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## Proton repulsion and thallium displacement in $Tl^{2+}$ -doped $RbH_2AsO_4$ investigated by electron paramagnetic resonance

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**Abstract.** The electron paramagnetic resonance of the paramagnetic centre  $Tl^{2+}$  in the  $Rb^+$  site in  $RbH_2AsO_4$  was investigated in the temperature range 25–149 K. Similarly to what has already been observed in other members of the  $KH_2PO_4$  (KDP) family, in the ferroelectric phase the symmetry of the spectrum, at higher temperatures, is consistent with the  $C_2$  symmetry of the  $Rb^+$  site, whereas at low temperatures it changes to  $C_1$ . These observations support the general proposition that in the KDP family the  $Tl^{2+}$  centre causes, at low temperatures, an inversion of the Slater configurations for the protons in such a way that only one proton is connected to the neighbouring  $AsO_4$  group. The present study shows evidence, at low temperatures, of additional structures in the spectrum, which strongly suggest a superhyperfine interaction of the  $Tl^{2+}$  centre with one neighbouring proton and one neighbouring  $^{35}Rb$  nucleus. This gives important additional support to the idea of inverted Slater configurations and besides indicates that proton repulsion is accompanied by  $Tl^{2+}$  displacement.

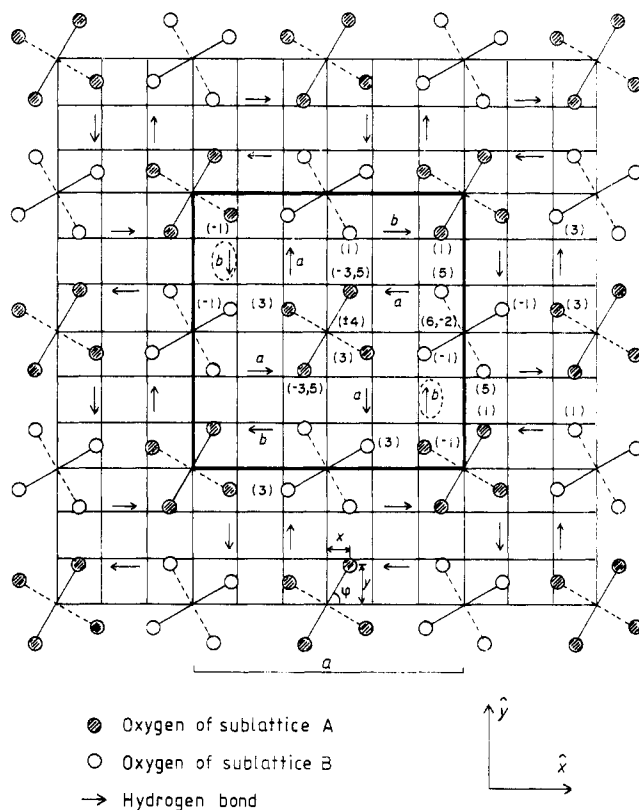
### 1. Introduction and theory

The  $Tl^+$  ion isomorphously replaces the cation in crystals of the  $KH_2PO_4$  (KDP) family, during growth by solution, and can subsequently be converted to  $Tl^{2+}$  by x-ray irradiation at liquid-nitrogen temperature [1]. This impurity centre has interesting properties as a paramagnetic probe and has been used to observe phase transitions in the KDP family. The hyperfine interaction is exceptionally large—of the order of 100 GHz—and small changes in its value result in significant changes in the spectra. Therefore, the electron spin resonance (ESR) spectra are very sensitive to local changes. The position of the lines in a magnetic-field sweep is far from  $g = 2$ , making it possible to identify easily the electron paramagnetic resonance (EPR) spectrum. Both isotopes  $^{203}Tl$  and  $^{205}Tl$  have almost equal magnetic moments, and therefore the respective EPR lines are not resolved, resulting in a very simple spectrum.

