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An electron spin-resonance study of ClO_3 radicals in NH_4ClO_4 single crystals

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Abstract. An ESR study of ClO_3 centres in x-irradiated ammonium perchlorate (NH_4ClO_4) single crystals is carried out that is aimed at resolving the controversy that has recently arisen over the possible occurrence of low-temperature phase transitions in the compound (room temperature structure: orthorhombic; space group $Pnma$). The ESR spectra are recorded as a function of the orientation of the magnetic field $\boldsymbol{H}$ in the three orthogonal crystallographic planes at 300 K, 77 K, and 4.2 K, and also as a function of temperature for $\boldsymbol{H}$ parallel to the principal z-component A_{zz}(Cl) of the ^{35}Cl hyperfine coupling tensor. The analysis of the spectra shows that while the $\mathbf{g}$-tensor remained axial over the entire temperature range ($g_\parallel = 2.0052(3), 2.0055(3), 2.0057(3)$ and $g_\perp = 2.0090(3), 2.0096(3), 2.0105(3)$ at 300 K, 77 K, and 4.2 K respectively), $\mathbf{A}$(Cl), which is rhombic at room temperature ($A_{zz} = 429.77(1.0)$ MHz, $A_{yy} = 316.15(1.0)$ MHz, and $A_{xx} = 325.98(1.0)$ MHz at 300 K) becomes more axial as the temperature is lowered ($A_{zz} = 441.90(1.0)$ MHz, $A_{yy} = 299.09(1.0)$ MHz, and $A_{xx} = 301.61(1.0)$ MHz at 77 K, and $A_{zz} = 445.55(1.0)$ MHz, $A_{yy} = 299.84(1.0)$ MHz, and $A_{xx} = 303.43(1.0)$ MHz at 4.2 K). No changes in the spectra attributable to any phase transition were observed, and we conclude that NH_4ClO_4 does not undergo any phase transition below room temperature. Furthermore, it is found that during $ClO_4^- \longrightarrow ClO_3$ radiative decomposition the mirror-related Cl–O bonds, even though weaker than the other Cl–O bonds, do not break, thus confirming our earlier conclusion that mirror symmetry is preserved during radiation damage.

1. Introduction

Ammonium perchlorate, NH_4ClO_4, has been extensively studied for nearly four decades [1]. The complex reorientational dynamics of both the anions and cations as well as the possible phase transitions have been the major points of interest. It is well established that NH_4ClO_4 undergoes a reversible crystallographic transition at 513 K from a high-temperature cubic structure to an orthorhombic structure which is then maintained down to room temperature [2]. The orthorhombic unit cell belongs to the space group $Pnma$ with $Z = 4$. A variety of experimental studies have shown that the ammonium ions execute either free rotations [3, 4] or rotations about the single threefold axis [5–8]. The barrier to rotation of the ammonium ions is found to be unusually low (1 kcal mol^{-1} or less). In addition there have been many reports of anomalous physical properties of the system at low temperatures as discussed in [9]. These anomalies are interpreted as either due to the influence of phase transitions [10–13] or due to a marked change in the reorientational behaviour of the NH_4^+ ion [14–17]. Chakraborthy *et al* [9] in their Raman study of single crystals of NH_4ClO_4 in

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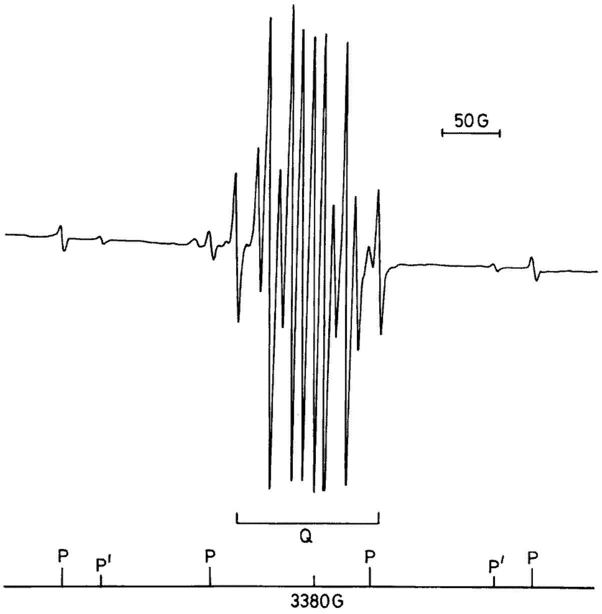

