Detection of spin-flip ESR transitions and Arrhenius behavior for the $AsO_4{}^{4-}$ center in the KH_2AsO_4-type ferroelectric compounds at high temperatures

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The normally forbidden electron-nuclear spin-flip ($\Delta M_S = \pm 1$, $\Delta M_I = \mp 1$) transitions have been detected in the ESR spectra of the $AsO_4{}^{4-}$ center, which is frequently used as a probe of the low-frequency molecular motion related to the ferroelectric or antiferroelectric phase transitions in KH_2PO_4-type compounds. It is suggested that the omission of the line broadening from these transitions had caused significant errors in the earlier reported motional correlation time τ in the "fast" motion regime for this probe in KH_2AsO_4 and related lattices. A simple procedure based on the modified Bloch equations is described which minimizes errors due to this broadening and illustrated by showing that the low-frequency ^{75}As fluctuations in KH_2AsO_4 and KD_2AsO_4 obey the Arrhenius law even over a wider temperature range than in earlier studies wherein a non-Arrhenius behavior had been reported. The activation energy and preexponential factor are 0.20 eV and 3.2×10^{-13} s for KH_2AsO_4 and 0.26 eV and 3.7×10^{-14} s for KD_2AsO_4, with an error of about 10%, and thus these parameters exhibit a definitive isotope effect and sensitivity of the probe to the lattice environment. This study also suggests a reexamination of the τ data for KH_2PO_4-type lattices as obtained via other probes, such as the $SeO_4{}^{3-}$ center, especially in the high-temperature ("fast" motion) regime.

INTRODUCTION

This paper reports the detection of the normally forbidden electron-nuclear spin-flip ($\Delta M_S = \pm 1$, $\Delta M_I = \mp 1$) transitions[1–3] in the ESR spectra of the $AsO_4{}^{4-}$ center,[4] a commonly used spin probe for ESR studies of phase transitions in the KH_2AsO_4 type of ferroelectric and antiferroelectric crystals.[5] Although the occurrence of the spin-flip ESR transitions has been known since 1954,[1] to our knowledge this is the first report of their detection and of their rather significant role in the ESR evaluation of the motional correlation time τ for the low-frequency ($\approx 10^{10}$ Hz) fluctuations in relationship to the ferroelectric transitions. Accurate experimental measurements of such low-frequency fluctuations in the KH_2AsO_4-type compounds, which are typical members of the KH_2PO_4 family of ferroelectrics, are of current interest[6] because of the recent discoveries of the proton glasses[7,8] [crystals exhibiting slowly relaxing features which are characteristic of glassy matrices) and the central-peak phenomenon[9] [detection of an unusually low frequency ($\approx 10^{10}$ Hz) peak in the inelastic neutron and light scattering studies of solids undergoing phase transitions[10]]. The $AsO_4{}^{4-}$ center was reinvestigated because, while this is the most commonly used spin probe in the ESR investigations of the KH_2PO_4 type of compounds,[11–23] we have noted significant differences in the reported[14,16,18] τ values and hence the conclusions derived for the origin of the detected motional processes are not definitive.[5,18] For example, it is still unsettled as to whether or not the τ's measured for KH_2AsO_4 and KD_2AsO_4 follow an Arrhenius behavior, $\tau = \tau_0 \exp(\Delta E / k_B T)$, ΔE being the activation energy and τ_0 the preexponential factor. Perhaps because of the large uncertainty in the reported τ values,[5,14,16,18] it has been conjectured[16,18] that the ESR spectra of the $AsO_4{}^{4-}$ center are not sensitive to fluctuations of the host lattice, and that they exhibit more or less the effects characteristic of the probe's motion, but somewhat modified by the host. The detection here of the spin-flip transitions and their significant effect on the linewidths suggest that at least some of earlier controversies can be traced to the omission of the line-broadening effect of these transitions. Specifically, in most of the earlier studies[5,14,16,18] the τ's have been evaluated from the line-shape analysis of essentially one ESR transition—the lowest field ($M_I = \frac{3}{2}$) component of the ^{75}As ($I = \frac{3}{2}$) hyperfine quartet,[4] without recognizing that the width of this transition has a large contribution from the nuclear spin-flip transitions. Moreover, while the spin-flip transitions contribute also to the other three ($M_I = \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$) hyperfine lines of the $AsO_4{}^{4-}$ center,[4] the lowest-field component is affected the most, because of the dependence of the spin-flip signal intensity on the Zeeman field H as H^{-2}, and because the spin-flip line separation is directly proportional to H.[1–3]

In this work it is first shown that the omission of the spin-flip line-broadening mechanism leads to a non-Arrhenius behavior if τ were deduced from the linewidth changes for only the lowest field component of the $AsO_4{}^{4-}$ center. Then we discuss a simple methodology which minimizes the error due to this line-broadening mechanism in the calculation of τ for the $AsO_4{}^{4-}$ center, illustrating it with the Arrhenius analyses for KH_2AsO_4 and KD_2AsO_4. The Arrhenius parameters obtained exhibit a definitive H→D isotope effect and thus confirm the sensitivity of this probe to the host-lattice environment. The relevance of these results to similar investigations via other spin probes is also pointed out.

