

On the indirect determination of ESR g -factors by NMR of paramagnetic crystals

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Abstract. Single crystal proton broadline NMR of the Tutton salt $K_2Co(SO_4)_2 \cdot 6H_2O$ is reported. From the analysis of the water proton dipolar tensor proton positions have been located, based on hydrogen bonding schemes. Besides, from an analysis of the paramagnetic proton shift tensors the g -tensor of the $[Co(H_2O)_6]$ chromophore has been evaluated. Comparison with directly measured g -tensor at 4.2 K is found to be good.

Keywords. Broadline NMR; paramagnetic shift tensor; g -tensor; paramagnetic resonance.

1. Introduction

The line shape and width of nuclear magnetic resonance absorption in solids depend on the magnetic field inhomogeneity and dipolar interaction of the surrounding magnetic nuclei with the resonant nuclei. The second moment analysis in solids will give information about the dipole-dipole interaction (Van Vleck 1948). If the dipole-dipole interaction is larger than the linewidth one can observe dipole split line and this was observed first in proton magnetic resonance study of hydrated gypsum $CaSO_4 \cdot 2H_2O$ crystal by Pake (1948). Later many authors (Pedersen and Holcomb 1963; Padmanabhan *et al* 1974) extended this technique to hydrated salt crystals to determine directions of the water protons and their positions.

In most of the hydrated salt crystals, the water molecules at ambient temperatures undergo a flipping motion about the bisector of the HOH angle (Ketudat *et al* 1956), resulting in two dipolar split lines for each water molecule as a result of magnetic equivalence of the two protons in diamagnetic systems. This motion can be arrested by cooling the system down to low temperatures. Bloembergen (1950) observed ten unresolved component lines in $CuSO_4 \cdot 5H_2O$ at 4.2 K due to the non-equivalence of the water protons in this paramagnetic host. In diamagnetic lattices, however, these dipolar split lines will occur symmetrically about the free proton resonance. This interaction, being purely dipolar, follows a $(1-3 \cos^2 \theta)/r^3$ dependence. With the chemical intuition about hydrogen bonding schemes and by following the dipolar splitting of the proton resonance lines in hydrated salts as a function of crystal orientation one can easily map out the proton positions which are otherwise very difficult to accurately determine by x-ray diffraction. Only neutron diffraction can give precise positions of the protons. In cases where neutron diffraction data is not available, broad line NMR is a tool to elucidate proton positions accurately in hydrated crystals.

Although diamagnetic salt hydrates have been subjected to broad line measurements, very little work has been done in paramagnetic salt hydrates where the centre of gravity

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of the dipolar split lines will be shifted due to the susceptibility shifts of the paramagnetic metal ion. This shift is anisotropic in nature. In many high spin non-S-state ions due to fast spin lattice relaxation ESR measurements have to be carried out at ultra-low temperatures. However, proton NMR can be done at room temperature and the very process which makes EPR spectra unobservable at room temperature makes NMR of lattice protons observable. So in paramagnetic salt hydrates apart from locating precisely the proton positions one can get the shift tensor (Padmanabhan *et al* 1974; Sato *et al* 1980; Raj *et al* 1982) and hence indirectly the g -tensor of the paramagnetic moiety.

In this paper we estimate g -tensor in $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ by analysing the paramagnetic shift tensor and proton positions. The present system, however, contains twelve water molecules per unit cell, of which six are magnetically distinct in general orientations except for b -axis rotation. Accurate analysis of the dipolar anisotropy and shift tensor is difficult due to many overlapping features. However, it is shown that fairly reliable g -values can be extracted from measurements of paramagnetic hydrated salts. Chidambaram and Raghavarao (1963) reported the direction cosines of the p - p -vectors in the isomorphous diamagnetic zinc and magnesium tutton salts.