Figure 1. A room temperature ESR spectrum of x-irradiated NH_4ClO_4 single crystal for $\boldsymbol{H} \parallel \boldsymbol{c}$. P: signals due to $^{35}ClO_3$; P′: signals due to $^{37}ClO_3$; and Q: signals due to NH_3^+.

the temperature range 10–300 K observed anomalous behaviour of some internal and lattice modes at around 180 and 40 K, and concluded that these anomalous changes arise from the occurrence of phase transformation around these temperatures. However, Bastow *et al* [18] in their chlorine and deuterium nuclear spin-relaxation studies of NH_4ClO_4 do not see any evidence of a phase transition near 180 K. Recently Bastow and Stuart [19], from a nuclear magnetic resonance study of ^{14}N and ^{35}Cl in NH_4ClO_4, and Brown *et al* [20], from a heat capacity study, find no evidence of any phase transition below room temperature. A detailed single-crystal and powder neutron diffraction study and a Raman spectroscopic investigation at low temperatures by Prask *et al* [21] rule out the occurrence of any phase transitions in the temperature range 10 to 298 K except for changes in the dynamics of the NH_4^+ group.

Electron spin resonance (ESR) is a very powerful technique for studying structural changes. Therefore we have taken on a detailed ESR study of NH_4ClO_4 with a view to clarifying the controversy. Paramagnetic centres necessary for ESR are most conveniently introduced into NH_4ClO_4 by irradiation with x-rays or γ-rays. A host of free radicals are generated on irradiation, NH_3^+ and ClO_3 being the most prominent [22]. Of these, the NH_3^+ is more stable (lifetime $\approx$ a few months) than the ClO_3 radical (lifetime $\approx$ a few hours). Although NH_3^+ in NH_4ClO_4 has been studied extensively using ESR [23], the short lifetime seems to have come in the way of detailed ESR of ClO_3 centre in NH_4ClO_4. The only ESR study of the ClO_3 radical in NH_4ClO_4 is a preliminary report by Cole [22]. In fact, since the ClO_3 ion is heavier than NH_3^+, it is expected to probe a different range of timescales of the dynamics in the compound. This paper presents the results of an ESR study of ClO_3 radicals over the temperature range 4.2 K to 300 K.

An ESR study of the radicals generated in the solid state consequent upon high-energy irradiation is also a useful technique for elucidating the nature of radiation-induced

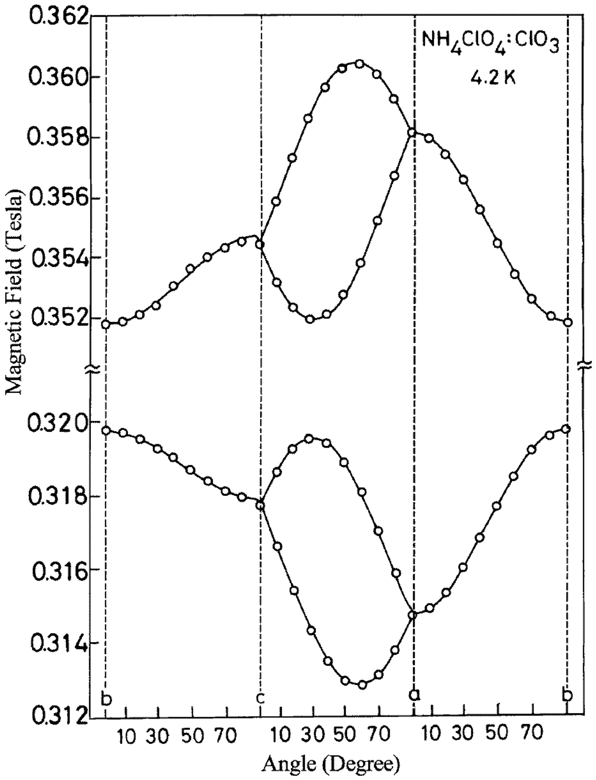

Figure 2. Rotation patterns of a $^{35}ClO_3$ centre in three mutually orthogonal planes at 4.2 K. The circles are experimental points, and the lines are fits to the Schonland equation [24].

decomposition. The latter is not well understood, though it is generally believed that the total crystal environment and the orientation of the molecular ions largely determine the decomposition pathways. A recent study of the NH_3^+ centre in NH_4ClO_4 has given convincing evidence for the relevance of the symmetry of the ion to the nature of the radiation-induced decomposition [23]. The present study of the ClO_3 radical in NH_4ClO_4 also supports this conclusion.

