

Hg⁺ (6s¹) Ions in KH₂PO₄ and NH₄H₂PO₄: New Paramagnetic Probes of Cationic Dynamics Near Phase Transitions in Hydrogen-Bonded Ferroelectrics and Antiferroelectrics

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We present here electron paramagnetic resonance (EPR) evidence to show that Hg⁺ ions can be substituted for K⁺ in KH₂PO₄ (a hydrogen-bonded ferroelectric) and for NH₄⁺ ions in NH₄H₂PO₄ (a hydrogen-bonded antiferroelectric¹). This study was undertaken because, while the (solid–solid) structural phase transitions in these compounds have been considered as models of structural and ferroelectric/antiferroelectric phase transitions, the microscopic details of their own transition mechanisms are not yet understood.² Current theoretical models of structural phase transitions need data on the low-frequency (~10⁸–10¹¹ Hz) motion as well as the higher frequency lattice vibrations. The low-frequency motion falls in the domain where EPR spectroscopy is most effective for studying motional effects. Consequently, EPR spectroscopy has been extensively used for studying the dynamics of the anions (PO₄³⁻) as well as the cations (K⁺, NH₄⁺, etc.) in the KH₂PO₄-type compounds.² In using the EPR technique for studying these (diamagnetic) compounds, of course, it has been necessary to introduce a suitable paramagnetic ion (or free radical) into their lattices. We noticed that the probes used for studying the role of the cations K⁺, Cs⁺, NH₄⁺, etc., were Cr³⁺ (3d³), Fe³⁺ (3d⁵), Cu²⁺ (3d⁹), and Ti²⁺ (6s¹) ions. It is thus seen that all these probes have one or two units of positive charge higher than that of the alkali cation they are supposed to replace. Because of this extra charge, these ionic probes would exhibit a local electrostatic potential different from that of the substituted cations. Thus the

local dynamic and structural properties seen by the probe would be expected to be different from that of the original lattice. We, therefore, searched for a monovalent paramagnetic ion and have found that Hg⁺ (6s¹) ions might represent such a probe.

The Hg(I) ions were incorporated into KH₂PO₄ or NH₄H₂PO₄ by doping these compounds with Hg(CH₃CO₂)₂·2H₂O (5% by weight), growing single crystals from aqueous solution, and γ irradiating the doped crystals with a 500-Ci source for a few hours (exact time not critical). The crystals turned yellowish after γ irradiation, an indication that Hg⁺ centers had been formed, as reported earlier^{3,4} for Hg⁺ in Cd(CH₃CO₂)₂·2H₂O doped with Hg(CH₃CO₂)₂·2H₂O.

EPR measurements were made at X-band frequencies by using a Varian E-3 spectrometer. The microwave frequency was measured with a Hewlett-Packard 5345 L digital frequency counter, and the resonance fields were measured relative to the standard free-radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH). So that the spin Hamiltonian parameters could be determined, the variation of the EPR signals was investigated in the three mutually orthogonal crystal planes *ab*, *bc*, and *ca* of the tetragonal (*I42d*) phases of KH₂PO₄ and NH₄H₂PO₄.¹ The crystallographic axes were easily identified by noting that these crystals grow as "bricks" with the *c* axis as the longest direction. The *a* and *b* axes are parallel to the orthogonal edges of the crystals.

Figure 1 shows typical EPR signals from single crystals of KH₂PO₄ and NH₄H₂PO₄ at *T* = 300 K for \vec{H}/c , where \vec{H} is the externally applied (Zeeman) magnetic field. The spectra at other

(1) For a detailed discussion of ferroelectricity and antiferroelectricity, see M. E. Line and A. M. Glass, "Principles and Applications of Ferroelectrics and Related Materials", Clarendon Press, Oxford, England, 1977.

(2) See, for example, R. Blinc in "Magnetic Resonance of Phase Transitions", F. J. Owens, C. P. Poole, Jr., and H. A. Farach, Eds., Academic Press, New York, 1979, Chapter V.

(3) R. S. Eachus and F. G. Herring, *Can. J. Chem.*, 49, 2868 (1971).

(4) N. S. Dalal, J. A. Hebden, and C. A. McDowell, *J. Magn. Reson.*, 16, 289 (1974).

