Hg^+ IONS IN KH_2PO_4-TYPE LATTICES: NOVEL SUPERHYPERFINE INTERACTIONS AND $^{199}Hg/^{201}Hg$ HYPERFINE ANOMALY

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

Chemistry Department, West Virginia University, Morgantown, WV 26506

Abstract

Unlike earlier used paramagnetic probes for KH_2PO_4-type lattices, the Hg^+ ($6s'$) ions exhibit superhyperfine couplings to 4 ^{31}P nuclei. Detailed computer simulations of $^{199}Hg^+$ ($I = 1/2$) and $^{201}Hg^+$ ($I = 3/2$) hyperfine transitions yield a new value for the $^{199}Hg/^{201}Hg$ hyperfine anomaly, a difficult to measure but theoretically important parameter. Evidence is obtained for low symmetry excitations in the high temperature phases of $NH_4H_2PO_4$ and $ND_4D_2PO_4$, of significance for the development of new theoretical models.

I. INTRODUCTION

Paramagnetic probes have provided valuable, quantitative information on the role of the anionic fragments (PO_4^{3-} and AsO_4^{3-}) in the KD_2PO_4-type of ferroelectrics and antiferroelectrics. However, parallel studies of the cations (K^+, Rb^+, Cs^+ and NH_4^+) have not yet been possible, the progress being hampered mainly by the lack of suitable paramagnetic probes which could accurately simulate the cationic behavior. Previously used probes are Fe^{3+}, Cr^{3+}, Cu^{2+} and Tl^{2+}, all of which have an excess of positive charge compared with that of the substituted cations (1). This excess charge would necessarily lead to some structural deformation of the surroundings, and hence all these previously used ions might not be considered as faithful probes. Recently we reported (2) that Hg^+ ions can be stabilized in KH_2PO_4 and $NH_4H_2PO_4$. It was found that the Hg^+ hyperfine lines exhibited a 1:4:6:4:1 quintet superhyperfine structure for $T > T_c$, T_c being the para-ferro (or anti-ferro) electric transition temperature, 123 K for KH_2PO_4 and 147 K for $NH_4H_2PO_4$. While the preliminary results (2) showed that the Hg^+ ion couples strongly to the lattice and exhibits large spectral changes related to the lattice changes at T_c, the spin Hamiltonian parameters were not determined in that study because the very large (~35 GHz) hyperfine tensor made it difficult to obtain an accurate analytical expression for the EPR transition energy as a function of the applied Zeeman field. Moreover, it was not clarified whether the quintet/triplet superhyperfine pattern observed on each of the Hg^+ transitions was from the four hydrogen-bonded protons such as in AsO_4^{4-} in KH_2AsO_4 (1), or due to four ^{31}P nuclei of the nearby PO_4^{3-} units. In this paper we describe our measurements of Hg^+ centers in deuterated samples and show that in contrast to the AsO_4^{4-} center, the quintet/triplet superhyperfine structure on the Hg^+ ion arises from four ^{31}P nuclei (2,3). We also report accurate Hg^+ hyperfine parameters from both the ^{199}Hg and the ^{201}Hg nuclei and show evidence for a hyperfine anomaly for the ^{199}Hg, ^{201}Hg nuclei, a quantity of high theoretical interest and difficult to obtain experimentally (3).

II. EXPERIMENTAL PROCEDURE

Hg^+ ions were formed by γ-irradiating a nominally 1% Hg^{++}-doped KH_2PO_4 (or $NH_4H_2PO_4$) crystal. Hg^+ is formed by capturing a photoelectron by Hg^{++} ion as follows

$$KDP + \gamma\text{-rays} \rightarrow e^-$$

$$Hg^{++} + e^- \rightarrow Hg^+$$

All crystals were grown from aqueous solution at room temperature. D_2O was used for growing KD_2PO_4 and $ND_4D_2PO_4$. EPR measurements were made at X-band (10 GHz) frequency, using a Bruker EPR spectrometer, model ER 200D. The line positions were measured accurately with a Bruker field-tracking gaussmeter and a Hewlett-Packard frequency counter. A Bruker digital variable temperature accessory was used for controlling the sample temperature to an accuracy of ± 0.5 K.

III. RESULTS AND DISCUSSION

Figure 1 shows EPR spectra of Hg(I) centers in (a) KH_2PO_4, (b) $NH_4H_2PO_4$ and (c) $ND_4D_2PO_4$ for H//c at room temperature.

The quintet signal around 3400 G is from the Hg^+ which have I = 0 Hg isotopes (^{198}Hg, ^{200}Hg, ^{202}Hg etc.). The 5500 G signal is the hyperfine transition from the ^{199}Hg ($I = 1/2$) nucleus while that at 7450 G is assigned to the ^{201}Hg ($I = 3/2$) nucleus (1). The transition fields as well as the quintet superhyperfine splittings are fairly similar in KH_2PO_4, $NH_4H_2PO_4$

CH2358-0/86/0000-0490 $1.00 © 1986 IEEE

and $ND_4D_2PO_4$, showing that four ^{31}P nuclei and not the four (H-bond) protons cause the quintet superhyperfine splittings.

