Brief Reports

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Electron-spin-resonance line-shape studies of the AsO_4^{4-} center in RbH_2AsO_4 and RbD_2AsO_4

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A quantitative study of the electron-spin-resonance (ESR) line shapes of the AsO_4^{4-} center in RbH_2AsO_4 and RbD_2AsO_4 is presented. Analysis of the spectra at various temperatures, using a theoretical model and electron-nuclear double resonance (ENDOR) obtained superhyperfine (shf) couplings, shows the existence of a single correlation time with which the rubidium and hydrogen shf interactions are modulated. Further analysis of the ENDOR- and ESR-deduced shf couplings is shown to disallow any large-amplitude relative motions between the heavy atoms and the H_4AsO_4 units. It is suggested that fluctuations in the nonsymmetric distribution of the electron density are responsible for the observed ESR features in potassium dihydrogen phosphate-type systems.

The objective of the present paper is to obtain a quantitative insight into the electron-spin-resonance (ESR) spectra of the AsO_4^{4-} center in RbH_2AsO_4 (RDA) and RbD_2AsO_4 (DRDA) in order to provide a model, based upon ESR studies, of atomic dynamics in RDA, or more generally in KH_2PO_4- (KDP-) type systems which have been the focus of research for over three decades in connection with their phase-transition behavior from the high-temperature paraelectric to the low-temperature ferroelectric phase.[1-4] The ESR spectrum in RDA at low temperatures ($T < T^* < T_c$, paraelectric-ferroelectric phase-transition temperature) exhibits superhyperfine (shf) structure due to the various nuclei ^1H ($I = \frac{1}{2}$), ^{85}Rb ($I = \frac{5}{2}$), and ^{87}Rb ($I = \frac{3}{2}$), which is in contrast with the spectrum for CsH_2AsO_4 (CDA) where ^1H shf structure is overwhelmed by Cs shf interactions,[5-7] or for KH_2AsO_4 (KDA) where only ^1H shf structure is observed. RDA thus seems an ideal system for quantifying the nature of the coupled radical center-lattice motions, although the dynamics of the various nuclei even in CsH_2AsO_4 was earlier found to be correlated and of the soft-mode type (but on a longer time scale).[5-7] A key result emerging from the electron-nuclear double resonance (ENDOR) (and ESR) investigations of CDA has been the presence of significantly different superhyperfine couplings for the

two cesium atoms lying on the c axis (42 and 9 MHz).[5] The ENDOR and electron-spin echo envelope modulation (ESEEM) results on KDA also yield different coupling constants for the potassium nuclei.[8,9] This has been considered to imply a freeze-in of the "soft-mode motions" as structural displacements.[7,10] In the soft-mode picture, movement of the potassium and phosphorus along the c axis is tied to the movement of hydrogens in the double-minimum potential well. This leads to nearly equal mean-square thermal amplitudes for the potassium and phosphorus atoms along the c axis. However, in the recently revised soft-mode model, the mean-square thermal amplitude for K is zero, but the amplitude for P is increased by approximately a factor of 2.[1] Although experimentally observed relative displacement of Cs (or K) and As along the c axis is of the order of 0.1 Å, the observed difference in shf couplings of the two axial Cs or K atoms seems rather too large. While we were able to measure with ENDOR the two largest shf couplings for ^{133}Cs in CDA, the second largest couplings for both ^{85}Rb and ^{87}Rb were unobtainable due to the presence of a large number of overlapping lines at low frequencies. These couplings can, however, be determined from ESR line-shape simulations, as shown in the first half of this paper. Making use of the ESR- and
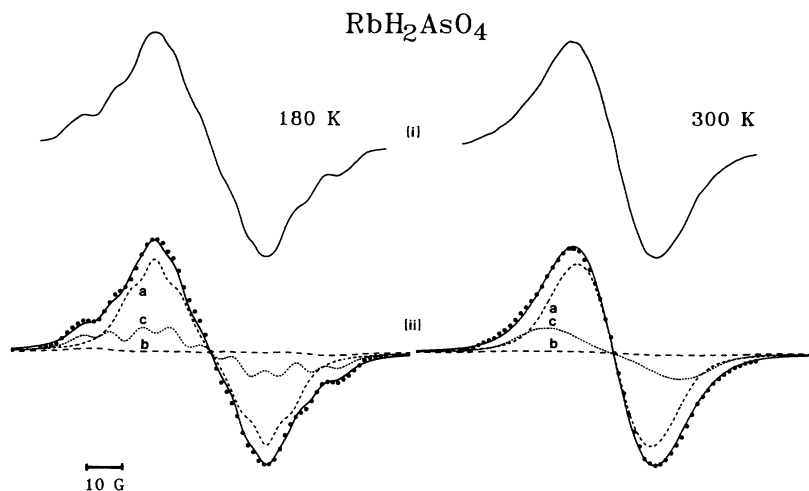
RbH$_2$AsO$_4$