The EPR spectra of  $Tl^{2+}$  may be described by the spin Hamiltonian

$$\mathcal{H} = H \cdot \mathbf{g} \cdot \mathbf{S} + S \cdot \mathbf{A} \cdot \mathbf{I} \quad (1)$$

where  $S = \frac{1}{2}$  and  $I = \frac{1}{2}$  for both Tl isotopes. On account of the high hyperfine interaction ( $A \sim 100$  GHz), at microwave frequencies of about 9 GHz two transitions are observed,



**Figure 1.** Projection of the structure of  $\text{RbH}_2\text{AsO}_4$  in the  $ab$  plane. The heavy full line is the contour of the  $\bar{1}42d$  unit cell. The  $\text{As}^{5+}$  ions, not shown in the figure, are at the centre of the  $\text{O}^{2-}$  tetrahedra and the  $\text{Rb}^+$  ions, also omitted in the figure, are displaced by  $(0, 0, \frac{1}{2})$  from the  $\text{As}^{5+}$  positions. The arrows indicate the ordering of the protons in a  $+z$  (pointing out of the page) ferroelectric domain. Numbers indicate the  $z$  positions of the ions in units of  $c/8$ . A  $\text{Ti}^{2+}$  centre may be supposed to substitute a  $\text{Rb}^+$  ion at the centre of the unit cell, then the  $y$  axis of the defect labelled  $\text{A}_\downarrow$  connects the defect to the  $b$  proton at the lower right side.

corresponding to  $(F = 1, m_F = -1) \rightarrow (F = 1, m_F = 0)$  and  $(F = 1, m_F = 1) \rightarrow (F = 1, m_F = 0)$ , where  $F = I + S$ . The two other allowed transitions are not observed.

$\text{RbH}_2\text{AsO}_4$  has a phase transition at 110 K from a high-temperature paraelectric phase to a low-temperature ferroelectric phase. As shown in figure 1, there are two  $\text{Rb}^+$  sites per unit cell, which will be denoted by A and B.

In the paraelectric phase the crystal belongs to the tetragonal  $\bar{1}42d$  space group. The two sites have symmetry  $S_4$ , and consequently the  $\text{Ti}^{2+}$  ions in these sites are magnetically equivalent and yield just one line in the EPR spectrum, for each transition. The spectrum is formed by a pair of lines, corresponding to the observed transitions, and is isotropic in the plane  $ab$ .

In the ferroelectric phase, the crystal belongs to the orthorhombic  $Fdd2$  space group and the symmetry of the  $\text{Rb}^+$  sites is  $C_2$ . Owing to the existence of two ferroelectric domains, there will be four magnetically inequivalent centres  $\text{A}_+$ ,  $\text{A}_-$ ,  $\text{B}_+$  and  $\text{B}_-$ , where the subscripts refer to the two ferroelectric domains. If the substitutional  $\text{Ti}^{2+}$  keeps the symmetry of the  $\text{Rb}^+$  site, four lines are expected for each transition, for a general

direction of the magnetic field. If the symmetry of the  $Tl^{2+}$  centre is lower ( $C_1$ ), there are eight magnetically inequivalent centres,  $A'_+$ ,  $A''_+$ ,  $B'_+$ ,  $B''_+$ ,  $A^+$ ,  $A^-$ ,  $B^+$  and  $B^-$ , where the superscripts distinguish centres that are transformed into each other by a  $C_2$  axis along the  $c$  axis of the crystal.

The EPR spectra of the  $Tl^{2+}$  ion in crystals of the KDP family show two patterns in the ferroelectric phase—a high-temperature pattern corresponding to defect centres with symmetry  $C_2$ , and a low-temperature pattern corresponding to defect centres with symmetry  $C_1$  [2]. At intermediate temperatures both patterns are observed.

To explain these experimental results, it has been proposed [3] that the proton-thallium interaction creates a temperature-dependent configurational potential with three minima. The central minimum corresponds to the normal Slater configuration with two near protons and two far protons around the  $AsO_4^{4-}$  radical. The external minima correspond to defective Slater configurations with one near proton and three far protons. Below a certain temperature  $T$ , this last configuration, which has symmetry  $C_1$ , is stable and the other, with symmetry  $C_2$ , is unstable. At  $T^*$  the situation is reversed. Around  $T^*$  the three wells of the configurational potential have the same depth and both defects may be observed simultaneously.

There has been a suggestion [4, 5] that the off-centre displacement of the  $Tl^{2+}$  impurity is important for the explanation of the additional local lowering of symmetry at low temperatures ( $T < T^*$ ). The study of  $RbH_2AsO_4$  was undertaken to verify the generality of the three-well model in the KDP family as well as to confront the two models—proton or  $Tl^{2+}$  displacement. In this work it has been observed that the changes of the EPR spectra at  $T^*$  and  $T_c$  are similar to the changes observed in other members of the family. Besides, the superhyperfine (SHF) interaction observed in  $RbH_2AsO_4$  adds new arguments in favour of proton displacement and suggests that the  $Tl^{2+}$  ion may suffer a displacement simultaneously with the proton.

