

Figure 1. Pen sketch of Jaina Kalpa Vriksha copied from Ravikumar (ref. 18).

of Jaina cosmology¹⁸, which has a similar structure. This, however, could not be tested because of lack of sufficient samples. Figure 2 shows chronological changes in D/L ratio of MLS from second-century (Jaina) to thirteenth-century (Hoysala) temples. It can be seen that this ratio has drastically decreased over a period of time. We propose that these MLS represent an entirely different model of Jaina culture whose D/L ratio was high. When this cult structure from North India was copied in South Indian temples (probably as a result of some Jaina kings converting to Vaishnavism) a 'copy error' was probably incorporated over a period of time, leading to a resemblance to maize ears.

Thus it may be inferred that the MLS at Somnathpur do not represent maize ears. Hence the implication

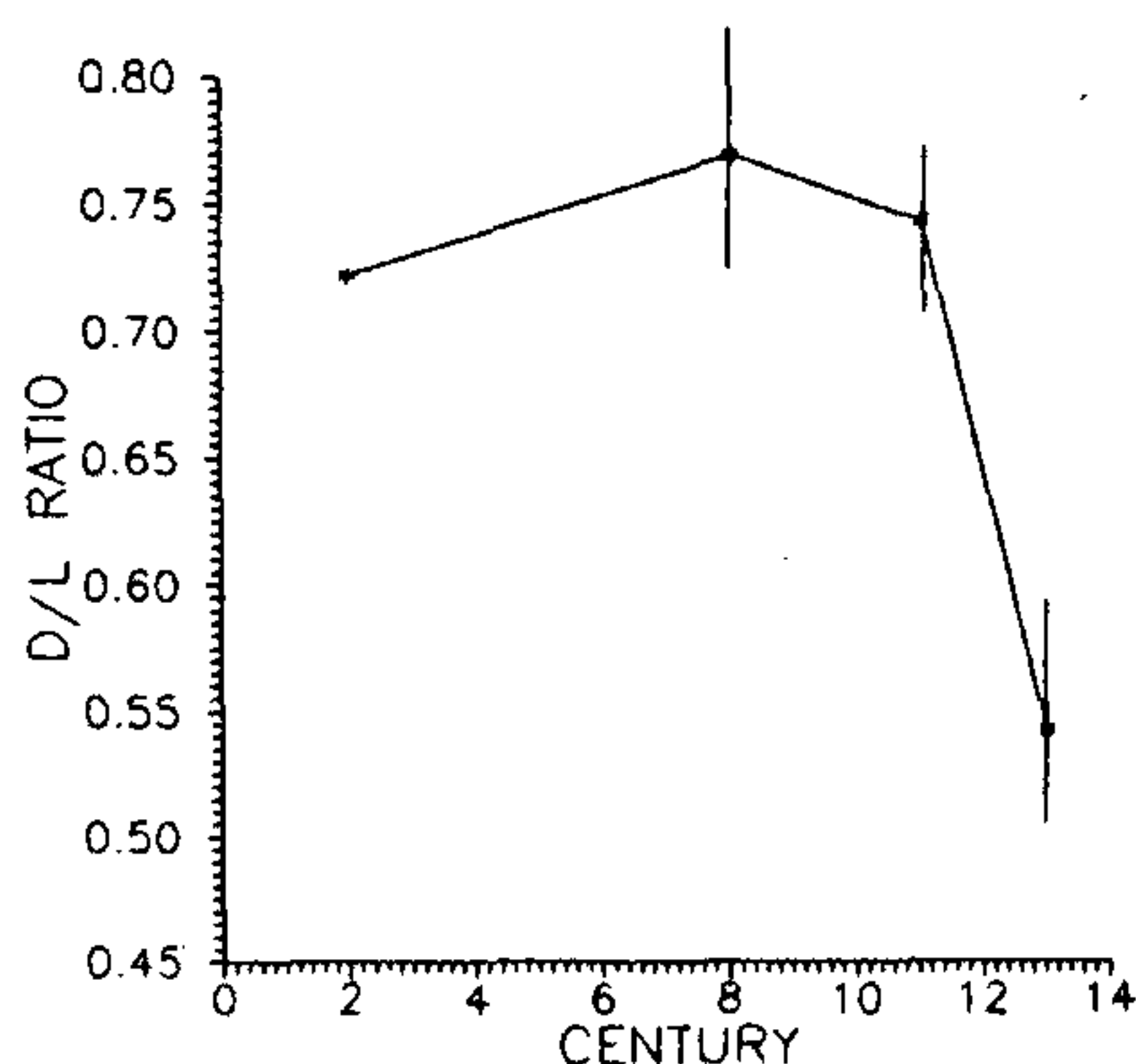


Figure 2. D/L ratios of MLS over centuries. Some of the data for a few centuries have been clubbed. Vertical bars indicate one standard deviation. Sources: second century, ref. 14; eighth century, refs. 14, 15; tenth century, refs. 19, 20; thirteenth century, present work, recorded at Somnathpur temple.