EXPERIMENT

Single crystals of KH_2AsO_4 (KDA) and KD_2AsO_4 (DKDA) were grown via slow evaporation of saturated solutions in H_2O or D_2O, respectively. As usual[5] the crystals grew as rectangular parallelpipeds with the c axis as the longest dimension. The $AsO_4{}^{4-}$ centers were formed via γ irradiation of the crystals to a dose of about 4 Mrad (not critical) at room temperature. All ESR measurements were made with Bruker X band and Q band ESR spectrometer systems, using a field-tracking NMR gaussmeter (Bruker, model ER 035M) and a Hewlett-Packard frequency counter, model 5340A. The sample temperature was controlled to within ± 0.5 K via the Bruker digital temperature controller, model ER 4111 VT. All linewidths were measured as peak-to-peak in the first derivative mode, using a 100-kHz magnetic-field modulation and phase detection system. An ASPECT 2000 computer was used for the data acquisition and line-shape simulations.

SPIN-FLIP TRANSITIONS FOR $AsO_4{}^{4-}$

As has been well documented earlier,[4,5,11–23] and shown in Fig. 1 here, the ESR spectra of the $AsO_4{}^{4-}$ center, henceforth referred to simply as $AsO_4{}^{4-}$, consist of a quartet of lines due to the hyperfine splitting from the ^{75}As ($I=\frac{3}{2}$) nucleus. At the X-band (≈ 9.5 GHz) frequencies, the resonance fields for the quartet components are approximately centered around 150, 210, 320, and 465 mT (1 mT = 10 G), respectively. As usual these signals are labeled 1, 2, 3, and 4 sequentially, as marked in Fig. 1 for both KDA and DKDA. Although not recognized earlier,[4,5,11–23] a clear evidence for the occurrence of the nuclear spin-flip ($\Delta M_S=\pm 1$, $\Delta M_I=\mp 1$) transitions[1–3] can be seen in Fig. 2(a), which shows a magnified version of the signals corresponding to line 4 in Fig. 1 for KDA. The spin-flip signals are the two weak satellites symmetrically disposed around the main signal at 465 mT. Their identification as the proton spin-flip transitions is based on the following arguments. First the signal separation for line 4 (at 465 mT), which exhibits the highest resolution, is exactly as given[1–3] by $2g_n\beta_nH$ (1.42 mT at $H=465$ mT) for protons. Second, the spin-flip signals are absent in deuterated lattices, as may be seen from the corresponding signal for DKDA, Fig. 2(b). Third, their separation decreases at lower fields in accordance with $2g_n\beta_nH$,[1–3] being 0.63 mT at $H=210$ mT for line 2 for KDA for which they are barely resolved [Fig. 2(c)]. Similarly the expected signal separation of approximately 0.5 mT at $H=140$ mT for line 1 for KDA is smaller than the inhomogeneous width for this line, therefore, they contribute only to its overall broadening as may be verified from Fig. 1. Finally, the signal identification was consistent with microwave power saturation behavior of the signals[1–3]—a rapid increase in their intensity with an increase in the microwave power incident on the sample, without any saturation even at levels where the main signal (for example, line 4) exhibited strong saturation behavior (decrease in the signal height and increase in the linewidth[1–3]).