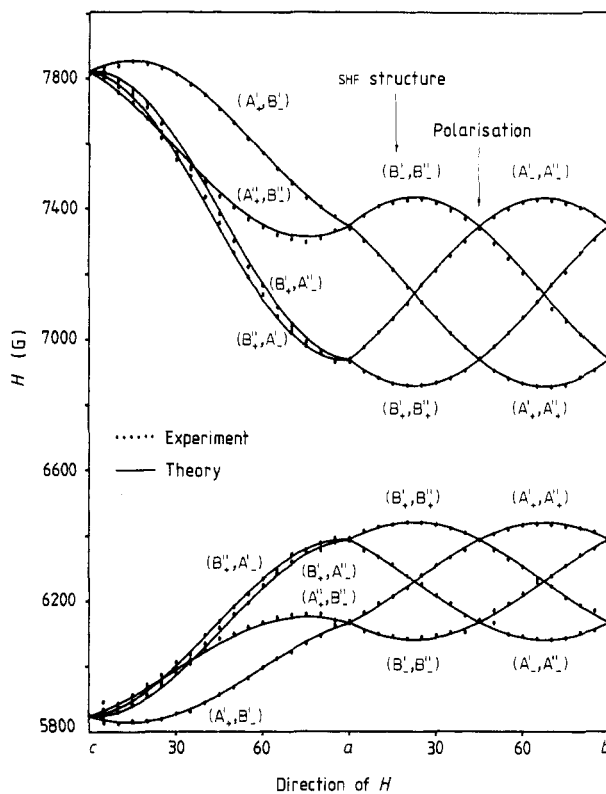
## 2. Results and discussion

The  $RbH_2AsO_4$  crystals, grown by slow evaporation of a solution containing approximately 2 mol. % of  $Tl^+$ , were irradiated at 77 K with x-rays (75 kV, 15 mA) for 3 h. The  $Tl^{2+}$  ions thus formed are destroyed at 250 K.

The angular dependence of the EPR spectra of  $Tl^{2+}$  was investigated in the paraelectric phase (149 K) and in the ferroelectric phase (25 and 100 K). They are similar to the angular dependences obtained by us for other members of the KDP family and reported previously [2, 3, 6–8]. The angular dependence at 25 K is shown in figure 2, and according to the symmetry arguments presented above demonstrates that the  $Tl^{2+}$  centre destroys the  $C_2$  axis of the  $Rb^+$  site. In fact, it is possible to show that if the  $C_2$  axis of the site is preserved, the centres  $A'_+$ ,  $A''_+$ ,  $B^+$  and  $B^-$  are magnetically equivalent in the plane  $ac$  and should yield just one line (similarly  $A^+$ ,  $A^-$ ,  $B'_+$  and  $B''_+$  would yield one line).

The  $g$  and  $A$  tensors, obtained by fitting the angular variations to the spin Hamiltonian (equation (1)), are given in table 1. It can be seen that the principal axes of the tensors are along the directions of the crystal axes in the paraelectric phase and are displaced from these directions in the ferroelectric phase.

In order to discuss the role of the bonding protons in the lowering of the symmetry, they are classified into two groups. As can be seen in figure 1, each  $Rb^+$  ion has eight neighbouring protons: four connect an  $AsO_4$  group just above or below the  $K^+$  ion to a lateral  $AsO_4$  group and will be labelled  $a$ ; the other four, labelled  $b$ , connect two  $AsO_4$



**Figure 2.** Angular dependence of the EPR spectra of  $\text{RbH}_2\text{AsO}_4:\text{Tl}^{2+}$  at 25 K and 9248 MHz. The spectra correspond to the defect with symmetry  $C_1$ . At 25 K the lines corresponding to the  $C_{2z}$  symmetric defect are very faint and are not shown. Only the angular dependence of the centre labelled  $A'_+$  was adjusted to the experimental points, the other continuous lines were obtained by symmetry operations. The arrows show the directions on which the SHF structure (figures 4 and 5) and the temperature dependence of polarisation (figure 3) are observed.

groups that are lateral with respect to the  $\text{Rb}^+$  ion. Protons a and b are at almost the same distance from the site of  $\text{Rb}^+$ , but protons b are a little nearer.

