NQR and Neutron Diffraction in Scheelites *

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Measurements of the spin-lattice relaxation time for rhenium in $KReO_4$ and NH_4ReO_4 are reported; relaxation rates are extremely fast due to the large quadrupole moment of Re. Calculations of the electric field gradient in $KReO_4$ show that the EFG is a very sensitive function of the orientation of the anion in the unit cell as well as of the unit cell dimensions, and that geometrical effects make a major contribution to the temperature dependence. Neutron diffraction in these two salts has been employed to determine the temperature dependence of structural parameters over a wide range of temperature, and preliminary results are reported.

Key words: NQR, Relaxation, Electric field gradient, Neutron diffraction.

I. Introduction

The anomalous properties of the ammonium scheelites [1] have been explained in terms of a pseudo-spin theory [2, 3] based upon the two possible orientations of the ammonium ions in the surrounding cage of eight oxygen atoms; a projection of part of the unit cell is shown in Figure 1. The two orientations are of different energy due to the difference in the N–O distances, and the energy splitting is assumed to be a function of one component of strain which measures the distortion of the unit cell. The work reported in this paper is directed towards experimental testing of the assumptions and predictions of this theory.

In Sect. II, measurements on spin-lattice relaxation of Re in $KReO_4$ and NH_4ReO_4 are reported. In Sect. III, point charge calculations are used to determine the dependence of the electric field gradient at the Re site on the structural parameters of $KReO_4$, and in Sect. IV, a preliminary report is given of some features of neutron diffraction of ND_4ReO_4.

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II. Spin-Lattice Relaxation

It is known from ^1H NMR relaxation time measurements that the ammonium ion in NH_4ReO_4 is in rapid rotation at all temperatures [4]. The analysis is not sensitive to details of the reorientational motion and uses a single correlation time, but the temperature dependence of T_1 and $T_{1\varrho}$ calculated from standard theory agrees well with the observations.

In the scheelite structure, each anion is surrounded by eight ammonium ions, four of them at the same height along the c-axis, and the other four displaced by $\pm c/4$ along the c-axis. At low temperature the ammonium ions are all oriented towards axial oxygen atoms [5], and so each anion is coordinated only to the NH_4^+ ions which are displaced along the c-axis. In this situation, reorientation of an NH_4^+ ion from an axial to another axial orientation is effective in proton relaxation but does not change the electric field gradient (EFG) at the anion (except during the jump), and so is ineffective in quadrupolar relaxation of Re. At higher temperatures, the pseudo-spin theory postulates that each NH_4^+ ion takes its equatorial orientation for some of the time, with a probability approaching 0.5 at high temperature. Thus each NH_4^+ ion adjacent to a given anion makes jumps from axial to equatorial and vice-versa. The result must be that the

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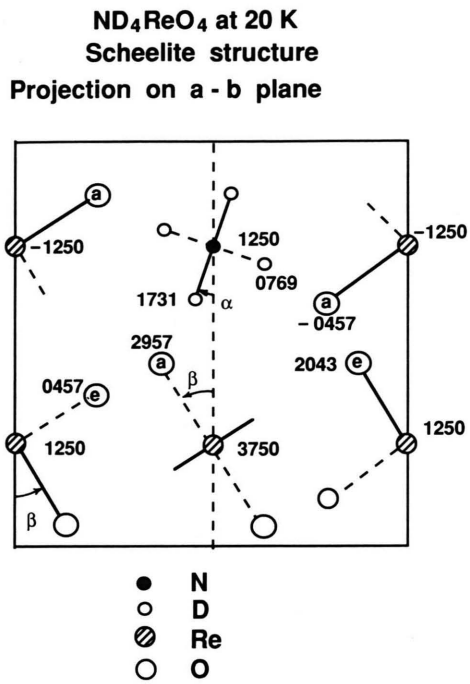

Fig. 1. Projection of part of the structure of ND_4ReO_4 at 20 K on the $a-b$ plane. The z fractional coordinate of each atom is indicated, multiplied by 10^4. The letters "a" and "e" indicate oxygen atoms which are classified as axial and equatorial with respect to the ammonium ion. The ND_4^+ ion is oriented so that the N–D bonds point towards the four axial oxygen atoms, which are labelled "a". The four equatorial oxygen atoms, labelled "e", are slightly more distant from the N atom, and define a second possible orientation for the ammonium ion.