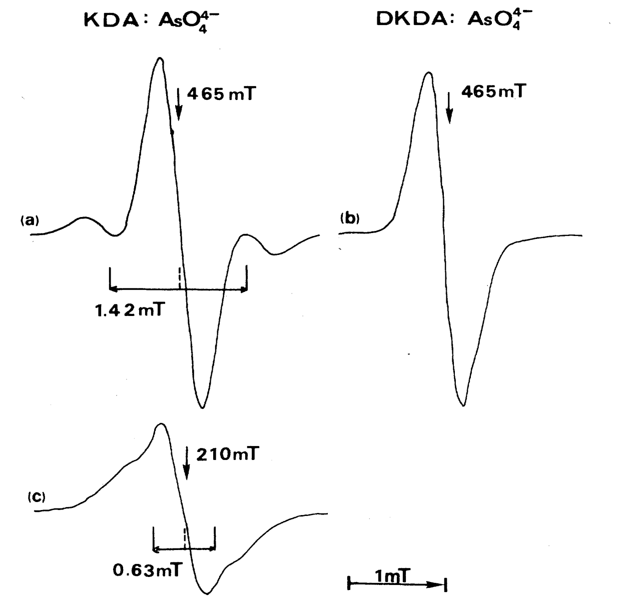

FIG. 2. ESR spectral features for the $AsO_4{}^{4-}$ center in KDA, $H\perp c$, exhibiting the spin-flip transitions: (a) line 4 exhibiting well-resolved satellites (indicated by sticks 1.42 mT apart) due to proton spin-flip transitions, (b) line 4 in DKDA showing absence of the proton spin-flip lines, (c) line 2, spin-flip transitions barely resolved.

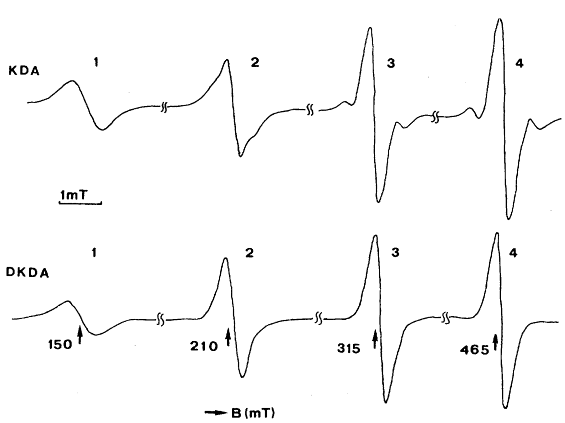

FIG. 1. Typical X-band, $H\perp c$, room temperature, ESR spectra of the $AsO_4{}^{4-}$ center in KH_2AsO_4 (KDA) and KD_2AsO_4 (DKDA) showing the four ^{75}As hyperfine transitions, labeled 1, 2, 3, and 4 as discussed in the text.

EFFECT OF SPIN-FLIP TRANSITIONS ON LINEWIDTHS AND τ

The above-discussed spin-flip broadening enters the calculation of the motional correlation time τ directly because in the spin-probe studies of crystals,[11–23] τ is usually deduced from line separation or linewidth changes via the modified Bloch equations.[24] Here we note that while more rigorous theoretical treatments have been discussed and applied to spin-probe studies of liquids,[25,26] the modified Bloch equations are still in common use in the spin-probe studies of phase transitions in crystalline solids,[5] perhaps because of the complexity of the probe's bonding in strongly anisotropic lattices. Thus, in the absence of other, simple line-shape analysis models, we shall continue using the modified Bloch equations[24] for motional studies of crystals, but with possible improvements in view. In particular, to incorporate the spin-flip broadening in the calculation of τ, we note that, generally, the τ is calculated via the solutions of the modified Bloch equations in two limiting cases, the limit of "slow" motion defined by the condition $\tau\Delta_{0i}/\gamma \gg 1$, and of "fast" motion, characterized by $\tau\Delta_{0i}/\gamma \ll 1$. Here Δ_{0i} is the splitting of the ith line in the rigid-lattice ($\tau \rightarrow \infty$) limit, and γ is the electronic gyromagnetic ratio. In the fast-motion limit, the following formulas are generally used:[24]

$$\Gamma_i = \Gamma_{0i} + k\gamma\tau(\Delta_{0i})^2/4 \tag{1}$$

or

$$\tau = 4(\Gamma_i - \Gamma_{0i})/(k\gamma\Delta_{0i}^2) , \tag{2}$$

where Γ_i is the observed peak-to-peak linewidth, Γ_{0i} is the residual (peak-to-peak) linewidth and k is a constant depending on the line shape; its value being 1.15 for a first derivative Lorentzian and 1.7 for a first-derivative Gaussian line shape. Equation (2) shows that the τ obtained via this procedure depends sensitively on the residual linewidth Γ_{0i}, especially at high temperatures, where the (motional) broadening contribution becomes comparable to Γ_{0i}.