Table I. Spin Hamiltonian Parameters for Hg^+ Centers for KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ ^a

host	T, K	g_{\parallel}	g_{\perp}	g_{iso}	$^{199}\text{A}_{\parallel}$, MHz	$^{199}\text{A}_{\perp}$, MHz	A^{S} , MHz	ref
KH_2PO_4	300	1.9965 ± 0.0004	1.9972 ± 0.0004	1.9965 ± 0.0005	$34\,174 \pm 6$	$34\,940 \pm 6$	13.4 ± 0.5	this work
$\text{NH}_4\text{H}_2\text{PO}_4$	300	1.9959 ± 0.0005	1.9950 ± 0.0005	1.9959 ± 0.0005	$33\,944 \pm 6$	$33\,973 \pm 6$	13.0 ± 0.5	this work
$\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$	300	1.9967 ± 0.0001	1.9900 ± 0.0001	1.9934 ± 0.0002	$29\,362 \pm 1$	$29\,127 \pm 2$		4

^a The direction of g_{\parallel} and A_{\parallel} coincides with that of the crystallographic c axis. $\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ is included for comparison. A^{S} is the superhyperfine coupling on each Hg^+ transition.

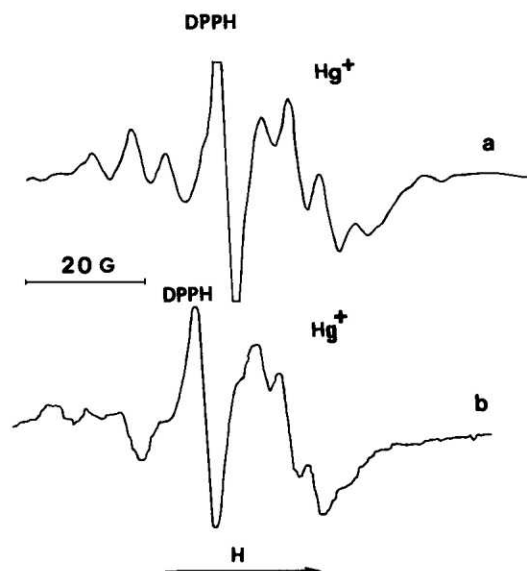


Figure 1. EPR spectra of the $^{198,200}\text{Hg}^+$ center in KH_2PO_4 (a) and $\text{NH}_4\text{H}_2\text{PO}_4$ (b) for $H//c$ at 300 K.

orientations were very similar. The angular variation of the signals was fitted to the spin Hamiltonian

$$\mathcal{H} = \beta \vec{H} \cdot \underset{(a)}{\mathbf{g}} \cdot \vec{S} + \vec{I}^{\text{Hg}} \cdot \underset{(b)}{\mathbf{A}} \cdot \vec{S} + \sum_{i=1}^4 \vec{I}_i^{\text{S}} \cdot \underset{(c)}{\mathbf{A}}^{\text{S}} \cdot \vec{S} \quad (1)$$

where \mathbf{g} is the electronic Zeeman tensor, $S = 1/2$, \vec{I}^{Hg} is the nuclear spin of a Hg nucleus, and \vec{I}_i^{S} is the nuclear spin of the i th proton or phosphorus. The three terms in eq 1 are roughly responsible for the three distinct features in the spectra: (a) strong lines near 3400 G, (b) a weak satellite around 5400 G, and (c) the small (~ 4 G) splitting on both of these signals. Feature a is due to the electron Zeeman interaction of the most abundant, non-magnetic Hg isotopes ($^{198,200}\text{Hg}$). Feature b is due to the hyperfine interaction of the electron spin with the ^{199}Hg ($I = 1/2$) isotope, and c is due to superhyperfine interaction of four (nearly) equivalent protons or phosphorus nuclei. The spin Hamiltonian parameters obtained are listed in Table I, which also contains data on Hg^+ ions in other hosts.