FIG. 1. (i) Experimental ESR spectra of the AsO$_4^{4-}$ center in RbH$_2$AsO$_4$ at 180 and 300 K for H∥c; (ii) comparison of the experimental (solid circles) and theoretically calculated (solid curve) ESR spectra. The component spectra (a–c) are discussed in the text.

ENDOR-obtained two largest shf couplings for the Cs and Rb nuclei, we then make estimates of the relative displacements of the type Cs-AsO$_4$ or Rb-AsO$_4$ and compare them with those observed experimentally.[1] An order of magnitude difference between the calculated and experimental values is argued in the second half of this paper to be suggestive of a different interpretation for the atomic motions.

The X-band ESR experiments on single crystals of RDA and DRDA (irradiated with γ rays at room temperature) were performed as a function of temperature using a Bruker ER200D spectrometer. ^{1}H, ^{85}Rb, and ^{87}Rb ENDOR experiments were also performed by aligning crystals in the magnetic field (H∥c) in order to fix the shf coupling constants.

Figures 1 and 2 show, respectively, the ESR spectra for the AsO$_4^{4-}$ center in RDA and DRDA corresponding to the highest-field line and for H∥c at both the low and high temperatures. A tremendous change on substitution of protons by deuterons clearly implies modulations of multinuclear shf interactions due to the various coupled nuclei. A successful interpretation of the ESR spectra for CDA, over the entire temperature range and for various orientations of the magnetic field, was earlier provided

with a model in which a paramagnetic spin-$\frac{1}{2}$ center was coupled to two nonequivalent, axial cesium atoms ($I=\frac{7}{2}$), two equivalent near protons ($I=\frac{1}{2}$), and two equivalent far protons ($I=\frac{1}{2}$),[5-7] and where cesium and proton shf interactions were modulated via "two-site" motions of these nuclei. As shown below, the same model but with a different interpretation for the motional times provides a quantitative understanding of the ESR line shapes in RDA and DRDA.

Rubidium occurs in two isotopic forms: ^{85}Rb ($I=\frac{5}{2}$) and ^{87}Rb ($I=\frac{3}{2}$) with natural abundance of 72.17% and 27.83%, respectively.[11] The two axial rubidium nuclei, located on either side of the H$_4$AsO$_4$ unit, can therefore be comprised of either both ^{85}Rb with relative probability 0.521, or both ^{87}Rb with relative probability 0.077, or one each of ^{85}Rb and ^{87}Rb with relative probability 0.402. The observed ESR spectrum is a superposition of these three situations with the above probabilities. To obtain shf couplings along the c axis due to the near and far protons [$A_c(^1H_{near})$ and $A_c(^1H_{far})$] and the rubidium nuclei [$A_c(^{85}Rb_l)$, $A_c(^{87}Rb_l)$, $A_c(^{85}Rb_s)$, or $A_c(^{87}Rb_s)$, to be abbreviated as $A_c(\alpha_{l,s})$ where α denotes the nucleus type, and the indexes l and s refer to the larger and to the
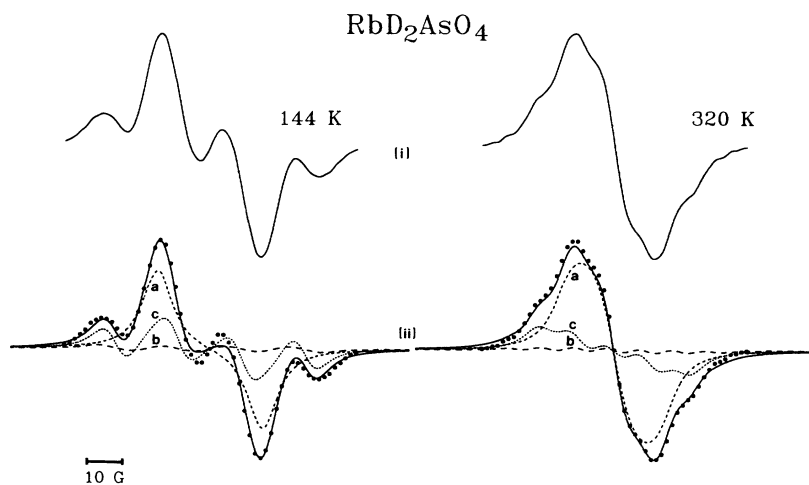
RbD$_2$AsO$_4$

FIG. 2. (i) Experimental ESR spectra of the AsO$_4^{4-}$ center in RbD$_2$AsO$_4$ at 144 and 320 K for H∥c; (ii) comparison of the experimental (solid circles) and theoretically calculated (solid curve) ESR spectra. The component spectra (a–c) are discussed in the text.