Table 1 shows that in the ferroelectric phase the  $x$  axis of the  $g$  and  $A$  tensors is only  $11^\circ$  off the direction that connects the  $\text{Rb}^+$  site to the proton. This kind of result has been observed by us in all crystals of the KDP family examined, except  $\text{NH}_4\text{H}_2\text{AsO}_4$  [7]—namely  $\text{KH}_2\text{PO}_4$  [2, 3],  $\text{KD}_2\text{PO}_4$  [3],  $\text{KH}_2\text{AsO}_4$  [3, 7] and  $\text{NH}_4\text{H}_2\text{PO}_4$  [6]—and led to the proposal [2] that one of the protons b that should be at the side of the double-well potential closer to the  $\text{Tl}^{2+}$  ion goes to the farther well, thus compensating the excess charge. This displacement of one proton breaks the  $C_2$  symmetry of the site and this is revealed in the EPR spectra by the observation of two lines labelled ' and ', instead of just one.

The variation of the spectrum with temperature was observed for the magnetic field in the  $ac$  plane at  $60^\circ$  from  $a$ ; in this direction the splitting of the lines  $A'_+$  and  $A''_+$  is large and there is no interference from other lines. At low temperatures (25 K) a faint line is observed between the two lines and its intensity is constant as the temperature is increased. At about 80 K the intensity of this intermediate line grows and the intensity of the lines  $A'_+$  and  $A''_+$  decreases, drastically modifying the spectrum.

According to our model [3], described briefly in section 1, this intermediate line corresponds to centres  $\text{Tl}^{2+}$ , which preserve the symmetry of the site, and  $T^* \sim 80$  K is the temperature where the three wells in the configurational potential of thallium–proton coupling have the same depth. These results are consistent with our previous

**Table 1.** Principal values and direction cosines of  $g$  and  $A$  tensors of  $RbH_2AsO_4:Tl^{2+}$ . The  $x$  principal axis is directed nearly along the line connecting the  $K^+$  site to a b proton.

Principal values			
	$g$	$A$ (MHz)	Direction cosines ( $\alpha, \beta, \gamma$ )
149 K (A)	1.994	104 990	$x: (1, 0, 0)$
	1.994	104 990	$y: (0, 1, 0)$
	1.985	104 220	$z: (0, 0, 1)$
25 K (A')	1.991	102 088	$x: (0.879, -0.377, -0.294)$
	1.998	102 867	$y: (0.387, -0.922, -0.025)$
	1.984	101 436	$z: (0.280, -0.092, 0.956)$
Line connecting $K^+$ site to b proton			(0.786, -0.558, -0.266)

measurements with other crystals of the KDP family, the only difference being that the  $C_2$  symmetric centre is observed in  $RbH_2AsO_4$  even at very low temperatures.

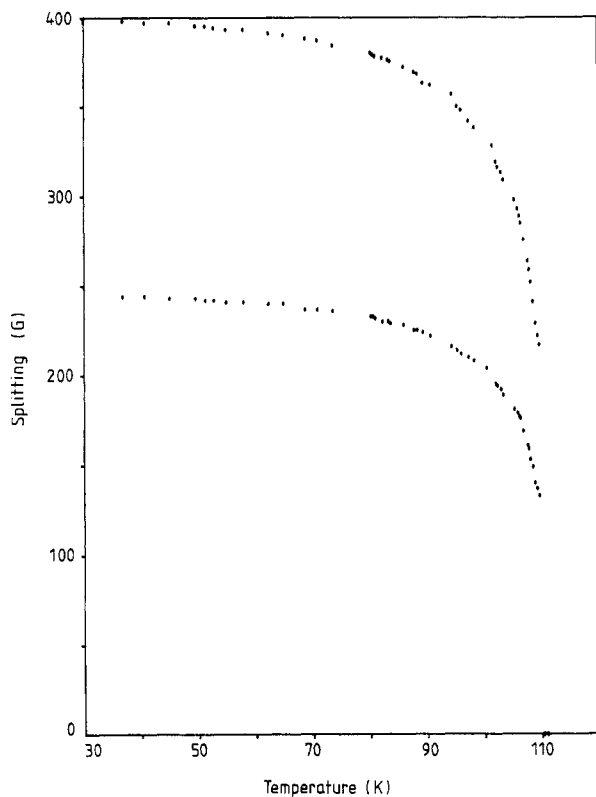
For the magnetic field oriented along the  $a^*b$  direction, only two lines are observed (figure 2), corresponding to centres ( $A'_+, A''_+, B'_+, B''_+$ ) and ( $A'_-, A''_-, B'_-, B''_-$ ), which belong to ferroelectric domains + and -, respectively. The splitting of the doublet is then expected to be, in a first approximation, proportional to the spontaneous polarisation, which is the order parameter of the ferroelectric transition. Figure 3 shows the variation of this splitting with temperature; it goes discontinuously to zero at  $T_c = 110$  K, indicating the first-order character of the transition. Measurements of spontaneous polarisation in crystals of the KDP family indicate that it saturates rapidly below  $T_c$ , unlike what happens with the splitting. It is thought that the local polarisation of the lattice by the  $Tl^{2+}$  defect is responsible for this different behaviour.