drawn thereupon that maize was being cultivated in South India in pre-Columbian times cannot be unequivocally supported on the basis of these structures; nor trans-oceanic trade contacts between the Old World and the New World during pre-Columbian times.

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Symmetry preservation during radiation damage

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An examination of radiation-damage processes consequent to high-energy irradiation in certain ammonium salts studied using ESR of free radicals together with the structural information available from neutron diffraction studies shows that, other factors being equal, nearly equal, symmetry-related bonds are preserved in preference to those unrelated to one another by any symmetry.

RADIATION-INDUCED decomposition of molecular ions in the solid state is not yet a fully understood phenomenon. As noted by Atkins and Symons¹, even though each quantum of radiation is much more energetic than the bond strengths of molecular ions, 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 expected if the weakest bond had undergone rupture. It is generally believed, and there is some experimental evidence, that the crystalline environment and the orientation of the molecular ion in the lattice play important roles in determining the decomposition pathways. According to Johnson², the decomposition is determined by what can be called 'the total crystalline environment', which might include factors such as crystal free-volume, cation size, impurities and lattice energies. But, as Jones remarks³, 'the total crystalline environment' is a concept and not a parameter and its dependence on any specific crystalline property and interaction is, at best, poorly known. Recently, from a detailed examination of bonds ruptured by high-energy radiations in certain ammonium salts, we have found evidence for 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 on radiation damage in preference to those unrelated to one another by any symmetry. The particular example discussed here concerns mirror symmetry. However, other symmetry operations may have similar effects. Our conclusion is based on our own electron spin resonance (ESR) study of NH_3^+ radicals in ammonium perchlorate NH_4ClO_4 , briefly described here (the details will be published separately), and also on some more examples available in the literature.

ESR study of free radicals is a well-established technique^{1,4}, which not only provides a useful local probe for determination of the structure and dynamics of the host compound in which the radical is trapped but also can give valuable information on the site symmetry and the nature of the free radical itself. NH_3^+ radicals generated when substances containing NH_4 groups are irradiated by X-rays or γ -rays have been studied by ESR in a number of systems^{5,6}, including NH_4ClO_4 (refs. 7–12). NH_3^+ is a planar radical with the unpaired electron residing in the $2p\pi$ orbital of the nitrogen atom along the three-fold symmetry axis¹⁰. At temperatures above about 77 K, because of the free rotations/jumping motions around the three-fold axis, the three hydrogens are equivalent and the ESR spectrum consists of a triplet of quartets, resulting from the hyperfine coupling of the unpaired electron to one nitrogen nucleus ($I = 1$) and the three equivalent hydrogens. The proton hyperfine tensor A_H is found to be essentially isotropic but the nitrogen hyperfine tensor A_N is either axial or rhombic, deviations

from axially occurring when the radical experiences an asymmetric crystal field or when it undergoes restricted rotation or limited librations about an axis other than the three-fold axis⁶. The Z-principal component of the A_N tensor is invariably along the line joining the nitrogen to the position of the hydrogen that is removed since this three-fold direction provides the unique axis of the NH_3^+ radical, leading to maximum anisotropy of the A_N tensor along this direction¹⁰. The X- and the Y-principal components lie in the plane perpendicular to this axis and are nearly equal to each other, the three remaining protons lying in this plane being equivalent to one another by virtue of their motion at all but very low temperatures. Therefore, the Z-principal component will be either the largest or the smallest⁵ principal component. These conclusions have been well established as a result of a number of investigations carried out on the NH_3^+ radicals over a number of years^{1,4–12}.