2. Experimental details

The single crystals of NH_4ClO_4 used in the present study were grown from an aqueous solution of commercially available AR-grade ammonium perchlorate by slow evaporation. Short-lived ClO_3 radicals are generated when the crystals are irradiated with x-rays (20 mA, 40 kV) at room temperature for about 1–2 h. A large number of crystals had to be studied due to the short lifetime of the ClO_3 centres. However, the reproducibility of the results from various crystals was excellent.

The crystallographic axes were identified by taking a Weissenberg photograph. A Bruker X-band ESR spectrometer (ER200D) was used to record the ESR spectra. An Oxford ESR900 continuous-flow cryostat was used for temperature variation (accuracy ±0.1 K). The spectra were recorded with the magnetic field varied in the three mutually orthogonal crystalline planes. In each plane the orientation of the field was changed by rotating (at 10°

intervals) the crystal mounted on a goniometer. The field was calibrated with a Bruker NMR Gaussmeter (ER035M) and the frequency was measured with a Hewlett–Packard frequency counter (5246L).

3. Results and discussion

ESR spectra of x-irradiated NH_4ClO_4 consist of signals due to NH_3^+, ClO_3, and ClO_2 radicals. These radicals have well-defined ESR spectra as described in the literature [22]. In figure 1 we show a typical spectrum recorded for the magnetic field $\boldsymbol{H} \parallel \boldsymbol{c}$ with signals due to NH_3^+, $^{35}ClO_3$, and $^{37}ClO_3$ marked. Signals due to ClO_2 radicals are observed in certain other orientations. Since the central transitions ($M_I = \pm\frac{1}{2}$) of the characteristic quartet spectrum of ClO_3 ($I(\mathrm{Cl}) = \frac{3}{2}$) overlap with the signals of NH_3^+, we have monitored only the two outermost ($M_I = \pm\frac{3}{2}$) signals as a function of orientation and temperature. The signals due to $^{37}ClO_3$ are weaker (due to the lower isotopic abundance of ^{37}Cl (24.47%) compared to that of ^{35}Cl (75.53%)). Furthermore, they do not contain any additional information. Therefore, in the following we analyse only the $^{35}ClO_3$ spectra. The rotation patterns from three crystallographic planes at 4.2 K are presented in figure 2. Similar rotation patterns (not shown) were obtained at 300 and 77 K. It is observed that in the *ac*-plane there are two magnetically inequivalent sites while in the *ab*- and *bc*-planes they merge into a single site. Even though a unit cell of NH_4ClO_4 has four molecules ($Z = 4$), the symmetry operations of the unit cell (space group *Pnma*) reduce them to equivalent ESR centres.

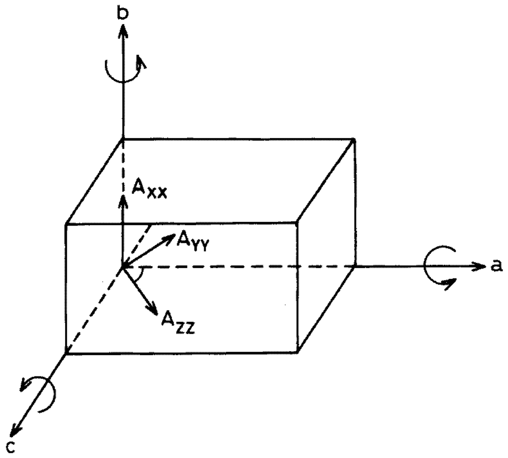

Figure 3. A sketch of the unit cell of NH_4ClO_4 indicating the rotation axes corresponding to the three rotation planes (*bc*-plane rotation corresponds to rotation around the *a*-axis and so on). The ClO_3 radical is assumed to be located at the origin for convenience.

The field positions have been analysed using the Schonland method [24] for each of the two transitions. The continuous lines in figure 2 are fits to the Schonland equation. The spectra are analysed using the spin Hamiltonian

$$\mathcal{H} = \beta \boldsymbol{S} \cdot \mathbf{g} \boldsymbol{B} + \boldsymbol{S} \cdot \mathbf{A} \boldsymbol{I}$$

where $\mathbf{A}$ is the hyperfine tensor due to the ^{35}Cl nucleus. We further assume that the $\mathbf{g}$- and $\mathbf{A}$-tensors are codirectional. Standard equations [24] for the transitions, taking into account second-order perturbation corrections to the spin Hamiltonian, are used. The values of the principal components thus obtained are presented in table 1, along with their direction cosines with respect to the a-, b- and c-axes obtained from the Schonland analysis. Figure 3 shows a sketch of the unit cell of NH_4ClO_4, indicating the rotation axes and the location of the principal components of the ^{35}Cl hyperfine tensor.