A superhyperfine (SHF) structure is observed on the lines corresponding to the centres  $A'_-, A''_-$  and  $A_-$ , when the magnetic field ( $H$ ) is in the  $ab$  plane oriented at approximately  $20^\circ$  from axis  $a$ . A doublet is visible at low temperatures ( $T < 70$  K) and a nine-line multiplet is observed from 85 to 100 K, approximately. A rotation of  $H$  from that privileged direction causes a decrease in the intensity of the structure and it disappears completely for a rotation of  $14^\circ$  on either side.

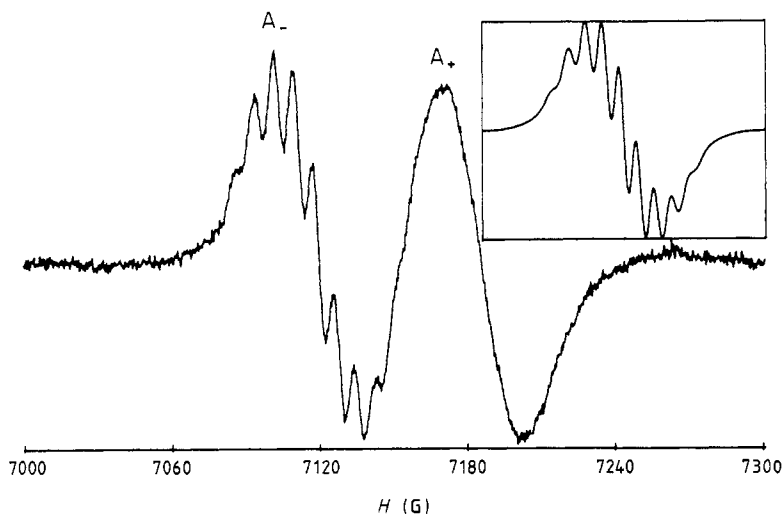
To interpret these experimental results, we must add to the spin Hamiltonian (equation (1)) the superhyperfine interaction term

$$\mathcal{H}_{SHF} = S \cdot A_n \cdot I_n. \quad (2)$$

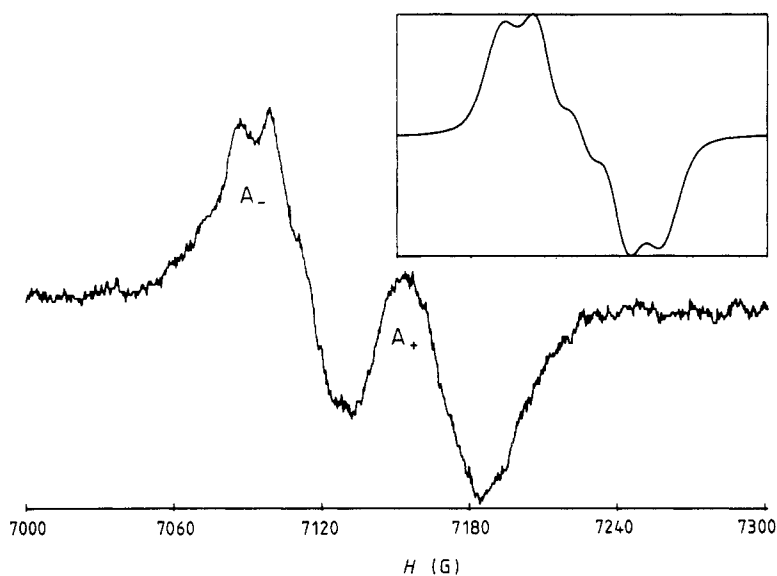
We remark that the SHF interaction associated with a neighbouring nuclear spin  $I_n$  is larger if the angle between the applied magnetic field and the line that links the defect and the nuclear spin  $I_n$  becomes smaller. The As nucleus cannot be responsible for this SHF structure since no structure is seen when  $H$  is directed along the  $c$  crystal axis, where the nearer As nucleus lies. The interaction with the proton should be more important than with protons  $a$  because the direction  $Tl^{2+}$ -proton is at  $15^\circ$  from the plane  $ab$  and



