EPR DETECTION OF HYPERFINE COUPLINGS FROM $^{203}Tl^{++}$ AND $^{205}Tl^{++}$ IONS AND FERROELECTRIC-SYMMETRY SIGNALS IN PARAELECTRIC KH_2PO_4 AND KD_2PO_4

P. J. Grandinetti*, D. Nettar** and N. S. Dalal

Chemistry Department, West Virginia University, Morgantown, WV 26506

Abstract

By using computer simulation techniques, it is possible to understand the rather unusual superhyperfine pattern on the hyperfine transitions of Tl^{2+} (6s') ions and to resolve transitions from $^{203}Tl^{2+}$ and $^{205}Tl^{2+}$ for the first time in the KH_2PO_4-type lattices. The detection of ferroelectric excitations in the paraelectric phase of partially deuterated KH_2PO_4 and their dependence on the H/D ratio could not be explained in terms of current theoretical models of ferroelectric transitions.

INTRODUCTION

Recent studies (1-7) have shown that Tl^{2+} (6s') can be formed in KH_2PO_4-type of compounds through X- or γ-irradiation at 77 K of Tl^{+} doped crystals. Even though Tl^{2+} has one unit of positive charge higher than K^{+}, it has the advantage of entering the lattice in the monovalent state, thus the doped lattice is formed without any distortion due to excess positive charge. The extra charge of the Tl^{2+} probe was explained by Gonzaga et al. (4-6) as being dynamically balanced by the displacement of a nearby proton. However, they made no mention of the proton superhyperfine structure, which could support this model. By detailed calculations of field positions and computer simulations of the superhyperfine structure we have produced results that only partially support the model proposed by Gonzaga et al. (4-6), but yield accurate values for the $^{203}Tl^{2+}$ and $^{205}Tl^{2+}$ nuclei for the first time in these lattices.

In addition, close examination of the spectra around T_c, but for $T > T_c$, shows evidence that the crystal breaks down into clusters of the low temperature (ferroelectric) phase and the high temperature (paraelectric) phase, and that these clusters occupy the whole lattice as the lattice orders below T_c.

EXPERIMENTAL

Potassium dihydrogen phosphate (KDP) and its deuterated analog crystallize as clear, colorless tetragonal crystals belonging to the $I\bar{4}2d$ space group.

Single crystals of KH_2PO_4 and KD_2PO_4 doped with Tl(I) were prepared as follows. A saturated solution of KH_2PO_4 in H_2O and D_2O was treated with about 1 mole % TlCl. The resulting turbid liquid was filtered and allowed to evaporate slowly at room temperature. After a few days, well formed single crystals of the KH_2PO_4-type salt were obtained. Tl(II) was created on the crystal lattice by gamma-irradiation from a ^{60}Co source at room temperature for approximately 24 hours (exact time not critical).

EPR measurements were made at X-band frequencies using a Bruker ER 200D spectrometer equipped with a TE_{102} cavity and interfaced to an Aspect 2000 minicomputer. The EPR SRC program was used on the Aspect 2000 to control the spectrometer and to do various data manipulation and spectral simulations. The microwave frequency measured with a Hewlett Packard 5340A digital computer. Variable temperature studies were carried out using a Bruker ER 411 T variable temperature unit accurate to $\pm$ 0.5 K. The magnetic field was calibrated with a Bruker field tracking gaussmeter.

RESULTS AND DISCUSSION

Typical EPR spectra of Tl(II) in the paraelectric phase of KH_2PO_4 and KD_2PO_4 for $H \perp C$ are shown in Figure 1.

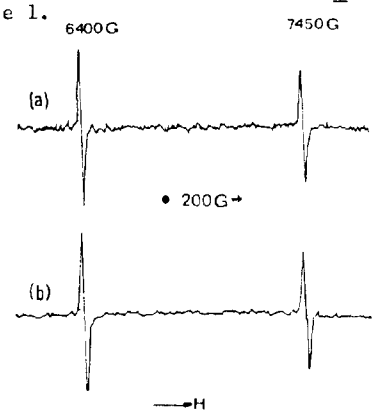

Fig. 1. Typical EPR spectra of Tl^{2+} in (A) KH_2PO_4 and (B) KD_2PO_4 at 300 K for H//a. The first resonance is around 6200 G and the second around 7200 G.

CH2358-0/86/0000-0503 $1.00

The spectrum consists of two main lines. These lines at 6200 G and 7400 G are due to the transitions between levels $|1, -1\rangle$ and $|1, 0\rangle$ and levels $|1, 0\rangle$ and $|1, 1\rangle$ ($\Delta m_F = \pm 1$) respectively, Figure 2.