2. Theory

The dipolar splitting between the two proton lines in a water molecule can be given by

$$\Delta B = 2\alpha[3 \cos^2 \theta_{12} - 1], \quad (1)$$

where $\alpha = 3/2 \mu r_{12}^{-3}$ in which μ is the proton magnetic moment, r_{12} is the distance between two protons and θ_{12} is the angle between the applied magnetic field B_0 and proton-proton (PP) vector. By transforming into laboratory coordinate system XYZ

$$\Delta B = 2\alpha[3 \cos^2(\phi - \phi_0) \cos^2 \delta - 1], \quad (2)$$

where δ is the angle between the PP vector and the plane perpendicular to the rotation axis, ϕ is the angle between B_0 and reference axis attached to the crystal and lying in the plane perpendicular to rotation axis and ϕ_0 is the angle between projection of the PP vector onto the above plane and reference axis (see figure 1). δ and ϕ_0 can be measured by rotating the crystal about a known crystallographic axis.

In the case of paramagnetic crystals the centre of gravity of the two lines from a particular water molecule will be shifted due to the dipolar field arising from the magnetic susceptibility of the metal ion as well as any transferred spin density onto the protons *via* the chemical bonds, though transferred spin density interaction is usually small and is a measure of contact hyperfine interaction at the site of proton. The susceptibility interaction is anisotropic in nature and the total shift B_s can be given as

$$B_s = a I \cdot S + \frac{\chi \cdot B_0}{R_{M-H}^3} (1 - 3 \cos^2 \omega), \quad (3)$$

where a is isotropic hyperfine coupling constant, χ is the susceptibility tensor and R_{M-H}^3 is the distance between metal ion and proton, ω being the angle between M-H direction and applied magnetic field. Expressing in terms of g -tensor, the anisotropic contribution can be written as

$$B_{as} \text{ (in gauss)} = \frac{g^2(\phi) \beta^2 \hat{S}(\hat{S} + 1)}{3kT} \frac{(1 - 3 \cos^2 \omega)}{R_{M-H}^3} B_0. \quad (4)$$

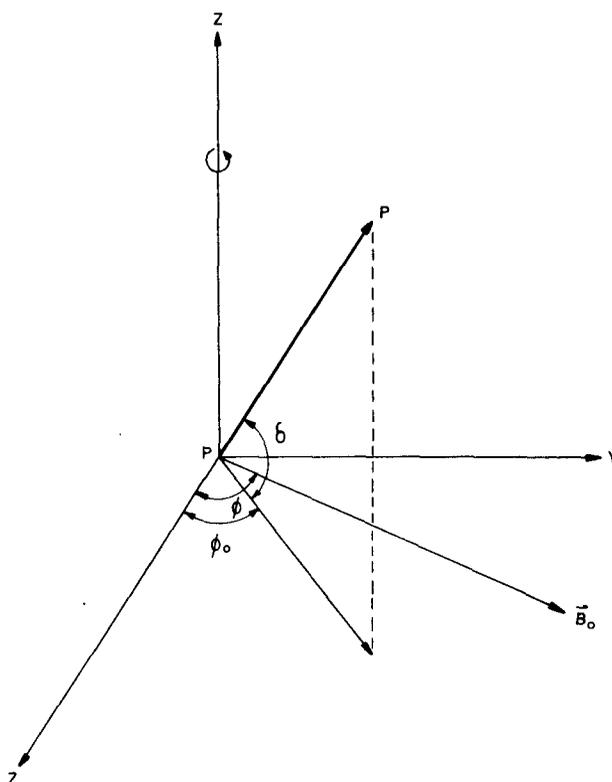


Figure 1. Representation of P-P vector in the laboratory coordinate system.

