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1994 J. Phys.: Condens. Matter 6 2971

(http://iopscience.iop.org/0953-8984/6/15/020)

J. Phys.: Condens. Matter 6 (1994) 2971–2974. Printed in the UK

COMMENT

Lattice-strain versus dynamic effects in electron spin resonance studies of $Rb_{1-x}(NH_4)_xH_2PO_4$

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Received 22 October 1993

Abstract. A methodology for investigating dynamics of various spin probes in mixed/glassy systems of the KH_2PO_4 type is developed. Using this methodology, electron spin resonance (ESR) features of the AsO_4^{4-} centre in the paraelectric phase of $Rb_{1-x}(NH_4)_xH_2PO_4$ are shown to arise from strain-broadening and motional-broadening effects. These conclusions are in disagreement with those of a recent study, which implicated the various features observed in the existence of ferroelectric–antiferroelectric fluctuations in $Rb_{1-x}(NH_4)_xH_2PO_4$. It is additionally shown that hyperfine couplings from Rb isotopes make the dominant contribution to the ESR spectra in Rb-containing compounds

A recent electron spin resonance (ESR) study [1] of the AsO_4^{4-} centre in the $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) proton glass has interpreted the observed ESR lineshape features in terms of fluctuations between local ferroelectric and antiferroelectric states of H_4AsO_4 units. This study also suggested that the phenomena of glass formation occurs due to progressive slowing down of these fluctuations. These conclusions have been drawn from the observed transformation of the quintet proton structure in $(NH_4)H_2PO_4$ (ADP) to the triplet proton structure in RADP at room temperature for x values of 0.95 and 0.90, and complete 'washing out' of the proton structure up to a temperature of 423 K for $x < 0.80$. The room-temperature proton triplet for $x = 0.85$ and 0.90, however, becomes a quintet around 315 K and 360 K, respectively.

The purpose of this comment is to show that a significant contribution to broadening of the ESR spectra in RADP arises from lattice strains, which, in combination with the paramagnetic centre's local dynamics, then lead to the observed features. We find that hyperfine couplings from the Rb isotopes, and not a single proton superhyperfine structure [2], make the dominant contribution to the ESR lineshape. No earlier studies of the AsO_4^{4-} centre in the Rb-containing compounds have taken the Rb hyperfine structure into account [1–4].

In order to obtain an insight into the ESR lineshapes of the AsO_4^{4-} centre in RADP, a quantitative understanding must first be obtained for the paramagnetic centre's lineshape and its local dynamics in the parent compounds, RbH_2PO_4 (RDP) or RbH_2AsO_4 (RDA), and ADP. This is especially true for understanding the lineshapes of the ESR spectra for RADP on the low-Rb side. The model discussed earlier for CDA [5] was therefore adapted appropriately for RDA. The modified model considers an $S = \frac{1}{2}$ centre coupled to two non-equivalent Rb atoms (^{85}Rb or ^{87}Rb with nuclear spins $\frac{5}{2}$ or $\frac{3}{2}$, respectively), two equivalent near protons,

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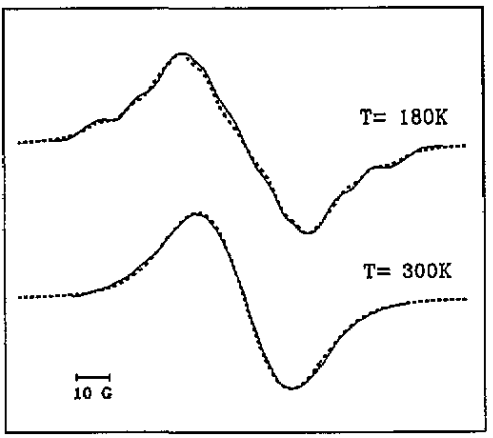

Figure 1. Temperature dependence of the ESR lineshapes of the AsO_4^{4-} centre in RDA. The continuous curve represents the experimentally observed spectra whereas the broken curve represents the calculated spectra.