EFG at the Re site fluctuates with a correlation time somewhat shorter than the correlation time determined from the proton T_1, and there should be a powerful quadrupolar relaxation mechanism operating in NH_4ReO_4 at intermediate and high temperature which is absent at low temperature and in $KReO_4$. The present measurements were undertaken to test this prediction.

The T_1 values are very short, due to the large quadrupole moments of both Re isotopes; T_2^* is also very short, and so an echo sequence must be used to measure the recovery of the magnetization following a "90°" pulse. Measurements were made on a Novex spectrometer using a $90°-\tau_1-90°-\tau_2-90°$ echo sequence. The pulse length was chosen by optimizing the echo height for a $90°-\tau_2-90°$ sequence. In most cases, τ_2 was 170 μs and the pulse length was about 8 μs. Results are shown in Table 1. The ratio $T_1(187)/T_1(185)$ for $KReO_4$ was 1.34 ± 0.2. For quadrupolar relaxation the expected ratio is 1.11 while for dipole-dipole relaxation the expected ratio is 0.98. The measured value is somewhat higher than expected, but indicates quadrupole relaxation.

Table 1. Spin-lattice relaxation times for Re in $MReO_4$.

Substance	Isotope	Transition	T [K]	T_1 [μs]
$KReO_4$	187	1/2–3/2	298.2	320±20
			213.3	898
			142.8	1660
			86.4	7880
	185	1/2–3/2	297.9	238
NH_4ReO_4	187	3/2–5/2	299.0	164
			149.6	406
			138.9	494
			118.6	1296
			103.4	2940

For $KReO_4$, T_1 varies approximately as T^{-2}, as expected for quadrupolar relaxation [6]. In NH_4ReO_4, T_1 is appreciably shorter than in $KReO_4$ for temperatures above about 100 K, but data is not yet available through the temperature range in which the quadrupole frequency is changing most rapidly with temperature.

III. Electric Field Gradient Calculations

The Re atom in the scheelite-structure is at a site of symmetry $\bar{4}$, and the electric field gradient at this site is a function of the lattice geometry. With a monatomic cation, and assuming fixed intra-ionic geometry of the anion, the lattice geometry is specified totally by the unit cell dimensions a and c, and the orientation of the anion relative to the unit cell edge, which is defined by the angle β in Figure 1. A point charge calculation of the EFG in $KReO_4$ as a function of a, c/a and β was undertaken to estimate the relative importance of these parameters. Further, the temperature dependence of a, c, and β was determined by neutron diffraction at three temperatures, as described in the next section. The lattice sums were computed using the program EFG5 which calculates the field gradient by direct summation over complete unit cells grouped as a greater unit cell, with a test of convergence and extrapolation to the infinite summation. The electric field gradient at Re can be expressed as

$$q = q^{(0)} + z q^{(1)},$$

where z is the charge on oxygen in units of the magnitude of the electronic charge. A reference lattice geometry was chosen, namely $a = 5.676$ Å, $c = 12.716$ Å, $\beta = 28.0°$, Re–O = 1.723 Å, O–Re–O = 110.8°, and the dependence of q on small deviations from this geometry was found to be described by the following equations:

$$q^{(0)} = -0.03790 + 0.020\,(\delta a/\text{Å}) - 0.00965\,\delta(c/a),$$

$$q^{(1)} = -0.06205 + 0.0365\,(\delta a/\text{Å}) + 0.0394\,\delta(c/a) + 0.001678\,(\delta\beta/\text{degrees}).$$