Here $g(\phi)$ is the g -effective at a particular orientation of B_0 , β is the Böhr magneton, k is the Boltzman constant, T is the temperature and \hat{S} is the fictitious spin angular momentum of the electron. In the case of paramagnetic ions with $S > \frac{1}{2}$ one has to use fictitious spin e.g. for Co^{2+} high spin $\hat{S} = \frac{1}{2} \cdot g^2(\phi)$ can be expressed as

$$g^2(\phi) = g_{11}^2 \cos^2 \phi_1 + g_{22}^2 \cos^2 \phi_2 + g_{33}^2 \cos^2 \phi_3. \quad (5)$$

ϕ_1, ϕ_2, ϕ_3 are the angles between B_0 and g_{11}, g_{22}, g_{33} , directions. The anisotropic susceptibility shift tensor will be traceless only when g -tensor is isotropic. The trace of B_{as} is due to the isotropic shift contribution from g -anisotropy. Since trace need not be zero as in most cases, it is difficult to exactly estimate isotropic transferred spin density contribution from the total centre of gravity shift (*i.e.* the experimental shift tensor).

3. Experimental

Large single crystals of $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ of $10 \times 8 \times 8$ mm size were grown from aqueous solution containing stoichiometric quantities of K_2SO_4 and $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$. The morphology of representative small crystals was determined using Enraf Nonius CAD-4 x-ray diffractometer. The morphological characteristics are similar to those reported by Wyckoff (1965). The compound belongs to monoclinic class with space group $P_{2_1/a}$ and cell parameters $a = 9.014 \text{ \AA}$, $b = 12.041 \text{ \AA}$, c

$= 6.079 \text{ \AA}$, $\beta = 104.97^\circ$, $z = 2$. The crystal structure is isomorphous to that of $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Kannan and Viswamitra 1965). Experiments were carried out on WL-210 sideline accessory of the Varian E-112 spectrometer. Measurements were done at 30 MHz. The crystal was fixed to the goniometer by means of quickfix and the quickfix proton signal was considered as the reference zero. Spectra were recorded for every 10° interval (for every 5° in some orientations) in three mutually perpendicular a , b , c^* ($= \mathbf{a} \times \mathbf{b}$) planes at room temperature. In b axis rotation, only three pairs of lines were observed implying that only three PP vectors out of twelve per unit cell are magnetically distinct. But in a and c^* rotations at arbitrary crystal orientations six pairs of lines were observed. Out of six pairs, two pairs most of the time get overlapped with other pairs.

The angular variation of proton peak positions in a and c^* axes rotations is shown in figures 2 and 3 respectively. Only 5 pairs for a axis and 4 pairs for c^* and all the 3 pairs for b axis rotation are followed. These experimental points are least square-fitted to following equation.

$$H = A\cos^2\psi + B\sin 2\psi + C, \quad (6)$$

where ψ is the laboratory rotation angle. These lines are asymmetrically shifted around free proton line due to paramagnetic shifts. But pair separation is not affected to first order by these shifts. Typical angular variation plots of pair separations for a and c^* rotations are shown in figures 4 and 5 respectively. The centre of gravity shifts for these