While reinvestigating the ESR of NH_3^+ in NH_4ClO_4 in connection with the recent controversy^{13–15} over the occurrence of low-temperature phase transitions in the compound, we were led to a detailed examination of the orientation of the A_N tensor with respect to the crystallographic axes and consequently the mechanism of the radiation damage creating the radical NH_3^+ . The question we sought to answer was: Which of the four protons of the NH_4 group is removed on irradiation with X-rays? An obvious expectation is that the hydrogen that is the most weakly bound would be the one to be lost. Our experimental results show, instead, that the two hydrogens bound with the weakest bonds, but related to each other by the mirror-symmetry operation of the NH_4ClO_4 lattice, survive the irradiation. A third hydrogen, which has a bond strength larger than or at least equal to those of the two mirror-related hydrogens, gets removed by the X-rays.

According to the neutron-diffraction study of Choi *et al.*¹⁶, which, together with the recent study of Prask *et al.*¹⁷ on ND_4ClO_4 , is probably the most reliable structure determination to date of NH_4ClO_4 [space group Pnma, $Z = 4$], two [H(1) and H(2)] of the four hydrogens of the NH_4 group lie on the *ac* mirror plane (Figure 1), and the other two [H(3) and H(4)] are related to each other by the mirror. The study also reports detailed N—H...O bond-lengths, which are reproduced in Table 1 which gives the bond-length data for NH_4ClO_4 at 10 K. The results were essentially confirmed by the study on ND_4ClO_4 (ref. 17) at different temperatures. As is evident from the table, the hydrogen bond N—H(1)...O(2) is significantly stronger than the mirror-related bonds N—H(3)...O(3). Consideration of the N—H covalent bonds also shows that, again, the N—H(1) bond is slightly stronger than the mirror-related N—H(3) and N—H(4) bonds.

We have carried out extensive ESR studies on the NH_3^+ radical trapped in NH_4ClO_4 at different temperatures