In order to examine the effect of the spin-flip transitions on the linewidth, we plotted the measured peak-to-peak linewidths Γ_i for lines 1, 2, and 4 for KDA for $H \perp c$. Line 3, being strongly overlapped by signals from other free radicals, is not suitable for a detailed linewidth analysis.[5] The data for KDA are shown in Fig. 3, where it can be noted that the width of line 1 (shown by Δ) is always larger than those of the other two lines. These plots also show that the widths of all three lines become nearly constant (though exhibiting a small increasing trend) in the higher-temperature range, as expected for motionally averaged signals.[24] Moreover, the excess width of line 1, about 0.5 mT, in the higher-temperature regime, is almost exactly the contribution expected from the proton spin-flip transitions for this line, as noted above. This conclusion was supported by deuteration studies. The deuteron spin-flip transitions are expected to make a relatively minor contribution to the linewidths because of their much smaller (about a factor of 3) end-to-end spread compared to those for protons at the same magnetic field. The measured peak-to-peak linewidth data for DKDA are shown in Fig. 4, where it can be seen that indeed the width of line 1 approaches those of 2 and 4 in the high-temperature regime.

We can now see that since Γ_{0i} contains a significant contribution from the proton spin-flip transitions for mainly line 1 in KDA, the τ's deduced from changes in the *peak-to-peak* width of this line would contain the largest systematic error. In particular, with an increase

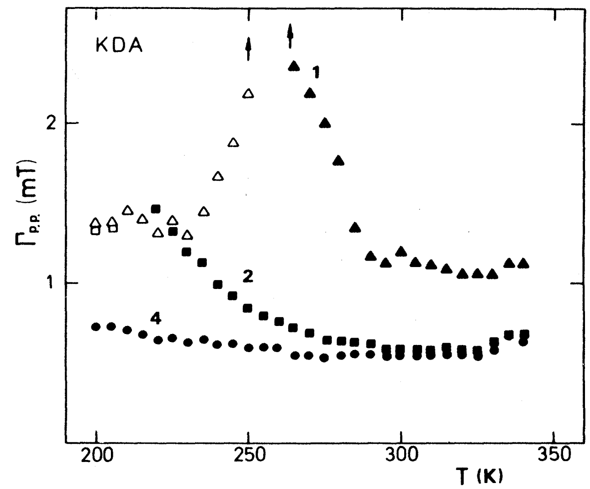

FIG. 3. Temperature dependence of the peak-to-peak linewidth of the AsO_4^{4-} hyperfine components for $\mathbf{H}\|(a+45°)$ for KDA. (▲) correspond to line 1 above coalescence and △ below coalescence, while ■,□ correspond to similar data for line 2 and ● to line 4.

in temperature, the rate of change of Γ_i and, hence, of τ will be smaller than that in the absence of spin-flip broadening. This mechanism can provide a qualitative explanation for the "flattening" of the $\ln\tau$-versus-T^{-1} plots at high temperatures for KDA as reported by Lamotte *et al.*[16] and the *high-temperature* nonlinearity noted for KDA and related compounds by Dalal and McDowell.[14]

To examine this conclusion quantitatively, the linewidth data were analyzed as differences, since this procedure highlights the role of the excess residual

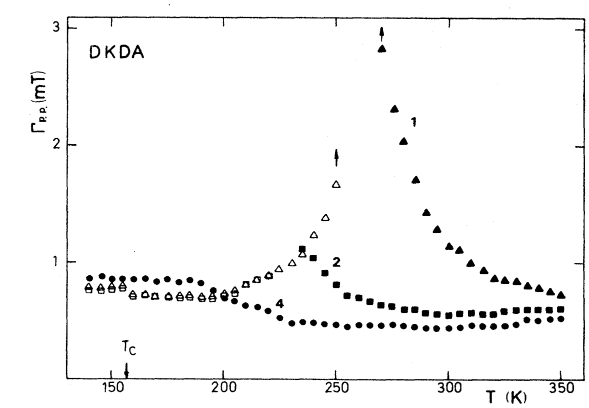

FIG. 4. Temperature dependence of peak-to-peak linewidth of the AsO_4^{4-} hyperfine components for $\mathbf{H}\|(a+45°)$ for DKDA. ▲ correspond to line 1 above coalescence and △ below coalescence. ■ and □ denote the corresponding data for line 2 and ● for line 4.

widths. Thus using Eq. (1) for lines 1 and 4, we can write

$$\Gamma_1-\Gamma_4=\Delta\Gamma_{14}=(\Gamma_{01}-\Gamma_{04})+k\tau(\Delta_{01}^2-\Delta_{04}^2)/4 \ . \quad (3)$$