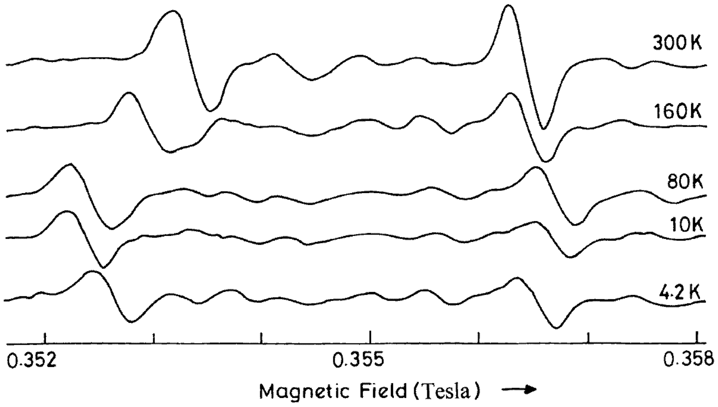

Figure 4. High-field hyperfine signals due to the $^{35}ClO_3$ centre along the principal z-axis of one of the two magnetically inequivalent sites as a function of temperature. The signal at the lower field is due to the second site.

While it was clear from the experiments at 300 K, 77 K, and 4.2 K that there was no increase in the multiplicity of sites below room temperature in any of the three crystallographic planes indicating a phase transition, to confirm this we have monitored the spectrum continuously as a function of temperature from 300 K to 4.2 K for $\boldsymbol{H} \parallel A_{zz}$ of one of the two sites in the ac-plane. In figure 4 we show the behaviour of the high-field ^{35}Cl hyperfine transitions at a few representative temperatures. It is clear that down to 4.2 K there is no further splitting of the lines, ruling out the possibility of any phase transition in this temperature range.

If NH_4ClO_4 does not undergo any phase transition below room temperature as concluded above, the question then arises as to the origin of the anomalies observed by several authors using different experimental techniques. An insight into what is happening could be obtained by comparing the ESR results of ClO_3 (the present study) and NH_3^+ [23] radicals. NH_3^+ ESR showed that at room temperature, in the ac-plane (as well as in the ab- and bc-planes), only a single magnetically inequivalent site is present. When the sample is cooled, at around 223 K the spectrum splits, indicating the development of two magnetically inequivalent sites. Normally, such a splitting would mean a lowering of the crystal symmetry (i.e., a phase transition) leading to a multiplicity of sites. However, with ClO_3 ESR, even at room temperature, we observe two magnetically inequivalent sites in the ac-plane. Noting that the NH_4^+ and ClO_4^- ions in NH_4ClO_4 have the same site symmetry, and also the fact that ClO_3 is a much heavier ion than NH_3^+, the results clearly point towards a dynamical origin of the splitting rather than a phase transition. This also explains why the anomalies reported earlier were observed to occur at different temperatures when different techniques were used to study the temperature dependence, as summarized in reference [9].

ClO_3 is a pyramidal (AB_3-type) radical and its electronic structure is well understood [25]. For a free ClO_3 radical (pyramidal AB_3-type) whose electronic structure is well understood [26], the hyperfine interaction tensor usually displays axial symmetry and a

Table 1. Principal components of the **g**-tensor.

Components	300 K	77 K	4.2 K
g_{zz}	2.0052(3)	2.0055(3)	2.0057(3)
g_{yy}	2.0089(3)	2.0095(3)	2.0100(3)
g_{zz}	2.0090(3)	2.0098(3)	2.0110(3)

Table 2. Principal components and direction cosines with respect to the crystallographic *a*-, *b*- and *c*-axes of the ^{35}Cl hyperfine tensor **A**, including second-order hyperfine corrections. The errors in the values of the principal components are ±1 MHz.

		Direction cosines		
Components	Values (MHz)	*a*	*b*	*c*
300 K				
A_{zz}	429.77	0.8855	0.0109	0.4645
A_{yy}	316.15	0.4643	0.0194	0.8855
A_{xx}	325.98	0.0187	0.9996	0.0121
77 K				
A_{zz}	441.90	0.8448	0.0044	0.5351
A_{yy}	299.09	0.5343	0.0463	0.8440
A_{xx}	301.61	0.0285	0.9989	0.0367
4.2 K				
A_{zz}	445.55	0.8456	0.0194	0.5339
A_{yy}	299.84	0.5335	0.0389	0.8449
A_{xx}	303.43	0.0186	0.9992	0.0344

Table 3. Bond lengths in Å of the ClO_4^- group. The 295 K data are from reference [26], and those at 78 K and 10 K are from reference [27].