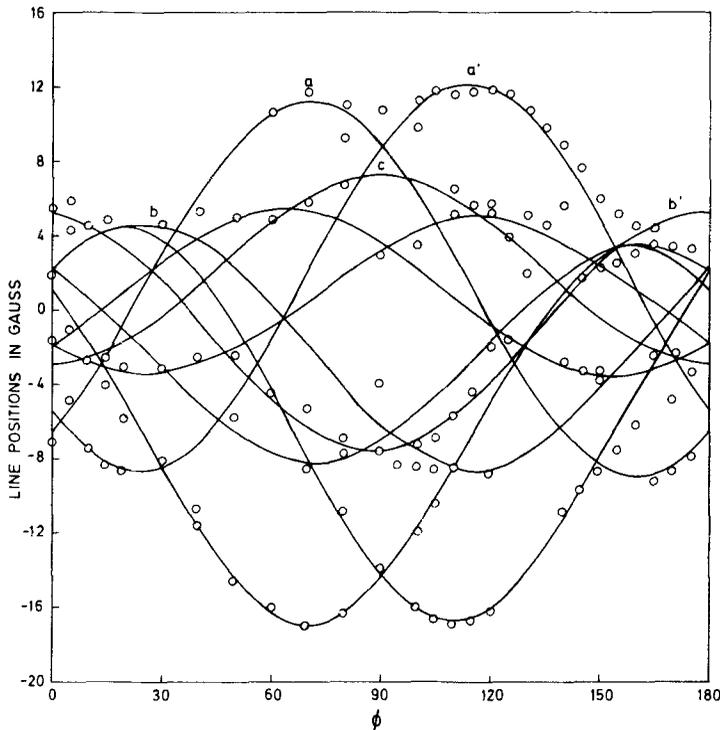


Figure 2. Angular variation of proton lines for a -axis rotation. Five pairs of resonances out of six expected could be followed in this rotation.

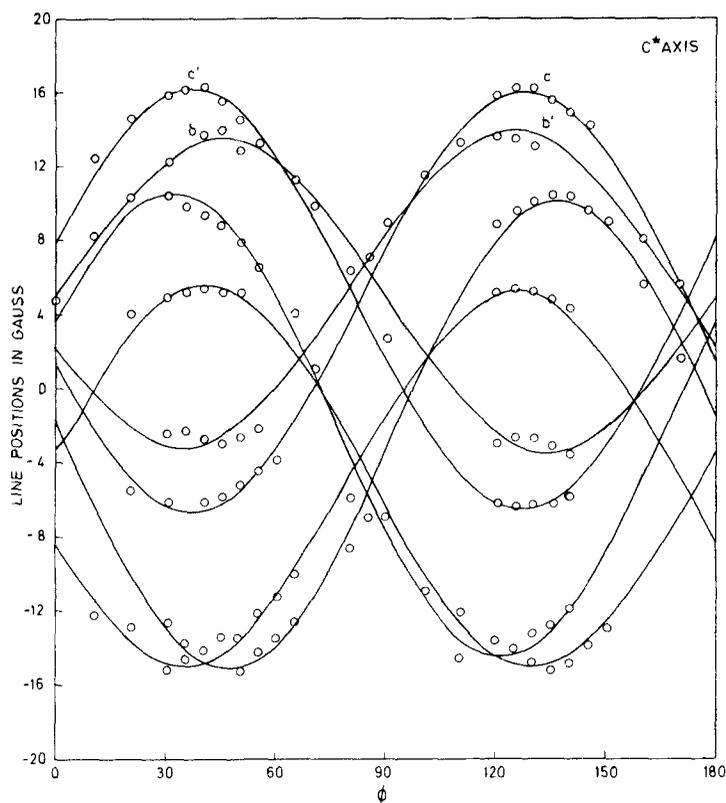


Figure 3. Same as in figure 2, but for c^* axis rotation. Only four pairs could be unambiguously identified.

rotations are shown in figures 6 and 7 respectively. Solid curves represent the theoretical fit and points the experimental values.

4. Discussion

4.1 Proton-proton vectors

When the pair separation was maximum, an exaggerated splitting was observed. This shift could be explained as due to the contribution from nonsecular terms which will shift both lines for a particular pair to the same distance in the opposite sign. This shift will be of the order of linewidth and this is also an angle and temperature-dependent factor. Considering a linewidth of 2 gauss, totally 4 gauss was subtracted from the maximum line separation and was used for calculating direction cosines of PP vector. The direction cosines of magnetically distinct PP vectors are listed in table 1. Other vectors can be generated using space group symmetry. Using the hydrogen bonding scheme introduced by El Saffar (1966) proton positions were calculated and these in fractional coordinates are listed in table 2. Hydrogen atoms H(1) and H(2) belong to O(5), H(3), H(4) belong to O(6) and H(5) and H(6) belong to O(7). Figure 8 shows the projection of complete unit cell including hydrogen atoms in ac^* plane.