Assuming that τ obeys the Arrhenius law, $\tau=\tau_0\exp(\Delta E/k_BT)$, Eq. (3) becomes

$$\Gamma_1-\Gamma_4=\Delta\Gamma_{14}=(\Gamma_{01}-\Gamma_{04})+k\tau_0(\Delta_{01}^2-\Delta_{04}^2)e^{(\Delta E/k_BT)}/4 \quad (4)$$

$$\cong k\tau_0(\Delta_{01}^2-\Delta_{04}^2)e^{(\Delta E/k_BT)}/4 \quad (5)$$

$$\text{if } \Gamma_{01}\approx\Gamma_{04} \ . \quad (6)$$

Equations (5) and (6) imply that a plot of $\ln\Delta\Gamma_{14}$ versus T^{-1} would be linear if τ obeyed the Arrhenius law, and if $\Gamma_{01}\approx\Gamma_{04}$ (i.e., if both lines had the same residual peak-to-peak linewidths due to the spin-flip transitions or other causes). The upper curve in Fig. 5 shows such a plot for KDA and a clear deviation from linearity is observed around 285 K, the region marked by the arrows in this figure. The observed nonlinearity indicates that either the Arrhenius law is not followed or the approximation $\Gamma_{01}\approx\Gamma_{04}$ [Eq. (6)] is not valid. As shown above, of course, Γ_{01} has a significant contribution from the proton spin-flip transitions whereas Γ_{04} does not, hence the breakdown of Eq. (6) seemed to be the likely cause of the nonlinearity in the upper curve in Fig. 5. This conclusion was verified in two ways. First, Eq. (6) was examined for lines 2 and 4 for which the peak-to-peak widths Γ_2 and Γ_4 are not significantly affected by the proton spin-flip transitions, especially in the higher-temperature regime where these lines become narrower than the separation between the spin-flip transitions [cf. Figs. 2(a) and 2(c)]. Thus any effects of the spin-flip broadening should be absent for Γ_{24}. The lower curve in Fig. 5 shows a plot of $\ln\Delta\Gamma_{24}$ versus T^{-1} for the same temperature range as used for Γ_{14}. The observed linearity for the $\ln\Delta\Gamma_{24}$-versus-T^{-1} plot suggested that the nonlinear behavior for $\ln\Delta\Gamma_{14}$ was indeed related to the proton spin-flip broadening for line 1. Second, a parallel analysis of DKDA data, as shown in Fig. 6, demonstrated that the plot of $\ln\Delta\Gamma_{14}$ versus T^{-1} is indeed more linear than the corresponding plot for KDA, providing further supports for the significant role of the spin-flip broadening in causing the nonlinear (hence non-Arrhenius) behavior of $\ln\Delta\Gamma_{14}$ versus T^{-1}.

Another significant advantage of the analysis based on the linewidth differences is that it provides a sensitive check on the validity of the approximations used in the formulas for deducing τ. The spectra shown in Fig. 7 for lines 1 and 2 for KDA provide a specific example. For a given temperature range, while line 1 is still a doublet (i.e., it exhibits features of slow motion), line 2 has already narrowed to a singlet (i.e., it shows a fast motion, motional narrowing, behavior). Thus one can check the τ values evaluated from the slow-motion approximation against those obtained for the fast motion for a given temperature range. Since at a given temperature τ should be characteristic of only the particular lattice-probe combination, and not of any particular line utilized, any differences in the τ obtained should serve a cautionary note on the breakdown, in the analysis procedure, of the approximation of either the slow- or the fast-motion limit.

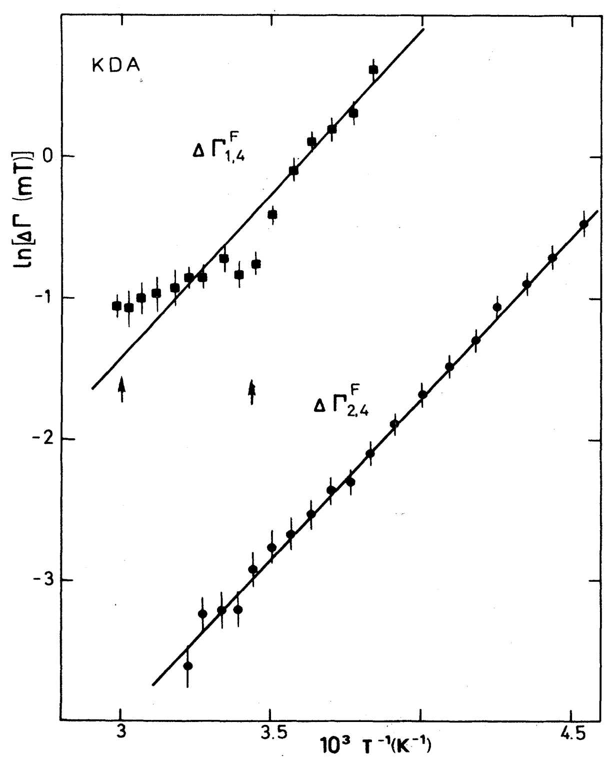

FIG. 5. $\ln\Delta\Gamma_{14}=\ln(\Gamma_1-\Gamma_4)$ and $\ln\Delta\Gamma_{24}=\ln(\Gamma_2-\Gamma_4)$ vs T^{-1} for KDA.