**Figure 3.** Temperature dependence of the splitting of lines corresponding to + and - polarisation (see figure 2). The spectrum is observed on the  $ab$  plane at  $45^\circ$  and the splitting of the doublet is measured as a function of temperature. The splitting goes discontinuously to zero at 110 K, indicating the first-order character of the ferroelectric transition.



**Figure 4.** The SHF structure on the line corresponding to the  $A_-$  defect is seen at  $T = 99$  K for  $H$  on the  $ab$  plane at  $20^\circ$  from the  $a$  axis. The line on the right side, without structure, corresponds to centre  $A_+$ , which is not privileged. The inset shows the computer simulation, with nine lines plus a broad line.



**Figure 5.** The SHF structure on the line corresponding to the  $A_-$  defect is seen at  $T = 27.7$  K for  $H$  on the  $ab$  plane at  $20^\circ$  from the  $a$  axis. The line on the right side, without structure, corresponds to centre  $A_+$ , which is not privileged. The inset shows the computation simulation, with five lines plus a broad line.

the direction  $Tl^{2+}$ -proton  $a$  is at  $50^\circ$  from the same plane. There are four nearest-neighbour Rb nuclei at a distance of  $4.3 \text{ \AA}$  from the  $Tl^{2+}$  and the angle of the direction  $Tl^{2+}$ -Rb $^+$  is at  $25^\circ$  from the  $ab$  plane. The  $^{37}\text{Rb}$  isotope ( $I = \frac{3}{2}$ , 27.3% abundant) has a magnetic moment of  $2.74 \mu_B$ , comparable to the proton magnetic moment, while the  $^{35}\text{Rb}$  isotope ( $I = \frac{5}{2}$ , 72.8% abundant) has a magnetic moment that is less than half this value and therefore will be neglected.

Let  $\gamma(^{35}\text{Rb})$  and  $\gamma(p)$  be the SHF coupling constants of the defect with the nearest-neighbour  $^{35}\text{Rb}$  nuclei and the bonding protons, respectively. For  $H$  lying on the  $ab$  plane, the largest value of  $\gamma(^{35}\text{Rb})$  will occur for  $H$  along the crystal  $a$  axis and the largest value of  $\gamma(p)$  will occur for  $H$  at  $33^\circ$  off the  $a$  axis. It is reasonable to assume that at an intermediate direction  $\gamma(^{35}\text{Rb}) = \gamma(p)$ . In this direction the SHF structure will correspond to an equal coupling to two protons and two  $^{35}\text{Rb}$  and will yield  $2 \times (2 \times \frac{3}{2} + 2 \times \frac{1}{2}) + 1 = 9$  lines. The coupling to two neighbouring  $^{37}\text{Rb}$  or one  $^{35}\text{Rb}$  and one  $^{37}\text{Rb}$  and two protons will yield a larger number of weaker lines, which would be observed as a broad line added to the nine-line structure.

This is what is observed experimentally. Figure 4 shows the observed spectrum for  $H$  in the  $ab$  plane, at  $20^\circ$  from the  $a$  axis, at 99 K, and the computer simulated spectrum.

At temperatures below  $T \approx 80$  K the nine-line SHF structure disappears. At these temperatures the defects with  $C_1$  symmetry become more stable than the defects with  $C_2$  symmetry. One of the protons is repelled to the farther well in the bond, and probably the  $Tl^{2+}$  ion is displaced to accommodate the new charge distribution. The SHF interaction is now effective with one proton and one Rb nucleus. Figure 5 shows the observed and simulated SHF structures at low temperatures ( $T < 70$  K).

In the paraelectric phase ( $T > 110$  K) the rapid movement of protons from one well to the other in the bond completely destroys the SHF structure.



### 3. Conclusions

In concluding, we remark that this model explains reasonably well the SHF structure observed in the three temperature ranges ( $T < T^*$ ,  $T^* < T < T_c$  and  $T > T_c$ ) and is compatible with the temperature-dependent three-minima potential well for  $Tl^2$ -proton coupling, proposed previously [3] to explain the EPR spectra.

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