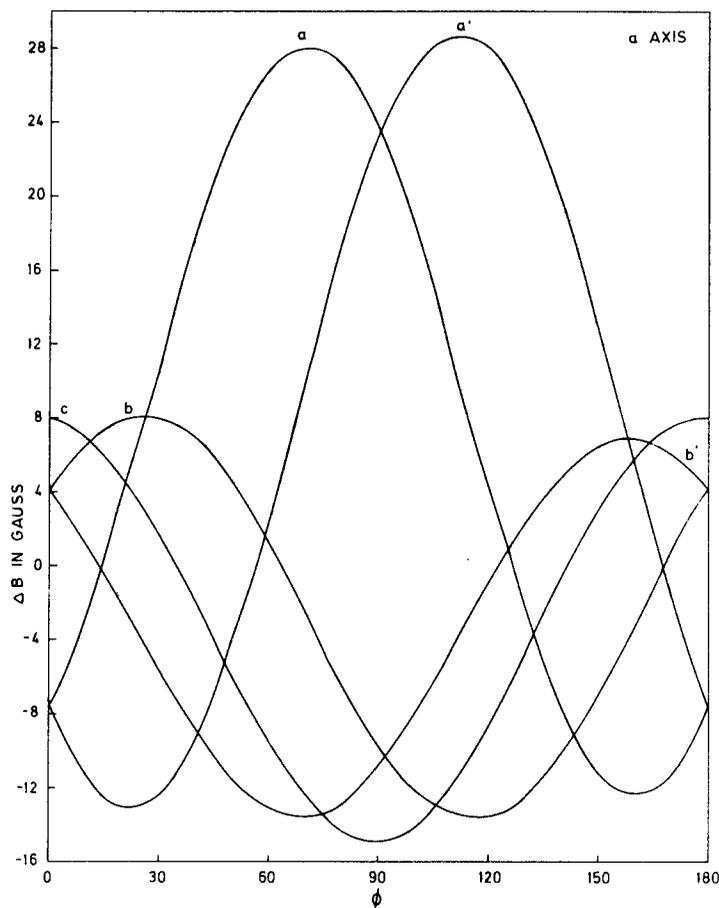


Figure 4. Angular variation of dipolar splitting for *a*-axis rotation for the five distinct P-P vectors.

4.2 *g*-tensor of the Co(II) moiety

Paramagnetic shifts also like any diadic symmetric tensor can be least square-fitted to equation (6). The coefficients *A*, *B* and *C* in each plane will give three of the shift tensor parameters. In case of *a* axis rotation

$$A = S_{aa}$$

$$B = S_{cc} - S_{bb'}$$

$$C = S_{bc} - \frac{1}{2}S_{aa}$$

and by cyclic permutation in the other axis we can extract the elements of the shift tensor in laboratory frame. This is then diagonalised to get the principal values and the direction cosines of the so-called shift tensor. Because of the overlapping of lines we were not able to follow all pairs in three rotations. The principal values of paramagnetic shift tensor and its direction cosines for one such pair *c* are given in tables 3 and 4 respectively.