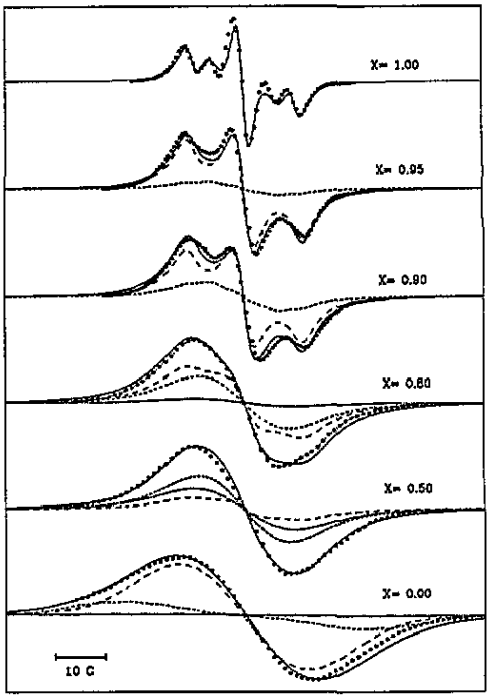

Figure 2. Concentration (x) dependence of the ESR spectra of the AsO_4^{4-} centre in RADP. The various curves plotted are discussed in the text.

and two equivalent far protons. The two axial Rb, located on either side of the H_4AsO_4 unit, can therefore consist of either both ^{85}Rb with relative probability 0.521 (case (i)), or both ^{87}Rb with relative probability 0.077 (case (ii)), or one each of ^{85}Rb and ^{87}Rb with relative probability 0.402 (case (iii)). Superhyperfine (SHF) couplings along the c axis due to near and far protons, and ^{85}Rb and ^{87}Rb, have been obtained in part from the ENDOR spectra recorded in the ab and ac planes as a function of temperature. The model calculations thus reduce to varying the rates $1/\tau_H$ and $1/\tau_{Rb}$ with which the proton and Rb SHF interactions are respectively modulated. It was found that the experimental spectra of the AsO_4^{4-} centre in RDA over the investigated temperature range were closest to those calculated with $\tau_H \simeq \tau_{Rb}$ ($= \tau$). Figure 1 shows a comparison between the experimental (continuous curve) and the calculated (broken curve) spectra at 180 K and 300 K, corresponding to τ values of 4.7×10^{-8} s and 1.0×10^{-9} s respectively. The experimental spectrum is in fact the result of superposition of three component spectra with appropriate probabilities, namely the spectra (i) when both ^{85}Rb nuclei lie on the c axis, (ii) when both ^{87}Rb nuclei lie on the c axis, and (iii) when one ^{85}Rb and one ^{87}Rb lie on the c axis. It was found that component (ii) makes an insignificantly small contribution to the experimental spectrum compared to the other two components. It is pointed out that the same model gives semi-quantitative agreement at various temperatures for RbD_2AsO_4 as well. The ESR behaviour of ADP, on the other hand, is that of a spin-$\frac{1}{2}$ centre coupled to two equivalent near protons ($I = \frac{1}{2}$) and two equivalent far protons ($I = \frac{1}{2}$). Figure 2 (corresponding to $x = 1.00$) shows a comparison

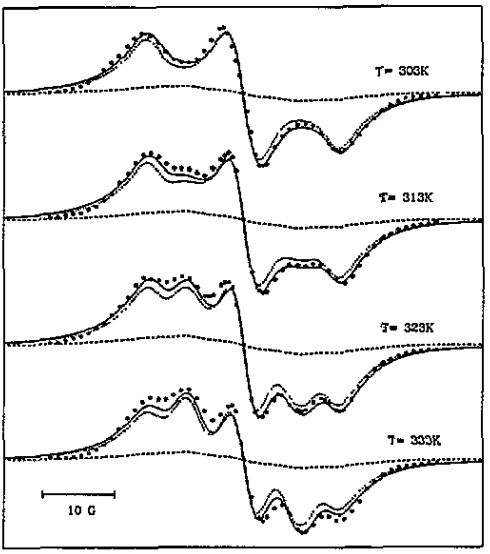

Figure 3. Temperature dependence of the experimental (filled circles) and calculated (continuous curve) ESR lineshapes of the AsO_4^{4-} centre in RADP. The component spectra (i) (dotted curve) and (iv) (broken curve) are also shown in the plot.

of our calculated (continuous curve) and the experimental (filled circles) results for ADP using $\tau = 4.7 \times 10^{-8}$ s, indicating that at room temperature the proton dynamics is much faster in ADP than in RDP.