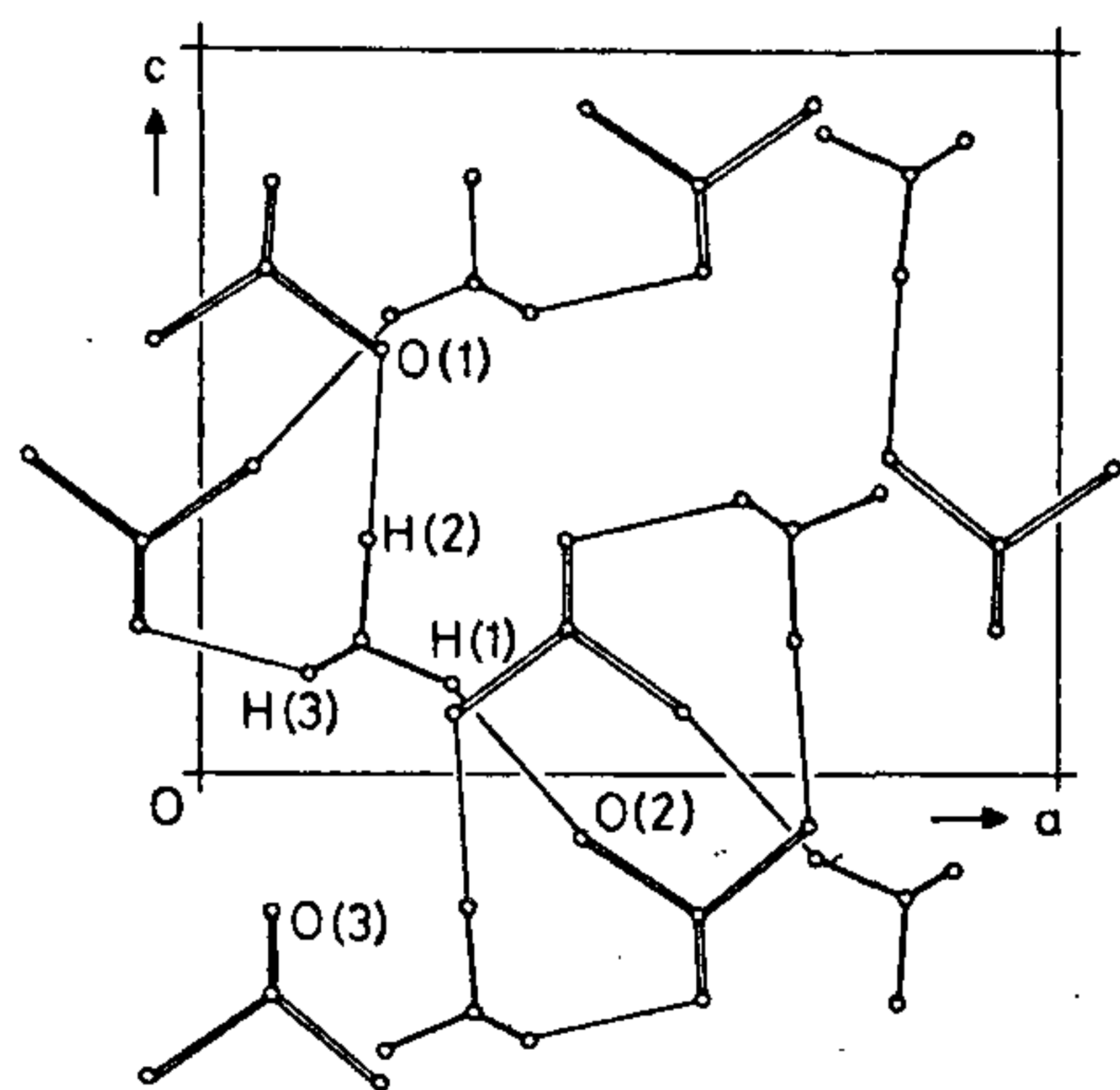


Figure 1. Structure of NH_4ClO_4 crystal projected onto the ac plane (from ref. 14). The hydrogen atom H(4) is directly below H(3) and is related to the latter by the ac mirror plane.

Table 1. The hydrogen bonds in NH_4ClO_4 at 10 K. The positions of the hydrogens are corrected for the rigid-body libration (from ref. 16).

Bond	N—H (Å)	H...O (Å)
N—H(1)...O(2)	1.028(6)	2.001(7)
N—H(2)...O(1)	1.058(5)	1.891(5)
N—H(3)...O(3)	1.031(3)	2.077(6)

(153 K $< T < 295$ K). At room temperature, the NH_3^+ spectrum of a single paramagnetic site is observed. Around 223 K, in the ac plane the $M_I(\text{N}) = \pm 1$ transitions begin to split, indicating the development of two paramagnetic sites. The splitting goes on increasing with decreasing temperature. As will be shown in a detailed analysis to be published elsewhere, this splitting is not due to any phase transition but is caused by an inadequate averaging-out of the anisotropies of the librational motions of the three-fold axes of the NH_3^+ centres. Here we only summarize the conclusion of the analysis in Table 2. At room temperature, all the three components of the A_N tensor are aligned with the crystallographic axes within experimental error. At 153 K, the Z -principal component of the A_N tensor makes an angle of about -10° with the a -axis and lies in the ac -plane. The Y -component is always along the b -axis, indicating that the ac mirror is still intact at the local level

also, even after irradiation. Considering this fact with the structural result^{16,17} that the direction N—H(1) makes angles of -26.2° , -25.1° , -21.92° , -20.4° and -16.1° at temperatures of 20, 30, 45, 60 and 75 K respectively, we associate the orientation of the Z -component of the A_N tensor with the N—H(1) direction and conclude that it is the H(1) hydrogen that is lost on irradiation. The orientations determined by ESR and neutron diffraction are not expected to be exactly the same since a slight reorientation of the NH_3^+ radical is likely to take place compared to the orientation of the parent NH_4^+ group.

Our ESR results conclusively rule out the possibility that one of the mirror-symmetric hydrogens is lost, since, if that were the case, the Z -principal component (the largest or the smallest component) of the A_N tensor would be along the direction joining the position of the N atom with that of the lost hydrogen. This would lead to the loss of the mirror locally and therefore no principal component need be along the crystallographic b -axis, as experimentally observed. The possibility of a slight rearrangement of the remaining three hydrogens such that the Z -principal component of the A_N tensor gets aligned with the b -axis is ruled out because, as seen in Table 2, it is the Y -principal component of intermediate value that is along the b -axis. Our conclusion is further corroborated by the fact that the A_N tensor shows very little anisotropy in the bc plane, which follows from the near-parallelism of the plane containing the hydrogens H(2), H(3) and H(4) with the bc plane.