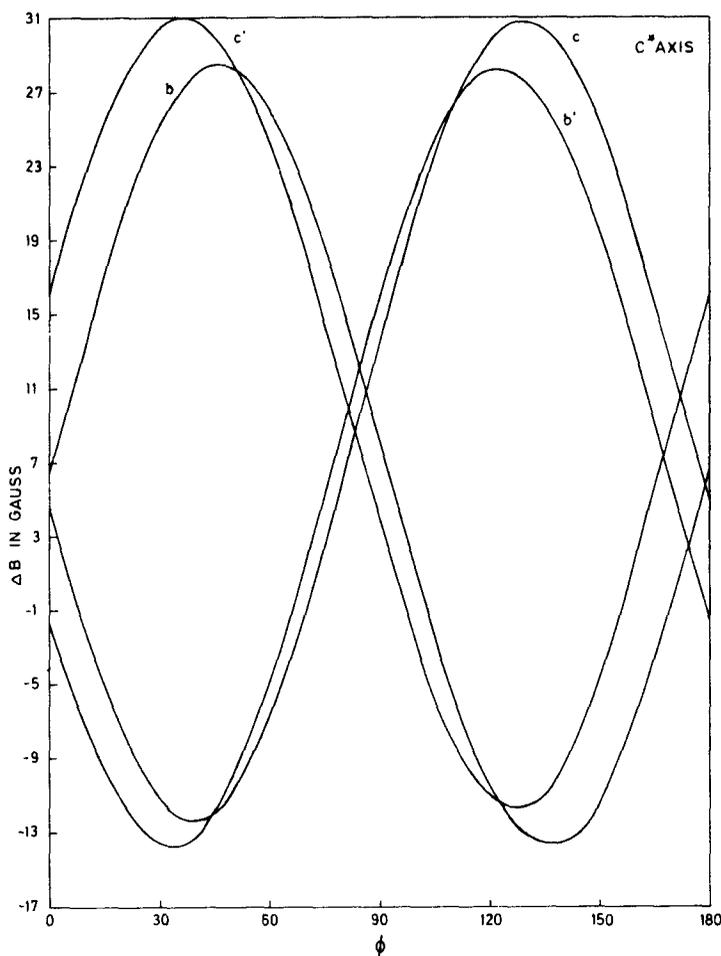


Figure 5. Same as in figure 4, but for c^* axis rotation for the four distinct P-P vectors.

These values are comprised of anisotropic susceptibility shifts and a pseudocontact shift and contact shift at the site of protons. The second term is very difficult to calculate from the principal values because the susceptibility tensor itself is non-traceless due to anisotropic g -value of cobalt. But ^{19}F NMR experiments by Harakawa (1964) on directly bonded fluorine to $3d$ metal ions showed the transferred spin density of the order of 0.5% equivalent to 5 gauss. Since in hydrated crystals water protons are not directly attached to metal ions we assumed 0.08% spin density and extracted the dipolar shift tensor based on this. It may be added here that similar transferred hyperfine density in the range of 0.02 to 0.1% is observed by ENDOR studies on $[\text{La}(\text{C}_2\text{H}_5 \cdot \text{SO}_4)_3 \cdot 9\text{H}_2\text{O}]$ (De Beer *et al* 1976).

4.3 Comparison with reported g -values

EPR experiments on Co^{2+} doped potassium tutton salts at 4.2 K were done by Abragam