TABLE I. Values of $A_c(^{85,87}\mathrm{Rb}_l)$ and $A_c(^{85,87}\mathrm{Rb}_s)$ obtained from ENDOR and ESR experiments.

Temperature (K)	$A_c(^{87}\mathrm{Rb}_l)$ (MHz)[a]	$A_c(^{87}\mathrm{Rb}_s)$ (MHz)[b]	$A_c(^{85}\mathrm{Rb}_l)$ (MHz)[a]	$A_c(^{85}\mathrm{Rb}_s)$ (MHz)[b]
144	66.4	8.8	19.9	2.7
180	65.3	8.7	19.6	2.6
300[c]	61.3	8.2	18.4	2.5
320[c]	61.1	8.1	18.3	2.4

[a]From ENDOR experiments.
[b]From ESR experiments and simulations.
[c]From linear extrapolation of the low-temperature shf values.

smaller of the two shf couplings, respectively], the EN-DOR spectra were recorded as a function of temperature in the ab and ac planes, with the microwave field applied to all the ESR transitions of the quartet. Linear extrapolation of the temperature-dependent ENDOR-obtained shf couplings was done to obtain shf values at higher temperatures where ENDOR experiments are not feasible. Table I lists various shf couplings $A_c(^{85,87}\mathrm{Rb}_l)$ for RDA at $T=144$ and 180 K (from ENDOR) and at $T=300$ and 320 K (from extrapolation). The same corresponding values for the rubidium shf couplings were used in simulations for both RDA and DRDA. The couplings $A_c(^{85,87}\mathrm{Rb}_s)$ were unobtainable from analysis of the EN-DOR spectra and were found, after numerous ESR lineshape calculations, to be smaller than $A_c(^{85,87}\mathrm{Rb}_l)$ by a factor of about 7.5. On the other hand, values for the $^2\mathrm{H}$ shf couplings were obtained from the $^1\mathrm{H}$ shf couplings by using a factor of 6.5, as given by the ratio of their isotropic hyperfine couplings, i.e., 1420 MHz/218 MHz.[11]

Experimental spectra over the investigated temperature range were found to be closest to the ones calculated with the correlation times $\tau_\mathrm{H}\approx\tau_\mathrm{Rb}(=\tau)$. A comparison between the two for both RDA and DRDA is shown in Figs. 1 and 2. As discussed above, the experimental spectrum is the result of superposition of three individual spectra with appropriate probabilities, namely, the spectra when both $^{85}\mathrm{Rb}$ nuclei lie on the c axis (curve a), when both $^{87}\mathrm{Rb}$ nuclei lie on the c axis (curve b), and when one $^{85}\mathrm{Rb}$ and one $^{87}\mathrm{Rb}$ lie on the c axis (curve c). Contributions (a)–(c) are also shown in Figs. 1 and 2. Contribution (b), that due to the arrangement $^{87}\mathrm{Rb}$-$\mathrm{H_4AsO_4}$-$^{87}\mathrm{Rb}$, is insignificantly small compared to that for either the atomic arrangement $^{85}\mathrm{Rb}$-$\mathrm{H_4AsO_4}$-$^{85}\mathrm{Rb}$ (contribution a) or the arrangement $^{85}\mathrm{Rb}$-$\mathrm{H_4AsO_4}$-$^{87}\mathrm{Rb}$ (contribution c).

It thus turns out that rubidium nuclei (either $^{85}\mathrm{Rb}$ or $^{87}\mathrm{Rb}$) lying on the c axis, one each on either side of $\mathrm{H_4AsO_4}$, show a significant difference in their shf couplings, i.e., $A_c(\alpha_l)/A_c(\alpha_s)\approx7.5$. This compares with a value of ≈4.6 for Cs nuclei in CDA. Fluctuations present in RDA or DRDA must therefore modulate shf couplings by a factor of ≈7.5 and in CDA by a factor of ≈4.6. The following approximate calculation shows that if fluctuations leading to modulation of the shf interaction by this amount were due to relative motion between the Rb (or Cs) and the $\mathrm{H_4AsO_4}$ units, the amplitude of the involved fluctuations must be unusually large.