Thus, even though the mirror-symmetric hydrogens H(3) and H(4) are more weakly bound than (or at best as strongly bound as) the hydrogen H(1), on irradiation they survive, and it is the hydrogen H(1) that gets removed. The final effect is the preservation of the mirror symmetry under irradiation. Further confirmation of the stability of the mirror-related bonds is available in the literature although the significance of the mirror plane does not appear to have been recognized so far. ESR studies of NH_3^+ , CrO_3^- and SeO_3^- (the latter two generated respectively by irradiating samples containing CrO_4^{2-} and SeO_4^{2-} doped for SO_4^{2-}) centres in single crystals of $(\text{NH}_4)_2\text{SO}_4$ have been reported some time ago¹⁸⁻²¹. A comparison of the results with the structure determined

Table 2. The principal components of the nitrogen hyperfine tensor of NH_3^+ in NH_4ClO_4 and their orientations with respect to the crystallographic axes at 295 K and 153 K.

Principal component	Magnitude (MHz)	Direction cosines			Temperature (K)
		a	b	c	
$(A_N)_Z$	61.53	0.9997	0.0181	-0.0135	295
$(A_N)_Y$	53.30	-0.0179	0.9996	-0.0206	
$(A_N)_X$	48.95	0.0139	-0.0204	0.9997	
$(A_N)_Z$	76.65	0.9847	0.0247	+0.1727	153
$(A_N)_Y$	49.25	0.0268	0.9996	+0.0098	
$(A_N)_X$	38.22	+0.1724	+0.0143	0.9849	

Table 3. Anticorrelation between symmetry and radiolytic decomposition.

Compound	Radical	Parent ion	Bond lengths of the parent ion (Å)	Bond broken	Reference Structure	ESR
NH ₄ ClO ₄	NH ₃ ⁺	NH ₄ ⁺	N-H(1): 1.028 N-H(2): 1.058 N-H(3): 1.031* N-H(4): 1.031*	N-H(1)	16	This work
(NH ₄) ₂ SO ₄	NH ₃ ⁺	NH ₄ ⁺	N(1)-H(1): 1.08 N(1)-H(2): 1.04 N(1)-H(3): 1.09* N(1)-H(4): 1.09* N(2)-H(5): 1.05 N(2)-H(6): 1.06 N(2)-H(7): 1.07* N(2)-H(8): 1.07*	Either N(1)-H(1) or N(1)-H(2) Either N(2)-H(5) or N(2)-H(6)	22	18, 19
(NH ₄) ₂ SO ₄	SeO ₃ ⁻	SeO ₄ ²⁻	S-O(1): 1.49 S-O(2): 1.49 S-O(3): 1.49* S-O(4): 1.49*	S-O(1) for (SeO ₃ ⁻) _I and S-O(2) for (SeO ₃ ⁻) _{II}	22	21
(NH ₄) ₂ SO ₄	CrO ₃ ⁻	CrO ₄ ²⁻	Same as above	S-O(1)	22	20

*Mirror-related bonds.

by neutron diffraction²² shows (Table 3) that the mirror symmetry-related hydrogens of NH₄⁺ and oxygens of SO₄²⁻ survive even though they are bound more weakly than or at best as strongly as the atoms that are lost on irradiation. In fact, the role played by symmetry in chemical reactions is very well recognized²³. For example, it is known that reaction pathways in which the symmetry of the bonds that are made is the same as that of the bonds that are broken are preferred²³. An extension of such ideas to the radiolytic decomposition in solids does not seem unreasonable, especially since (i) in solids the minimum-energy configuration is the one in which the constituents conform to the symmetry imposed by the lattice and (ii) the decomposition is preceded by the excitation of the molecule to higher vibrational states, the nature of which is determined by both the molecular and the lattice symmetry. Thus the decomposition would be determined by the selection rules influenced by the symmetry constraints. However, a possibility that cannot be ruled out with certainty at this stage is that the radical is formed by the breaking of the weakest bond but the radical reorients to conform to the lattice symmetry. This would require the NH₃⁺ radical, lacking in mirror symmetry when formed, acquiring it subsequently, amounting to an improvement in its symmetry. Even though in principle it is a possible outcome, it would be a slightly uncommon process, the more common occurrence being the reduction of the local symmetry of the lattice consequent to doping with a low-symmetry impurity. Ultrafast-spectroscopic techniques, which can detect this 'transient symmetry' of the radical during the time interval between its formation and its subsequent locking into the lattice (if such a process is indeed

taking place), would be required to decide between two possibilities. In the absence of such result cannot conclusively say that the mirror-symmetry bonds are not broken at all. However, one can conclude that, ultimately, mirror symmetry is preserved in radiation-induced decomposition processes involving molecular ions in solids. It would be interesting to examine the possibility of such symmetry preservation in more complex situations like biological systems.