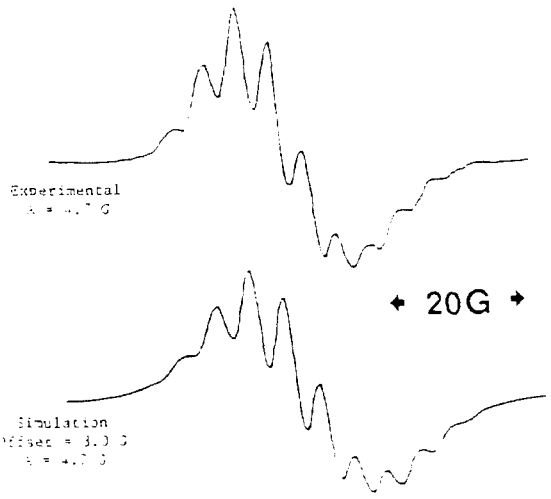

Fig. 2. Experimental and simulated proton superhyperfine structure for the "high" field transition of Tl^{2+} in KH_2PO_4.

The 7500 G line has an intensity 70% of that at 6200 G. This was unexpected because the Boltzmann factors were about the same for the two lines. However, a detailed analysis of the wavefunctions and energy levels obtained with the computer programs FIELDS and LSF (8-14) showed that the intensity differences were due to the different microwave induced transition probabilities, related to the mixing of the spin wavefunctions via the rather large (~100 GHz) Tl^{2+} hyperfine couplings. The spectra were analyzed as discussed elsewhere (8-14) using the computer programs FIELDS and LSF (11-13), and the spin Hamiltonian

$$= \underset{(a)}{\beta_e \underset{\sim}{H} \cdot \underset{=}{g} \cdot \underset{\sim}{\hat{S}}} + \underset{(b)}{\sum_i \underset{\sim}{\hat{I}}^i \cdot \underset{=}{A}^i \cdot \underset{\sim}{\hat{S}}} - \underset{(c)}{\sum g_N^i \beta_N \underset{\sim}{H} \cdot \underset{\sim}{\hat{I}}^i}$$

Here (a) is the electronic Zeeman term, (b) is the hyperfine coupling and (c) the nuclear terms. The summation on (b) and (c) is over the Tl isotopes and protons.

Table 1 lists the spin Hamiltonian parameters calculated using the LSF program and the calculated spin densities for $^{205}Tl^{2+}$ by using the computer simulation of proton superhyperfine structure as discussed below.

Table 1

Spin Hamiltonian Parameters* and Electron Spin Densities for $^{205}Tl^{2+}$

Host Crystal	Principal Values		Estimated rms error in fitting line positions (G)	C_s^2/C_p^2
KH_2PO_4 (295 K)	g_x	$=1.994\pm0.001$	0.2	
	g_y	$=1.994\pm0.001$		
	g_z	$=1.991\pm0.001$		
	g_{iso}	$=1.993\pm0.002$		
	A_x	$=116419\pm26$		0.63/0.39
	A_y	$=116428\pm26$		$=1.62$
	A_z	$=115936\pm26$		
	A_{iso}	$=116261\pm45$		
KD_2PO_4 (295 K)	g_x	$=1.993\pm0.001$	1.0	
	g_y	$=1.993\pm0.001$		
	g_z	$=1.990\pm0.001$		
	g_{iso}	$=1.992\pm0.002$		
	A_x	$=116402\pm44$		0.63/0.39
	A_y	$=116421\pm44$		$=1.62$
	A_z	$=115911\pm44$		
	A_{iso}	$=116245\pm76$		

*A_x, A_y, A_z and A_{iso} are in units of MHz, θ and φ are the polar and azimuthal angles in the crystal-fixed a, b, c axis system.

Figure 3 shows the proton superhyperfine structure on the Tl(II) transitions in KH_2PO_4 at 124 K.

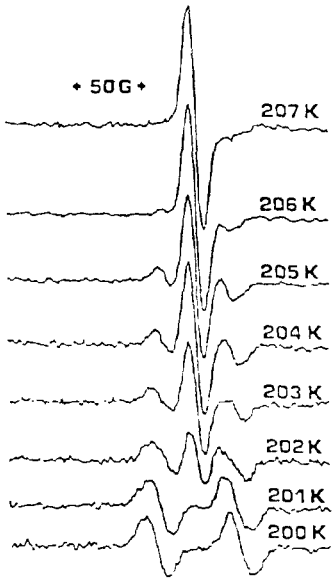

Fig. 3.