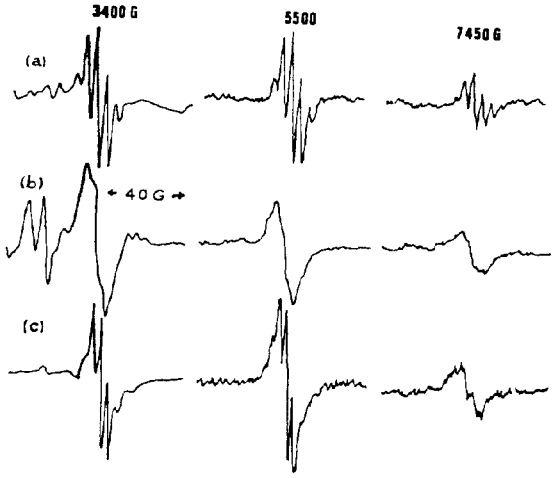

Fig. 1. EPR spectra of Hg(I) in (a) KH_2PO_4, (b) $NH_4H_2PO_4$, and (c) $ND_4D_2PO_4$ at 300 K. Lines shown left to right are from the ^{200}Hg (I = 0), ^{199}Hg (I = 1/2) and ^{201}Hg (I = 3/2) isotopes.

The effects of the phase transition on the Hg^+ spectra are presented in Figure 2 for $NH_4H_2PO_4$, T_c = 147 K. The 7450 G ($^{201}Hg^+$) line is chosen for this study.

At least two somewhat novel results can be noted from Figure 2. First, over a range of about 5° around T_c (~147 K), the spectra consist of (simultaneously present) features representing the high ($T > T_c$) temperature (paraelectric) and the low ($T < T_c$) temperature (antiferroelectric) lattice. Second, the 1:4:6:4:1 quintet representing four equivalent ^{31}P nuclei for $T >> T_c$ changes to a 1:2:1 triplet for $T << T_c$, thus reflecting the symmetry lowering due to the phase transition.

Since the ^{31}P superhyperfine was rather unexpected, detailed temperature and computer-simulation studies were carried out for the superhyperfine structure for $ND_4D_2PO_4$. Figure 3 shows a typical spectrum for H//c at 115 K, in the antiferroelectric phase of $ND_4D_2PO_4$.

It is clear that the superhyperfine structure is due to 4 ^{31}P nuclei which are equivalent for $T > T_c$ and become nonequivalent (2 groups of 2) at $T < T_c$. Detailed studies are

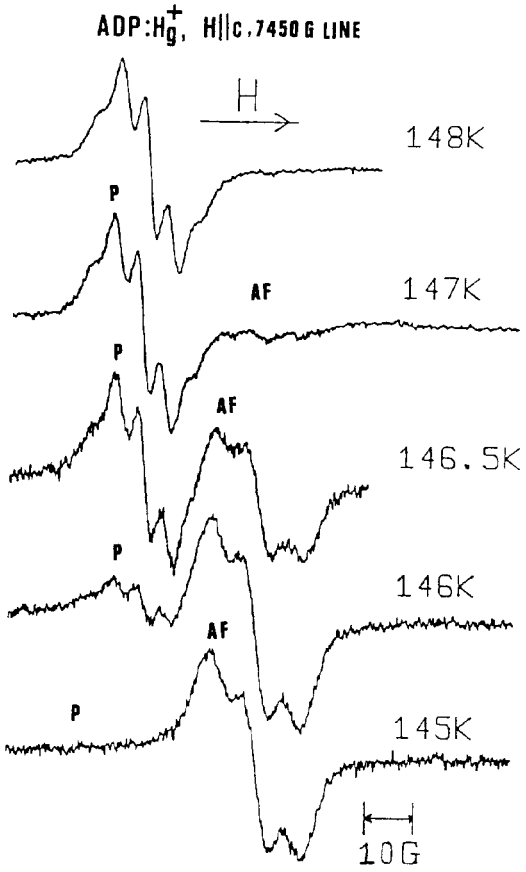

Fig. 2. Typical EPR spectra of Hg(I) near T_c (~147 K) for $NH_4H_2PO_4$ (ADP). The spectra exhibit superposition of the paraelectric and antiferroelectric phases around T_c (≈147 K).