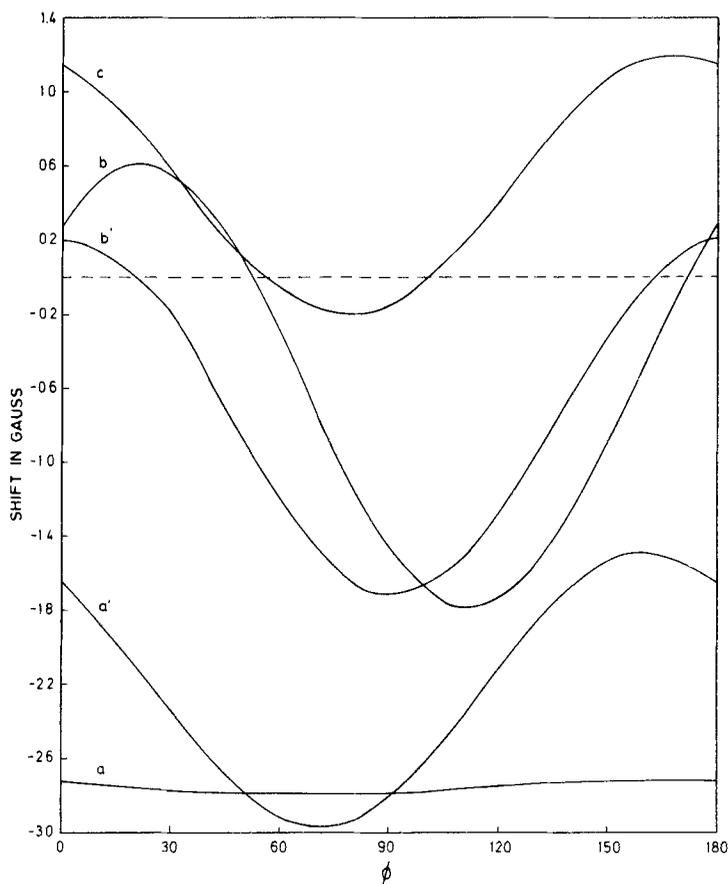


Figure 6. Angular variation of paramagnetic shift corresponding to the centre of gravity of the doublet dipolar lines for *a*-axis rotation.

and Pryce (1950). The reported values are

$$g_{xx} \geq 3.35; g_{yy} \leq 2.3 \text{ and } g_{zz} = 6.55.$$

Since the direction cosines of the cobalt(II) *g*-tensor are not reported, based on the octahedral symmetry of the $[\text{CoO}_6]$ chromophore we have assumed different combinations of the *g*-tensor principal directions along Co-O₅, Co-O₆ and Co-O₇ directions and calculated the susceptibility shift tensor at both the protons of the water molecule. This was further averaged to consider the fast-flipping motion about C₂ axis of the water molecule. This shift tensor values for the combination which has *g*_{zz} along shortest Co-O direction was found to give shift tensor values in close agreement with the experimental values. The *g*-values were back-calculated from the experimental shifts and were close to that of EPR reported values at 4.2 K. The experimentally derived *g*-tensor principal values are

$$g_{xx} = 3.27 \pm 0.2, g_{yy} = 2.18 \pm 0.2, g_{zz} = 6.35 \pm 0.2.$$

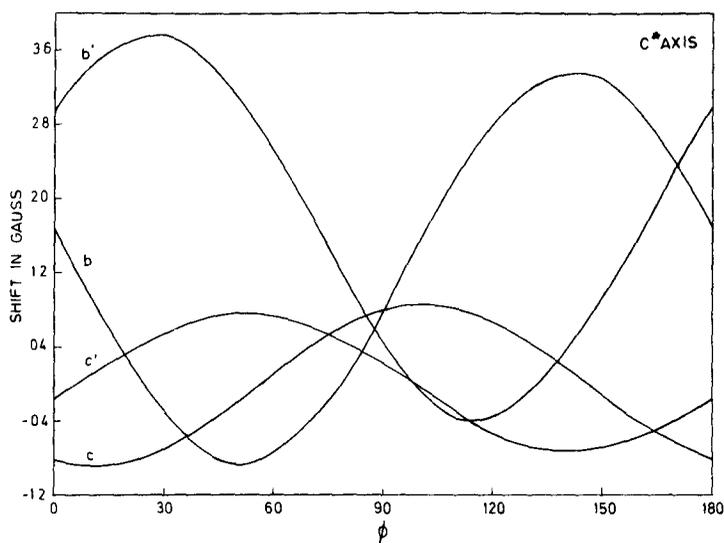


Figure 7. Same as in figure 6, but for c^* axis rotation.

Table 1. Magnitude and direction cosines of PP vectors.

PP Vector	PP distance			Direction cosines		
	A	ϕ_0	δ	a	b	c^*
a	1.43 ± 0.03	$70^\circ \pm 2^\circ$	$19^\circ \pm 2^\circ$	0.3256	0.3233	-0.8884
b	1.46 ± 0.03	$28^\circ \pm 2^\circ$	$43^\circ \pm 2^\circ$	0.6444	0.6837	0.3426
c	1.50 ± 0.03	$92^\circ \pm 2^\circ$	$40^\circ \pm 2^\circ$	-0.7656	0.6428	0.0267

Table 2. Proton positions in fractional coordinates derived from dipolar tensor.