Comparison of the \mathbf{g} - and \mathbf{A} -tensor components of the center reported here with those of $\text{Hg}(\text{I})$ in $\text{Cd}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (cf. Table I) and the fact that the intensity of the observed signals is proportional to the amount of $\text{Hg}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ doped into KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ hosts strongly suggests that the center reported here is a Hg^+ ($6s^1$) ion. That the lines around 3400 and 5400 G belong to the same center is proved by the observation that the intensity of the 5400 G line is $\sim 10\%$ of that of the former, corresponding to the isotopic abundance ratio of ^{200}Hg and ^{199}Hg , and that both lines have virtually identical superhyperfine structure. This superhyperfine structure, better resolved for $\text{NH}_4\text{H}_2\text{PO}_4$, is a 1:4:6:4:1 quintet which can be ascribed to the splitting from four equivalent $I = 1/2$ nuclei. This quintet superhyperfine splitting changed to a 1:2:1 triplet at 148 K, the phase transition temperature of $\text{NH}_4\text{H}_2\text{PO}_4$, for $H//c$, as shown in Figure 2. This observation is somewhat analogous to the quintet-triplet proton superhyperfine splitting in the EPR spectra of the AsO_4^{4-} centers in KH_2AsO_4 , and in KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ doped with KH_2AsO_4 .^{5,6} It is noted that these earlier studies^{5,6}

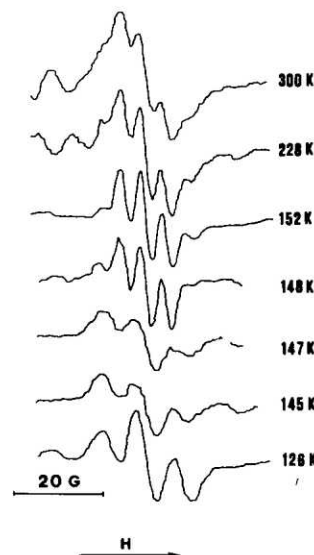


Figure 2. Temperature dependence of the quintet-triplet superhyperfine structure on the $^{199}\text{Hg}^+$ hyperfine line in $\text{NH}_4\text{H}_2\text{PO}_4$ for $H//c$. Note the change in the line shape below 148 K, the phase-transition temperature.

have yielded important dynamical data on the role of protons and the anions in causing the ferroelectric transition. The present results imply that the Hg^+ center is a potential tool for elucidating the ordering and hence the role of the cations in the phase-transition mechanism.

The hyperfine transition from the ^{201}Hg ($I = 3/2$) isotope is expected⁴ to occur around 6700 G, which is outside the range of our E-3 spectrometer. However, the evidence presented above is believed to be sufficient for showing that the paramagnetic center is indeed a Hg^+ ion.

The near isotropic symmetry of the observed \mathbf{g} tensor, ^{199}Hg hyperfine coupling, and even the quintet superhyperfine structure shows that the Hg^+ ion is located at a site of S_4 point symmetry of the $\bar{I}42d$ space group of the KH_2PO_4 -type crystals. This result indicates that perhaps Hg^+ ions substitute the K^+ (or NH_4^+) ions without appreciable local distortion of the host lattice. Further interpretation of the definite site position and the nature of the superhyperfine structure could be obtained from studies on KD_2PO_4 , $\text{ND}_4\text{D}_2\text{PO}_4$, and other crystals (such as $(\text{NH}_4)_2\text{SO}_4$, CsH_2PO_4 , RbH_2PO_4 , KH_2AsO_4 , $\text{NH}_4\text{H}_2\text{AsO}_4$, and their deuterated analogues). Although such studies are currently in progress in our laboratory, the results reported here should stimulate research by others interested in understanding the role of cations and the central peak phenomenon^{5,7} in the phase-transition behavior of these compounds. This is the first time that a paramagnetic probe has been found that has the same charge and local site symmetry as that of the host. Detailed ENDOR studies will be useful for further investigating the structure of this probe and to extend the time scale of EPR, as was done for the AsO_4^{4-} , CrO_4^{3-} , and SeO_4^{3-} centers.^{4,6}

It is noted, however, that since Hg^+ is a much heavier ion than the replaced ion (K^+ or NH_4^+), the actual dynamics observed via Hg^+ might be somewhat different. Detailed studies are underway to investigate this question.⁸

(5) N. S. Dalal, *Adv. Magn. Reson.*, in press.

(6) R. Blinc, P. Cevc, and M. Schara, *Phys. Rev.*, **159**, 411 (1967).

(7) For a review of the newly discovered, central peak phenomenon, see A. D. Bruce and R. A. Cowley, *Adv. Phys.*, **29**, 219 (1980).

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Registry No. Hg⁺, 22542-11-6; KH₂PO₄, 7778-77-0; NH₄H₂PO₄, 7722-76-1.

(8) We thank a referee for suggesting this point.