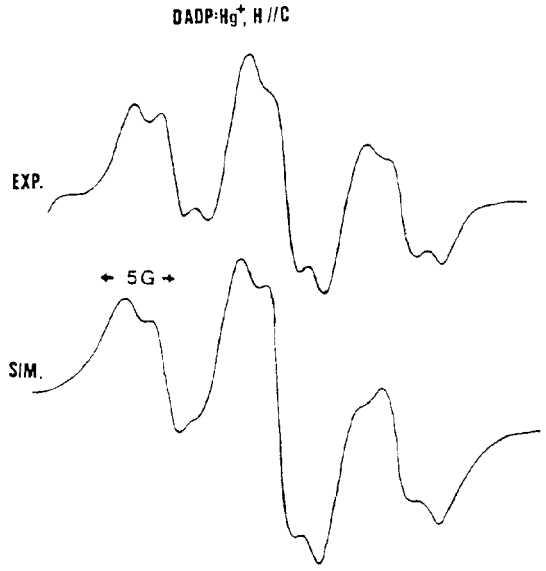

Fig. 3. Experimental and simulated ^{31}P superhyperfine spectra for Hg(I) in $ND_4D_2PO_4$ at 115 K ($T < T_c$).

currently in progress for measuring the motional dynamics of the cations which have not yet been performed for any of the KH_2PO_4-type of crystals.

We now discuss the $^{199}Hg/^{201}Hg$ hyperfine anomaly which has been determined via an accurate computer simulation of the observed EPR transitions. The analysis procedure and the computer program used has been described earlier (3,4).

^{199}Hg-^{201}Hg Hyperfine Anomaly, Δ:

Normally for two isotopes, 1 and 2, the ratio of their hyperfine constants, A_1 and A_2, is directly proportional to their nuclear g-factors g_1 and g_2, i.e.,

$$\frac{A_1}{A_2} = \frac{G_1^N}{G_2^N} \qquad (1)$$

This relationship assumes that the nuclei are point charges. However, for heavy nuclei, such as ^{199}Hg and ^{201}Hg, one expects the nuclei to have finite sizes. In that case equation (2) becomes

$$\frac{A_1}{A_2} = \frac{G_1^N}{G_2^N}(1 + \Delta^{BW} + \Delta^{RB}), \qquad (2)$$

Here Δ^{BW} is the difference of the so-called Bohr-Weisskopf hyperfine anomaly (5,6) for the two isotopes, Δ^{BW} takes into the distribution of the magnetic moment within the nuclei, and Δ^{RB}, the so-called Rosenthal-Breit term (7-9) relates to the differences in the coulomb field due to the nuclear shapes. The total correction term, Δ_{total}, can be written as

$$\Delta_{total} = \Delta^{RB} + \Delta^{BW} \simeq \frac{^{199}A_{iso}}{^{201}A_{iso}} \times \frac{^{201}g_N}{^{199}g_N} - 1$$

This value is included in Table 1 for various hosts. Interestingly it is seen that Δ_{total} is influenced by the antiferroelectric phase transition. While similar measurements are in progress using other hosts, the present study shows that Δ^{RB} makes a dominant contribution to Δ_{total}, and is perhaps of the opposite sign than Δ^{BW}. To our knowledge this is the first such detailed measurement of Δ for the mercury isotopes, and it shows that in heavy metals the shapes of the nuclei are affected by dielectric polarizations below T_c.

Table 1

Hyperfine Structure Anomaly (Δ) for $^{199}Hg(I)$ and $^{201}Hg(I)$

Host Crystal	$^{199}A_{iso}$/MHz	$^{201}A_{iso}$/MHz	Δ(%)
KH_2PO_4 (297 K)	35347 ± 5	-13084.7±1.2	-0.28±0.02
$NH_4H_2PO_4$ (297 K)	35540 ± 9	-12783.9±1.0	-0.27±0.03
$ND_4D_2PO_4$ (297 K)	34913 ± 10	-12816.5±2.6	+0.56±0.04
$NH_2H_2PO_4$ (120 K)	35878 ± 12	-13204.9±1.2	+0.30±0.04
$ND_4D_2PO_4$ (130 K)	35671 ± 42	-13174.9±1.9	-0.06±0.12

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

References

*M.S. Student 1983-84. Currently at Chemistry Department, University of Illinois, Urbana-Champaign, IL.

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

1. N. S. Dalal, Advan. Magn. Reson. 10, 119 (1982), is a recent review of EPR studies of KH_2PO_4-type crystals.
2. N. S. Dalal, D. Nettar, and P. J. Grandinetti, J. Am. Chem. Soc. 104, 2054 (1982).
3. P. J. Grandinetti, M. S. thesis, Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045 (1985).
4. N. S. Dalal, J. A. Hebden and C. A. McDowell, J. Magn. Reson. 16, 289 (1974).
5. See, for example, M. M. Stroke, B. J. Blin-Stoyle and V. Jaccarino, Phys. Rev. 123, 1326 (1961).
6. G. Busch, Helv. Phys. Acta 11, 269 (1938).
7. J. E. Rosenthal and G. Breit, Phys. Rev. 41, 459 (1932).
8. G. Breit, Phys. Rev. 42, 348 (1932).
9. G. Racah, Nature, 129, 723 (1932).