Atom	x	y	z
H (1)	0.2567	0.1344	0.1040
H (2)	0.2417	0.0965	0.3187
H (3)	-0.1499	0.1914	0.0083
H (4)	-0.2701	0.1095	-0.0809
H (5)	-0.0992	-0.0655	0.3585
H (6)	0.0274	-0.1449	0.3517

5. Remarks and conclusions

Proton positions in paramagnetic hydrated crystals $K_2Co(SO_4)_2 \cdot 6H_2O$ were calculated. It was observed that the g -values derived experimentally are in good agreement with the reported values within experimental error, proving that this technique is useful

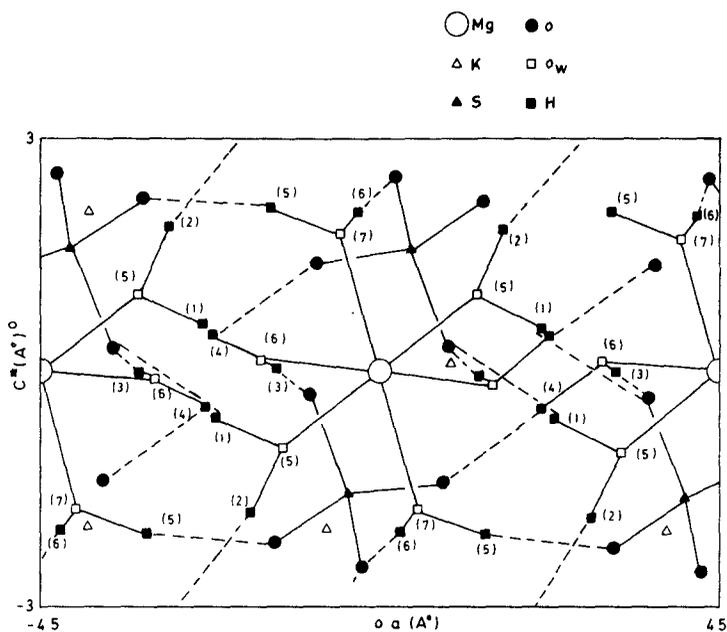


Figure 8. Projection of a unit cell of $K_2Co(SO_4)_2 \cdot 6H_2O$ lattice on to the ac^* -plane showing the derived proton positions and the hydrogen bonding schemes (dotted lines) derived from the NMR results. Filled circle represents oxygen atoms connected to sulphur while unfilled squares represent water oxygens.

Table 3. Shift parameters for PP vector c (all in gauss).

Principal values of shift tensor	B_s	B_{as}	B_{as} calc. using EPR parameters
S_{xx}	-1.3 ± 0.05	-2.1 ± 0.05	-2.2
S_{yy}	2.4 ± 0.05	1.6 ± 0.05	1.67
S_{zz}	0.823 ± 0.03	0.023 ± 0.03	0.025

Table 4. Direction cosines of shift tensor.

	a	b	c^*
S_{xx}	0.8745	-0.0621	-0.4811
S_{yy}	0.1401	0.9819	0.1278
S_{zz}	0.4644	-0.1792	0.8673

in cases such as non s -state high spin transition metal salt hydrates which will have fast spin lattice relaxation time at room temperature.

But if the number of spatially distinct water molecules per unit cell is greater there

will be considerable over-lapping of lines and the analysis will be difficult. In such cases experiments at high frequency and low temperatures like 77 K will give correct information, although the arresting of the water-flipping motion will lead to a doubling of the lines.

The interesting feature is that g -tensor is extracted for the pure system, while in EPR the presence of spin-spin interaction would entail diamagnetic dilution in an isomorphous host lattice. And it is not always possible to retain the exact geometry of a dopant ion in a foreign lattice. An additional bonus comes by way of not requiring ultra-low temperature measurements. However, not all systems will be amenable since in some cases the spin lattice relaxation may not be ideal since further modulation *via* paramagnetic relaxation due to fluctuating dipolar interaction can give rise to considerable broadening, making accurate shift tensor measurements rather difficult. Nevertheless, it is pleasing to note that one could extract EPR parameters *via* NMR of a dipolar coupled neighbour.

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