflexion both before and after domain reversal. The ratio of the structure factors before (F) and after (F') application of a reversing field is:

$$R_o = \frac{|F|}{|F'|}.$$

The constant of proportionality relating $F . F^*$ to I is identical for both measurements since both are made on the same reflexion under identical conditions. Hence

$$R_o = \left(\frac{I}{I'}\right)^{1/2}.$$

If the structure inverts on switching by a reversal of the c direction the hkl reflexion becomes the $hk\bar{l}$ reflexion and since $|F_{hk\bar{l}}| \equiv |F_{h\bar{k}\bar{l}}|$ in the space group $Pna2_1$,

$$R_o^2 = \frac{I}{I'} = \frac{I_{hkl}}{I_{hk\bar{l}}} \equiv \frac{I_{hkl}}{I_{\bar{h}\bar{k}\bar{l}}}.$$

The values of x/y [$= R_c^2(b)$] and y/x [$= R_c^2(c)$] can be calculated from the known structure and compared with the observed values R_o^2. Values of R_c^2 can also be calculated for the mechanism in which only the hydrogen atoms move along the chain by calculating values of I from the coordinates of Padmanabhan & Balasubramanian (1967) and values of I' from a similar model in which H(2) is moved to the opposite end of its hydrogen bond. A third possibility is that no change occurs in the crystal and in this case $R_c^2(a) \equiv 1$ for all reflexions.

Experimental method

$^6Li(N_2H_5)SO_4$ single crystals were prepared by evaporation from an aqueous solution of isotope separated $^6LiCO_3$ (at.% ^6Li, 95.54) and $N_2H_6SO_4$. A crystal which measured approximately $4 \times 7 \times 8$ mm was chosen and mounted on a goniometer with poling electrodes on its (001) faces. Intensity measurements were made on a four-circle neutron diffractometer using an ω scan and a wavelength of 1.062 Å.

Values of Fc_{hkl} and $Fc_{\bar{h}\bar{k}\bar{l}}$ were calculated using the scattering lengths given by the Neutron Diffraction Commis-

Table 1. *Observed and calculated values of the ratio of the structure factors*

hkl	R_o	σ	$R_c(a)$	$R_c(b)$	$R_c(c)$	$R_c(d)$	$R_c(e)$
031	1.015	0.025	1.000	1.062	0.942	1.376	1.396
0$\bar{3}$1	0.980	0.033	1.000	1.062	0.942	1.376	1.396
151	0.976	0.024	1.000	0.959	1.043	1.064	1.065
1$\bar{5}$1	0.981	0.027	1.000	0.959	1.043	1.064	1.065
$\bar{1}$51	1.021	0.025	1.000	0.959	1.043	1.064	1.065
$\bar{1}\bar{5}$1	1.040	0.030	1.000	0.959	1.043	1.064	1.065
113	1.010	0.062	1.000	1.051	0.952	0.985	0.984
113	1.088	0.046	1.000	1.051	0.952	0.985	0.984
1$\bar{1}$3	0.997	0.044	1.000	1.051	0.952	0.985	0.984
1$\bar{1}$3	0.962	0.038	1.000	1.051	0.952	0.985	0.984
$\bar{1}$13	1.060	0.063	1.000	1.051	0.952	0.985	0.984
$\bar{1}\bar{1}$3	1.002	0.053	1.000	1.051	0.952	0.985	0.984
$\bar{1}\bar{1}$3	0.909	0.071	1.000	1.051	0.952	0.985	0.984

sion (1969) and the coordinates of Padmanabhan & Balasubramanian (1967). From these a set of reflexions was chosen which showed significant Friedel inequalities. The crystal was poled and the intensity of the Bragg reflexion I measured. The crystal was then poled in the opposite sense and the new intensity I' measured. This was repeated on a set of 10 reflexions. From these intensities the ratios R_o $[=F_o/F'_o=(I/I')^{1/2}]$ were calculated.

Discussion

The ratio R_o of the observed structure factors and the error σ in R_o arising from counting statistics are shown in Table 1. Also shown are calculated values of the ratio R_c for several cases: (a) no structural change, (b) inversion of the cell, hkl to $hk\bar{l}$, (c) inversion of the cell, hkl to hkl, (d) reorientation of the hydrogen bonds from along $-\mathbf{c}$ to $+\mathbf{c}$ (e) reorientation of the hydrogen bond from along $+\mathbf{c}$ to $-\mathbf{c}$.

The correctness of each model was tested using a χ^2 test:

$$\chi^2 = \sum_{i=1}^{n} \frac{(R_{oi}-R_{ci})^2}{\sigma^2}$$

where the sum is performed over the 13 independent measurements.

Table 2 shows the values of χ^2 and the probability that a second experiment would have a larger value of χ^2 if the model is correct. It is evident that model a is overwhelmingly more probable and that no structural change occurs on reversal of the poling field. After we had finished our experiment Schmidt, Drumheller & Howell (1971) published the results of their extensive investigation of the dielectric properties of $Li(N_2H_5)SO_4$ which they conclude is not ferroelectric. They are able to account for the hysteresis loops by a mechanism of partially blocked conduction along the hydrogen bond chains. Our failure to observe any permanent alteration in the molecular structure of the crys-

tal as a result of poling is in agreement with their results and confirms the fact that it is not possible to reverse the permanent dipole moment of $Li(N_2H_5)SO_4$.

Table 2. *The values of χ^2 and probability for each model*

Model	χ^2	Probability
(a)	11·19	59%
(b)	36·53	< 1%
(c)	37·67	< 1%
(d)	376·73	≪ 1%
(e)	414·72	≪ 1%

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International Union of Crystallography

Report of Executive Committee for 1971

Personal Notes

The crystallographic world lost three of its most distinguished members in 1971. Professor Dame Kathleen Lonsdale died on 1 April. She was Professor of Chemistry and Head of the Crystallography Laboratory, University College, London from 1949 to 1968. Her many contributions to crystallography included her work as General Editor of the three volumes of *International Tables for X-ray Crystallography*. She was one of the first women to be elected Fellow of the Royal Society and the first woman President of the British Association for the Advancement of Science. As President of the International Union of Crystallography she chaired the sessions of the Seventh General Assembly in Moscow, in 1966.

On 1 July Sir Lawrence Bragg died at the age of 81. In conjunction with his father, Sir William Bragg, he carried

out the earliest crystal structure determinations by X-ray spectrometry, receiving for this work the Nobel Prize for Physics in 1915. It was as a result of these investigations that it first became possible to obtain absolute values of lattice parameters. Sir Lawrence and his school thereafter developed the quantitative aspects of X-ray diffraction techniques and worked out large numbers of more complicated crystal structures, especially those of silicate minerals. Sir Lawrence took a leading part in the formation of the International Union of Crystallography in 1947, and was its first President.

Professor J. D. Bernal died in September at the age of 70. He was a pioneer in the application of crystallographic methods to biological materials and carried out some of the early work on hormones and vitamins. His X-ray photographs of pepsin in 1933 were the first ever taken of single crystals of a protein. Professor Bernal was for many years