The present methodology for calculating ESR lineshapes in RDA and ADP was then extended to RADP. The experimental spectrum in RADP at a given x is the result of superposition of six component spectra with appropriate probabilities, namely the spectra when on the c axis and on either side of the H_4AsO_4 units we have (i) two NH_4 groups, (ii) two ^{85}Rb atoms, (iii) two ^{87}Rb atoms, (iv) one NH_4 and one ^{85}Rb, (v) one NH_4 and one ^{87}Rb, and (vi) one ^{85}Rb and one ^{87}Rb. Component spectrum (i) was shifted toward high fields by 3–5 G before summing up all the six component contributions with correct probabilities. This approximately takes into account the fact that the resonant field for ADP is higher than that for RDP. Furthermore, component spectrum (i) for all values of x was calculated using $\tau = 7.0 \times 10^{-8}$ s, whereas for all the other component spectra (ii)–(vi) τ was taken as 1.0×10^{-9}, the value obtained for RDA. Results of the calculations (continuous curve), shown in figure 2 at different values of x, reproduce clearly all the observed lineshape features including asymmetry. For the spectra corresponding to $x = 0.90$ and 0.95, significant contributions arise from the components (i) (long-dashed curve) and (iv) (short-dashed curve)†. On the other hand, the spectra at $x = 0.80$ and 0.50 do have significant contributions from the component (ii) (dotted curve) as well. Figure 3 compares the calculated (continuous curve) and experimental (filled circles) ESR spectra in RADP for $x = 0.95$ at four different temperatures. The contributions from the components (i) (dotted curve) and (iv) broken curve) are also shown in this plot. The values of τ at these temperatures have been taken from the linear plots of $-\ln \tau$ versus $1/T$ for ADP and RDA. We wish to point out that the calculations also reproduce well the ESR features in RADP for $x = 0.90$.

† See the *Note added in Proof.*

A slight difference between room temperature τ values in RADP with $x = 1.0$ and 0.95 (4.7×10^{-8} s and 7.0×10^{-9} s, respectively) is most likely due to changes in the charge and spin densities brought about by increased lattice strains. This is consistent with our recent analysis of the ENDOR and ESR investigations of RDA, DRDA, and CDA, according to which fluctuations probed by ESR are those involving redistributions of local spin/charge densities at the rate $1/\tau$. Also, the lattice strain increases the width of the ESR lines, which has been introduced into our calculations via the $1/T_2^*$ contribution to each spectral line; the value of $1/T_2^*$ increases from 2.4 G to 3.6 G in going from $x = 1.0$ to 0.95. Since in KDP-type systems the ESR-deduced correlation time τ for hopping of the O–H···O protons (and heavy nuclei) above T_c follows an Arrhenius behaviour [4] and strain-broadening effects are significant, possible emergence of the proton quintet in the ESR spectrum of RADP ($x < 1.0$) will take place, depending upon the values for $1/\tau$ and $1/T_2^*$, at increased temperatures.

In our conclusion, a methodology for investigating the dynamics in mixed/glassy systems of the KDP type has been developed. Using this methodology, it is shown that ESR features of the AsO_4^{4-} centre in the paraelectric phase of RADP result from a combination of strain-broadening and motional-broadening effects. Our conclusions are in disagreement with those of a recent study [1] wherein the same effects were ascribed to ferroelectric–antiferroelectric-type fluctuations. In addition, we believe that the presently discussed methodology opens up a new avenue for investigating the ESR dynamics of other spin probes coupled to many other nuclei with high spin quantum numbers.

This research was supported by grants from the Research Corporation to PKK, from the Air Force Office of Scientific Research to NSD, and a William Randolph Hearst Foundation Award of the Research Corporation to MBC.

Note added in proof. It is noted that the contribution (iv) (see page 2973) to the resultant spectrum at either $x = 0.95$ or $x = 0.90$ is still relatively small and that the spectra are dominated by the component (i) with slightly slowed-down dynamics but with increased spectral linewidth. The observation that the ^{75}As hyperfine constant A obeys the relationship $A_{RADP} = (1 - x)A_{RDP} + xA_{ADP}$ over the entire composition range does not, in our view, prove conclusively the existence of ferroelectric–antiferroelectric fluctuations, since the ESR spectra for small values of x are almost completely determined by the component (i) and what is needed to simulate the spectra is increased spectral linewidth together with slightly increased motional time.

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