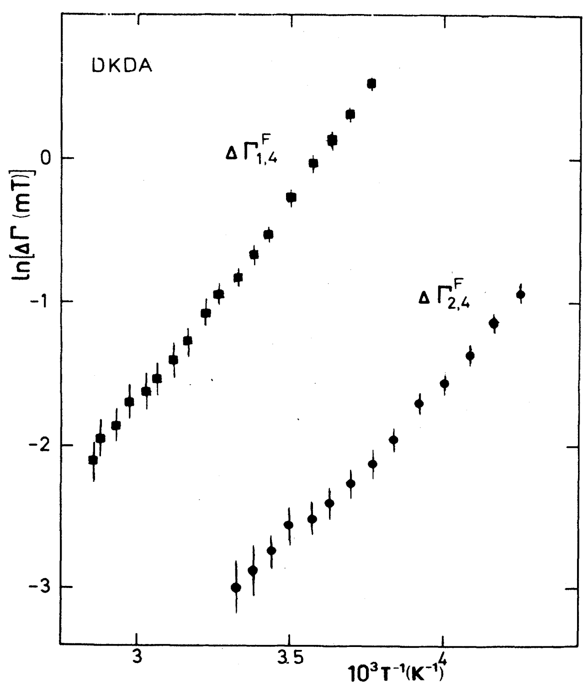

FIG. 6. $\ln\Delta\Gamma_{14}=\ln(\Gamma_1-\Gamma_4)$ and $\ln\Delta\Gamma_{24}=\ln(\Gamma_2-\Gamma_4)$ vs T^{-1} for DKDA.

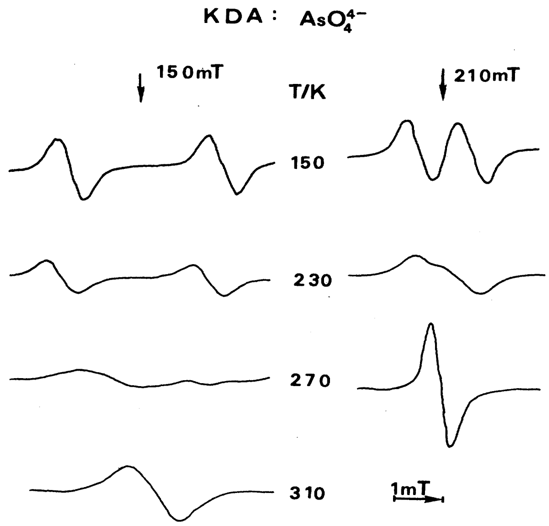

FIG. 7. ESR spectra of the AsO_4^{4-} center in KDA for lines 1 and 2 exhibiting different coalescence temperatures.

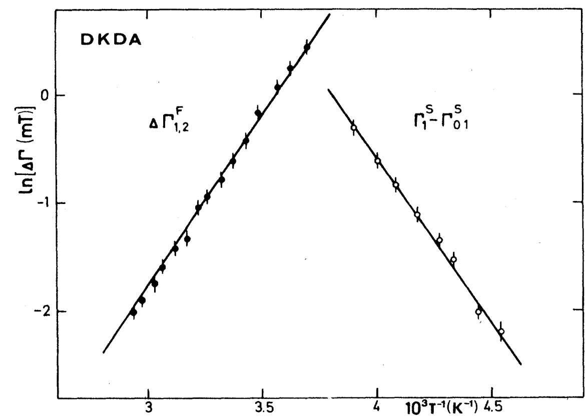

FIG. 8. Semilogarithmic plot of the difference between the linewidths $\Delta\Gamma_{12}=\Gamma_1-\Gamma_2$ and $\Gamma_1-\Gamma_{01}$ vs T^{-1} for DKDA. ○ denote the differences below the coalescence temperature and ● above coalescence.

We checked in detail the above-mentioned procedure of using the linewidth differences for the DKDA lattice. As mentioned above, while the plot of $\ln\Delta\Gamma_{12}$ versus T^{-1} is fairly linear (Fig. 8), that of $\ln\Delta\Gamma_{24}$ (or $\ln\Delta\Gamma_{14}$) versus T^{-1} shows a deviation from linearity. This was surprising at first, being opposite to the case for KDA (Fig. 5). However, further analysis showed that this was another, perhaps more striking confirmation of the effects of broadening of Γ_{0i} by the deuteron spin-flip transitions: the combination of lines 1 and 2 is the best for DKDA because while taking the linewidth differences, the effects of deuteron spin-flip broadening cancel out moreso for this combination (because the Zeeman field separation is the smallest for this pair) than for any other. It may be recalled that this is in contrast to the case for KDA where the best combination was that of lines 2 and 4.