The dependence of a, c/a, and β on temperature have been determined by neutron diffraction measurements on $KReO_4$ at three temperatures, 15 K, 150 K and 298 K, and a detailed report will be published elsewhere. The average temperature dependences over the range 150–298 K are

$$da/dT = +1.39 \times 10^{-4}\ \text{Å K}^{-1},$$

$$d(c/a)/dT = +6.53 \times 10^{-5}\ \text{K}^{-1},$$

$$d\beta/dT = -5.7 \times 10^{-3}\ \text{degrees K}^{-1}.$$

The resulting logarithmic temperature dependence of q, $d \ln q/dT$ is plotted as a function of oxygen atom charge, z, in Figure 2. This is of course only the static contribution, and further negative dynamic contributions [7] should also be considered. The measured value of $d \ln q/dT$ derived from the NQR temperature dependence [7] is $-20 \times 10^{-5}\ \text{K}^{-1}$, so it is clear that static contributions to the temperature dependence of ν_Q at constant pressure are considerable. Further, the dependence of q on the internal coordinate β is a major one, accounting for more than half the total for any charge on the oxygen atom between -1 and -2. Thus the apparent linear relationship between q and the strain in NH_4ReO_4 [3] has to be interpreted with care, for the strain is a function of the unit cell dimensions only, and does not reflect "internal coordinates" such as β.

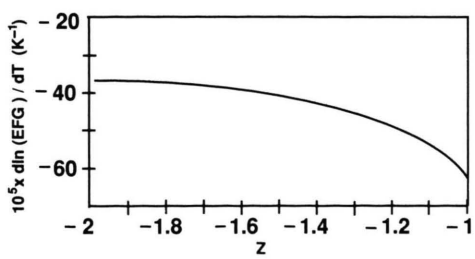

Fig. 2. The logarithmic temperature dependence of the electric field gradient as a function of the charge z on the oxygen atom as calculated from the dependence of EFG on lattice geometry, and the dependence of the lattice geometry on temperature as determined by neutron diffraction.

IV. Neutron Diffraction Study of ND_4ReO_4

A direct test of the pseudo-spin theory was undertaken, using powder neutron diffraction of ND_4ReO_4, in order to folllow the development of the structural parameters as a function of temperature and to determine whether the two orientations of the ammonium ion can be observed dircetly. Powder diffraction data were collected at a series of temperatures from 20 K to 240 K at 20 K intervals, and at room temperature, on the E3 powder diffractometer with the 30-element detector at the NRU reactor at Chalk River. Data analysis was carried out using a Rietveld program [8], and full results will be reported elsewhere.

In the analysis, a single deuterium site was assumed and satisfactory refinement was obtained at all temperatures. The deuterium position defines, in addition to the N–D bond length and D–N–D bond angle, the orientation of the cation with respect to the unit cell basis and the nearby oxygen atoms; in Fig. 1 the cation orientation is determined by the angle α. The results of the analysis confirm the conclusion of the previous neutron diffraction experiment [5] that at low temperatures the ND_4^+ ion is oriented so that the N–D bonds are directed towards the axial, rather than the equatorial, oxygen atoms. The situation at 20 K is shown in Figure 1. As the temperature increases, the anomalous thermal expansion [9] begins at about 100 K, and the average orientations of both the anion and cation change. The angle β specifying the anion orientation decreases by about 3 degrees, as shown in Fig. 3, as compared with a reduction of 1.1 degrees in $KReO_4$ over the same temperature range.