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Occurrence of soda trachyte near Kudangulam village, Tamil Nadu, South India

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I report chemical composition and petrography of a fine-grained, grey, degassed trachytic tuff from Kudangulam area, South India.

A fine-grained grey coloured trachytic tuff was collected from a pit sunk on a very coarse-grained apatite-phlogopite-bearing sovitic carbonatite¹ in charnockite about 2 km south of Kudangulam village (8° 11' N, 77° 43' E) and 20 km northeast of Cape Comorin. The trachyte occurs in a feeder dyke 15 cm wide. It cuts across the charnockite along N 80° W-S 80° E with a dip of 85° NE. The dyke contains reddish-stained chilled margins (1-5 mm). Contact aureoles (10-20 cm) have developed owing to baking effect on the wall rock of charnockite. Along nallah cuttings similar dykes of trachyte, alkali basalts, sovites (Figure 1), phlogopite-carbonatitic breccias and lavas are noted¹. An occurrence of black-coloured vesicular carbonatitic lava also is exposed, with jagged spinose fragments resembling furnace clinker with a rough irregular surface covered over a Mio-Pliocene shell limestone² which contains 1-3-cm large crystals of Icelandspars in cavities. Floats of volcanic bombs, ash-tuffs and breccias with fine three- or four-pointed splinters bounded by concave and vesicular surfaces are strewn over terri sands. These show wide variations in specific gravity from 1.35 to 2.69. The country rocks are extensively kaolinized.

In thin sections (Figure 2), trachyte shows microlites of twinned anorthoclase (carlsbad law on (010) twin plane).

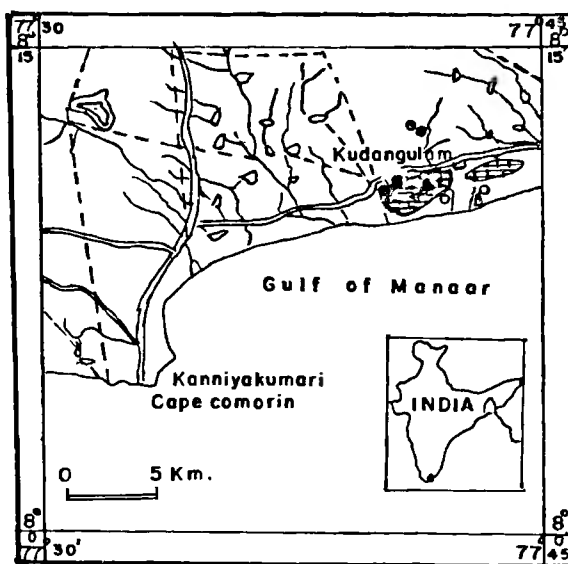


Figure 1. Map showing the location of soda-trachyte and other volcanic rocks. Δ , Soda-trachyte; \circ , sovite; \blacksquare , carbonatite-lava; \blacktriangle , cavity-filled Icelandspars; \bullet , Alkali basalt; \odot , amygdaloidal alkali basalt; \oplus , shell limestone; ---, fault.

Phenocrysts ($0.184 \times 0.025 \text{ mm}^2$) are set in an aphanitic matrix (42% vol.) composed of microgranules of carbonate and felsic materials. Slender prisms of accessory aegirine ($0.110 \times 0.010 \text{ mm}^2$) are also seen. Occasionally a few anhedral quartz grains are found in the interstitial spaces of anorthoclases. Anhedral

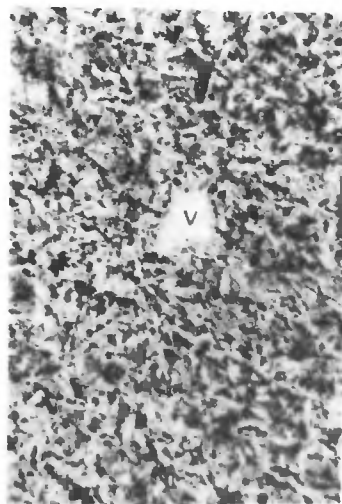


Figure 2. Photomicrograph showing anorthoclase microlites amidst a fine-grained aphanitic quartz normative matrix in a trachyte. An irregular-shaped isolated vesicle ($0.316 \times 0.210 \text{ mm}$) is found at the centre.