A further check on the methodology was made via calculations of τ for the slow-motion regime below T^* (273 K) for DKDA. As usual in this regime it was appropriate to use the well-established relationship[24]

$$\Gamma_i=\Gamma_{0i}+k/2\gamma\tau \ . \qquad (7)$$

Again, if τ followed an Arrhenius behavior, then a plot of $\ln(\Gamma_i-\Gamma_{0i})$ versus T^{-1} should show linear dependence with the same slope as for the fast-motion regime but with an opposite sign. Using $\Gamma_{01}=0.48$ mT [peak-to-peak width of line 1 at low temperatures $(T \ll T^*)$], a plot of $\ln(\Gamma_1-\Gamma_{01})$ versus T^{-1} for, this slow-motion region for DKDA is shown in Fig. 8 (open circles). The data exhibit the expected linear behavior and the appropriate activation energy (given in Table I), thereby supporting the above-discussed analysis procedure of linewidth differences in the fast-motion limit.

PROCEDURE FOR MEASURING τ

The above results indicate that the earlier used procedure for deducing τ from the line-shape changes in line 1 alone[5,14,16,18] or line 1 and 4 together[16] can be improved by including the linewidth data from the other lines. Moreover, if the ESR measurements are to be made at the X band, as is done usually,[5,18] then the procedure must include either line 1 or 2 (or both), together with other lines, because only these lines exhibit the domain splitting large enough to permit the τ measurements over a wide enough temperature range[5] (encompassing both the slow- and fast-motion regions). Additionally, since the proton spin-flip transitions cause qualitatively different line-shape changes [generally, separate lines as satellites, Fig. 2(a)] than do the deuteron spin flips [an inhomogeneous broadening of all four lines, cf. Fig. 2(b)],

TABLE I. Arrhenius activation energy ΔE, preexponential factor τ_0, and the temperature range ΔT for KH_2AsO_4 (KDA) and KD_2AsO_4 (DKDA).

Lattice	ΔT (K)	ΔE (eV)	τ_0 (s)	Ref.
KDA	220–310	0.20±0.02	3.2×10^{-13}	Present work
	218–286	0.15	1.0×10^{-12}	14
	225–295	0.21±0.03	2.8×10^{-13}	16
DKDA	217–330	0.26±0.02	3.7×10^{-14}	Present work
	218–286	0.25	1.0×10^{-13}	14
	235–295	0.27±0.03	2.8×10^{-14}	16

the line combination ideally suited for the measurements of τ for KDA would not necessarily be so for DKDA. It was clear nevertheless that a procedure based on the linewidth differences would improve the accuracy of the τ measurements.

We noted, however, that while the slopes and the intercepts of the linear plots in Figs. 5 and 8 yielded fairly consistent values for ΔE and τ_0, respectively, their absolute values depended on the line-shape factor k. This was significant since the observed line shapes were neither pure Lorentzians nor pure Gaussians and thus there was the possibility of some systematic error in the calculated τ values. It was thus considered important that the τ's obtained be calibrated against at least one value deduced by a fairly absolute procedure. This was achieved by calculating τ using the well-established relationship of the simple theories of motional narrowing (such as the formalism of the modified Bloch equations[24]): at the coalescence temperature T^* [i.e., the temperature at which a doublet (of signals being motionally averaged) just coalesces to a singlet], the value of τ is given by $\tau=2^{1/2}/\gamma\Delta_0$, Δ_0 being the line splitting in the limit of no motion (i.e., in the limit $\tau\rightarrow\infty$). In agreement with earlier reports,[5,14,16,18] T^* was measured as 260 K for KDA and 273 K for DKDA. Using the measured values of Δ_{01} (3.4 mT) for KDA as well as DKDA, we obtain the τ values of 2.4×10^{-9} s for KDA at 260 K and for DKDA at 273 K. Insertion of these τ values in $\tau=\tau_0\exp(\Delta E/k_BT)$, with $\Delta E=0.20\pm0.02$ eV for KDA and 0.26 ± 0.02 eV for DKDA (obtained from Figs. 5 and 8), yielded $\tau_0=3.2\times10^{-13}$ s for KDA and 3.7×10^{-14} s for DKDA. These values are collated in Table I where the data from earlier studies[14,16] are also included. It can be seen in Table I that both of the Arrhenius parameters (ΔE and τ_0) exhibit a significant isotope effect. While such an isotope effect had been noted earlier,[14,16] the results were less reliable than obtained here because of the reported non-Arrhenius behaviors.[14,16] Figure 9 shows the Arrhenius, $\ln\tau$-versus-T^{-1}, plots for KDA and DKDA, the continuous lines being the theoretical plots generated using the above parameters while the points represent the experimental data. The observed linearity of the plots and the satisfactory fitting imply that the probe's motion follows an Arrhenius behavior even at higher temperatures than investigated before.[14,16]