The ratio of the measured A_c and the isotropic hyperfine coupling constant A_0,[11]

$$A_0 = (8\pi/3)(\beta g\beta_I g_I)|\phi(0)|^2 , \qquad (1)$$

are 4.84 MHz/231 MHz $\approx 2.12\times10^{-2}$ for $^{39}\mathrm{K}$ at 103 K,[8] 20.30 MHz/1012 MHz $\approx 2.00\times10^{-2}$ for $^{85}\mathrm{Rb}$ at 106 K, 67.60 MHz/3417 MHz $\approx 1.98\times10^{-2}$ for $^{87}\mathrm{Rb}$ at 106 K, and 41.88 MHz/2298 MHz $\approx 1.82\times10^{-2}$ for $^{133}\mathrm{Cs}$ at 110 K.[5] Since A_c/A_0 decreases with an increase in the distance $c/2$, it is argued that the electronic wave function and the shf coupling constant may be written as[12]

$$\phi(r)=C(1/r)\exp(-\lambda r) ,$$

$$A_c=C_{\alpha'}|\phi(r)|^2=C_\alpha(1/r^2)\exp(-2\lambda r) , \qquad (2)$$

where C, C_α, $C_{\alpha'}$, and λ are constants. If $^{133}\mathrm{Cs}$ and $^{85,87}\mathrm{Rb}$ (or equivalently $\mathrm{AsO_4}$ or $\mathrm{H_4AsO_4}$) were to move in a double-minimum potential well, with a relative displacement of $\pm\Delta$ about the equilibrium position $r_0(\alpha)$, the above equation can be written as

$$A_c(\alpha_l)=C_\alpha\{1/[r_0(\alpha)-\Delta]^2\}\exp\{-2\lambda[r_0(\alpha)-\Delta]\} , \qquad (3)$$

$$A_c(\alpha_s)=C_\alpha\{1/[r_0(\alpha)+\Delta]^2\}\exp\{-2\lambda[r_0(\alpha)+\Delta]\} , \qquad (4)$$

which leads to

$$A_c(\alpha_l)/A_c(\alpha_s)$$
$$=\exp\{4\lambda\Delta\}\{r_0(\alpha)+\Delta\}^2/\{r_0(\alpha)-\Delta\}^2 . \qquad (5)$$

The ENDOR-determined values for $A_c(\alpha_l)/A_c(\alpha_s)$ are ≈4.6 in CDA and ≈7.5 in RDA. Arguing that $\Delta(\mathrm{Cs})\approx\Delta(\mathrm{Rb})=\Delta$, the following equation can easily be obtained from Eq. (5):

$$7.5\{r_0(\mathrm{Cs})+\Delta\}\{r_0(\mathrm{Rb})-\Delta\}$$
$$=4.6\{r_0(\mathrm{Rb})+\Delta\}\{r_0(\mathrm{Cs})-\Delta\} . \qquad (6)$$

Taking $r_0(\mathrm{Cs})=c/2=3.94$ Å and $r_0(\mathrm{Rb})=c/2=3.60$ Å, Δ turns out to be 3.3 Å, which is over an order of magnitude larger than what is observed experimentally.

Since both x-ray- and neutron-scattering data[1] give at least one order of magnitude smaller value for the relative displacement of the heavy atoms, an altogether different mechanism for modulation of the shf interactions is implied. We suggest that redistribution of the spin density of the electronic cloud at a rate $1/\tau$, where $\tau=\tau_\mathrm{H}=\tau_\mathrm{Rb}$, leads to a simultaneous modulation of both the proton and Rb (or Cs) shf interactions. This interpretation provides support for the suggestion by Bystrov and Popova[13] that in unradiated KDP a nonsymmetric distribution of electronic density in nonequivalent P-O--H and P-O-H bonds is the major source of spontaneous polarization in KDP. As the protons move perpendicular to the polar axis, electron density in the P-O bonds is shifted in the direction of the polar axis.

In conclusion, a quantitative study of ESR spectra of the AsO_4^{4-} center in RDA and DRDA has been presented. The ENDOR and ESR data have been used to argue against any large-amplitude relative motion between the heavy atoms (K,Rb,Cs) and H_4AsO_4 units. Instead, fluctuations involving a redistribution of the spin density, most likely driven by movement of protons in the double-minimum potential well, have been argued to explain all the dynamical observations in the ESR investigations of KDP-type systems.

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