Bond	295 K	78 K	10 K
Cl–O(1)	1.441(1)	1.444(5)	1.449(3)
Cl–O(2)	1.422(1)	1.433(5)	1.440(3)
Cl–O(3)	1.431(1)	1.456(3)	1.446(2)

large isotropic component is to be expected together with a superimposed anisotropy with the largest magnitude along the C_3 axis. But our results indicate (tables 1 and 2) that in NH_4ClO_4 crystals, while the **g**-tensor is axial in the temperature range covered, the **A**-tensor displays a slight rhombicity at room temperature which goes on decreasing as the sample is cooled. If we examine the Cl–O bond lengths at 295 K [26], 78 K and 10 K [27] (table 3), we find that the bonds become more nearly equal as the temperature is decreased. This most probably causes the increasing axiality of the **A**-tensor as the sample is cooled.

Table 4 gives the spin densities at the ^{35}Cl nucleus at different temperatures which are calculated following standard procedure [25]. Here A_{iso} is the isotropic splitting, and $a_s^2 = A_{iso}/A_{iso}^*$ is the s component of the molecular orbital, with A_{iso}^* being the free-atom isotropic splitting. B is the anisotropic splitting, and $a_p^2 = B/B^*$ is the p component of the

Table 4. Spin densities of the unpaired electron at the ^{35}Cl nucleus.

Temperature	A_{iso} (MHz)	a_s^2	a_p^2	$a_s^2 + a_p^2$
300 K	357.36	0.062	0.23	0.30
77 K	347.58	0.061	0.26	0.32
4.2 K	349.66	0.061	0.26	0.32

molecular orbital, with B^* the maximum value of the dipolar coupling. The values of A^*_{iso} and B^* are taken to be 5723 MHz and 175.60 MHz respectively [28]. The values of the spin densities are comparable to those for ClO_3 radicals in other systems [29]. From tables 2 and 4 we see that the ^{35}Cl hyperfine tensor is comprised of a large isotropic component with an anisotropic component superimposed on it. The maximum anisotropy of the **A**-tensor is expected to be along the line joining the Cl nucleus to the position of the oxygen that is removed. As seen from table 2, A_{zz} makes an angle of 27.7° (32.3°) at 300 K (77 and 4.2 K) with the a-axis. This is nearly the same direction as that of the Cl–O(2) bond which makes an angle of 26.6° (33.6° and 31.4°) with the a-axis at 300 K (77 K and 4.2 K respectively). Therefore we conclude that it is the Cl–O(2) bond which is ruptured during $ClO_4^- \longrightarrow ClO_3$ radiative decomposition.

At this point we note that the radiation-induced decomposition of molecular ions in the solid state is not yet a fully understood phenomenon. As noted by Atkins and Symons [25], even though each quantum of radiation is much more energetic than the bond strengths, often, selective homolysis is the major outcome, leading to the formation and trapping of only one or two species. Further, the fragments detected are often not those that would have been expected if the weakest bond had undergone rupture. It is generally believed, and there is some experimental evidence for this, that the crystalline environment and the orientation of the molecular ion in the lattice play important roles in determining the decomposition pathways. According to Johnson [30], the decomposition is determined by what can be called ‘the total crystalline environment’, which might include factors such as the crystal free volume, cation size, impurities, and lattice energies. But as Jones remarks [31], “ ‘the total crystalline environment’ is a concept and not a parameter and its dependence on any specific crystalline property and interaction, at best, is poorly known”. Recently, from an ESR study of NH_3^+ centres in single crystals of NH_4ClO_4 [23] we have found evidence for the relevance of one important aspect of the crystal structure—namely, the symmetry—to the nature of the radiation-induced decomposition. Our results show that other factors being equal/nearly equal, symmetry-related bonds are preserved during radiation damage in preference to those that are not related to one another by any symmetry. This conclusion is borne out by the present study also. Even though the two mirror-related bonds Cl–O(3) and Cl–O(4) are weaker than Cl–O(2), we find that the former survive the radiation damage.

4. Conclusion

To summarize and conclude, our ESR study of ClO_3 centres in NH_4ClO_4 rules out the existence of any low-temperature phase transitions. It further brings into focus the relevance of the symmetry in determining the pathway of the radiation-induced decomposition. Upon irradiation of NH_4ClO_4 with x-rays at room temperature the weaker bonds Cl–O(3) and Cl–O(4) which are related by a plane of symmetry do not break, while a stronger bond, Cl–O(2), gets ruptured.

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