A major change in the average cation orientation with temperature is observed. Figure 4 shows the variation of the angle α with temperature between 20 K and room temperature; the total change is about 30 degrees. At room temperature the observed cation orientation results in the N–D bond pointing roughly halfway between the axial and equatorial oxygen atoms. There are also major changes in the parameters of the deuterium thermal ellipsoid. The directions of the principal axes of the ellipsoid remain approxi-

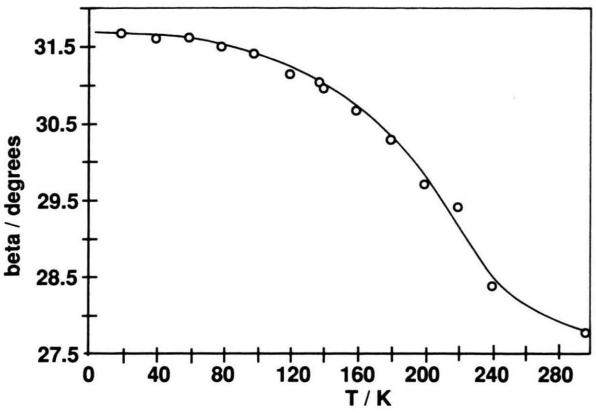

Fig. 3. The angle β (see Fig. 1) specifying the average orientation of the perrhenate ion in the unit cell, as a function of temperature.

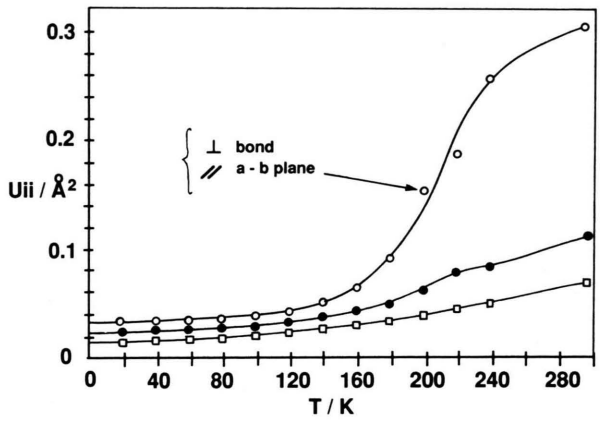

Fig. 5. The principal components of the thermal motion ellipsoid of the deuterium atom in ND_4ReO_4 as functions of temperature. The largest component is directed approximately perpendicular to the N–D bond but parallel to the a–b plane.

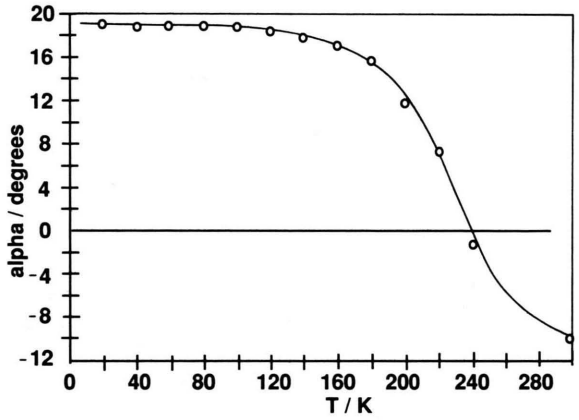

Fig. 4. The angle α (see Fig. 1) specifying the average orientation of the ammonium ion in the unit cell, as a function of temperature.

mately in a constant relationship to the N–D bond direction as the average orientation of the cation changes. One of the principal axes remains perpendicular to the bond direction but parallel to the basal plane of the unit cell; the thermal amplitude in this direction increases rapidly with temperature, as shown in Figure 5, and at room temperature, the corresponding r.m.s. amplitude of the thermal motion is as large as 0.5 Å.

At room temperature the average orientation of the cation and the large magnitude and anisotropy of the deuterium atom motion appear to be consistent with a deuterium atom which is split between the two possible orientations, axial and equatorial; the apparent change in the average orientation of the cation is a reflection of the changing occupations of the two possible orientations as the temperature changes. The results of the analysis using a single deuteriumn site are qualitatively consistent with the pseudo-spin theory. An attempt was made to fit the observed diffraction patterns with a "split" deuterium atom; the refinement was begun with two partial deuterium atoms in approximately the axial and equatorial positions, but led to unrealistic values for the bond lengths and bond angles, and was rejected. Satisfactory agreement with experiment was obtained only with a single deuterium site with highly anisotropic thermal motion.

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