An unexpected feature is that the resolution of the superhyperfine on the high field transition is much less resolved. These two spectra can be analyzed in terms of eight equivalent protons and the two Tl isotopes, ^{203}Tl and ^{205}Tl. This is done making the assumption that the calculated hyperfine coupling constant for Tl(II) is the coupling constant for the higher percentage isotope ^{205}Tl (70.5%) and that the electronic wavefunction at the nucleus is the same for both isotopes. Then the ratio of the magnetic moments of ^{203}Tl to ^{205}Tl is used to calculate the coupling constant of the lower percentage isotope $^{203}Tl^{2+}$.

$$^{203}A = (^{203}g_N/^{205}g_N) \cdot ^{205}A$$

Using the calculated coupling constant for ^{203}Tl with the program FIELDS, the magnetic fields are calculated for the two $^{203}Tl^{2+}$ transitions and can be compared to those for the $^{205}Tl^{2+}$ transitions. The difference between the field positions of the lines from the two isotopes is calculated for both transitions. A spectrum is simulated for a Tl^{2+} hyperfine transition with coupling to eight equivalent protons. This spectrum is offset from itself by the amount calculated previously and added to itself with an area proportional to its isotopic abundance. The experimental and simulated spectra are shown in Fig. 2. The comparison is quite good.

The temperature dependence of the hyperfine structure for Tl^{2+} was studied on three different crystals of KD_2PO_4, each of a different degree of deuteration. Figure 3 shows some typical spectra. The relative degree of deuteration is reflected by the apparent Curie temperatures of 197, 203 and 209 K. The % deuteration was estimated from the T_c versus % deuteration calibration curves of Hukuda (15). It was found that the range of temperature over which the spectra from the paraelectric and the ferroelectric phases are simultaneously present, denoted as ΔT_c - the coexistence temperature range, decreased as the % deuteration increases as shown below.

T_c/K	% Deuteration	ΔT_c/K
197 ± 0.5	70 ± 5	4.5 ± 0.5
203 ± 0.5	82 ± 5	3.5 ± 0.5
209 ± 0.5	88 ± 5	1.5 ± 0.5

IV. CONCLUSIONS

By combining computer simulation techniques with detailed EPR measurements as a function of temperature and crystal orientation, it has been shown that the Tl^{2+} ion has eight nearest neighbors rather than seven or nine as tentatively postulated earlier. The Tl^{2+} probe provides evidence for ferroelectric cluster formation in the paraelectric phase of partially deuterated KD_2PO_4 and this phenomenon depends strongly on the hydrogen content of KD_2PO_4.

The mechanism by which the residual hydrogens cause the ferroelectric excitations to appear in the paraelectric phase needs further theoretical and experimental investigation.

Acknowledgement. Partial support by the National Science Foundation is gratefully acknowledged.

References

*M.S. student 1983-84. Now at Chemistry Department, University of Illinois, Urbana-Champaign, Illinois.

**Postdoctoral Associate 1981-83. Now at AT&T Laboratories, New Jersey.

1. V. N. Efimov, N. I. Silkin, V. G. Stepanov, and V. A. Sovt. Phys. Solid State 21, 1464 (1979).
2. T. B. Bogatova, I. Kh. Salikhov, V. G. Stepanov, and L. A. Trofanchuk, Sovt. Phys. Solid State 25, 1591 (1983).
3. V. G. Stepanov and L. A. Trofanchuk, Sovt. Phys. Solid State 26, 532 (1984).
4. G. M. Ribeiro, L. V. Gonzaga, A. S. Chaves, R. Gazzinelli, R. Blinc, P. Cevc, P. Prelovsek, and N. I. Silkin, Phys. Rev. B 25, 311 (1982).
5. L. V. Gonzaga, J. F. Sampaio, G. M. Ribeiro, A. S. Chaves, R. Gazzinelli, and R. Blinc, J. Phys. Soc. Jpn. 51, 540 (1982).
6. L. V. Gonzaga, J. F. Sampaio, G. M. Ribeiro, R. Gazzinelli, and A. S. Chaves, J. Phys. Soc. Jpn. 52, 3215 (1983).
7. D. N. Domingues, A. S. Chaves, G. M. Ribeiro, and R. Gazzinelli, Sol. St. Commun. 47, 665 (1983).
8. N. S. Dalal, Advan. Mag. Reson. 10, 119 (1982).
9. N. S. Dalal, D. Nettar, and P. J. Grandinetti, Ferroelectrics 51, 15 (1983).
10. N. S. Dalal, J. R. Dickinson, and C. A. McDowell, J. Chem. Phys. 57, 4254 (1972).
11. N. S. Dalal, J. A. Hebden, D. E. Kennedy and C. A. McDowell, J. Chem. Phys. 66, 4425 (1977).
12. N. S. Dalal, J. A. Hebden, and C. A. McDowell, J. Mag. Reson. 16, 289 (1974).
13. N. S. Dalal, D. Nettar and P. J. Grandinetti, J. Am. Chem. Soc. 104, 2054 (1982).
14. S. Akahoshi, T. Fukami, Y. Matsumoto, and K. Hukuda, Jpn. J. Appl. Phys. 23, 943 (1984).