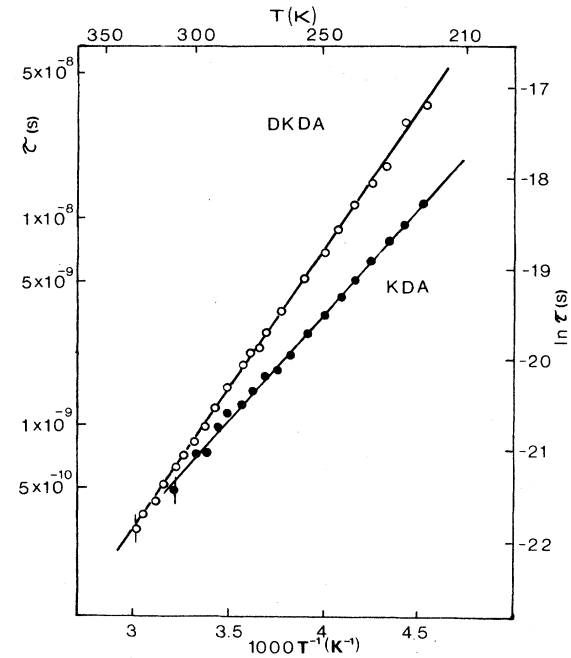

FIG. 9. Arrhenius plots of correlation times τ for the AsO_4^{4-} center in DKDA and KDA.

DISCUSSION AND CONCLUSIONS

This study demonstrates that proton spin-flip transitions make a significant contribution to the width of the lowest-field ^{75}As hyperfine transition (line 1) for the AsO_4^{4-} center in the KH_2AsO_4 type of lattices. The omission of this line-broadening mechanism appears to be the main cause for the non-Arrhenius behavior reported earlier for this probe in KDA and DKDA in the high-temperature region.[14,16] In contrast to the earlier methodologies based on line 1, this work suggests the following guidelines for the measurement of τ for AsO_4^{4-}: (a) one component must be line 1 or 2, and (b) the other component(s) should be picked so as to minimize the line-broadening effects of the spin-flip transitions. As discussed above, these results imply that the best combination for KDA (or the related protonated lattices) is provided by lines 2 and 4 (in contrast to the earlier procedure of using line 1 only[14] or lines 1 and 4[16]), while for DKDA (or the related deuterated lattices) the best combination is that of lines 1 and 2. The accuracy and the consistency of the results obtained here for KDA and DKDA now confirm a clear $H\rightarrow D$ isotope effect on the Arrhenius parameters of the AsO_4^{4-} probe. These data point to the sensitivity of the probe to the bonding and fluctuations of the host lattice and should serve as new data for the theoretical modeling[6] of the low-frequency fluctuations in relationship to the central peak,[9,10] or other cooperative phenomena in the KH_2PO_4 family of ferroelectrics and antiferroelectrics. The results will also be useful for future studies involving use of the AsO_4^{4-} center in probing low-frequency motion in the recently reported[27-29] proton and deuteron glasses based on the RbH_2AsO_4-$NH_4H_2AsO_4$ and RbD_2AsO_4-$ND_4D_2AsO_4$ systems.

We note, however, that this study could not be extended to the slow-motion regime, near T_c and for the proton quintet-triplet transitions,[11] where also deviations from the Arrhenius behavior have been reported.[5,14] Our preliminary data[30] now show that such deviations do occur but only in the close vicinity of T_c. Moreover, this work has some relevance to the other spin probes, such as SeO_4^{3-}, used[31-34] for investigating the mechanisms of the ferroelectric and antiferroelectric transitions in the KH_2 type of crystals,[5] since such forbidden transitions have been detected in the spectra of the SeO_4^{3-} center in KH_2PO_4.[17] Our preliminary analysis[30] indicates a need for a reexamination of the τ data for SeO_4^{3-} in KDP (Ref. 33) as well as in KDP-DKDP mixed crystals.[34]

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