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Thermally reversible transformation between free radicals in the paraelectric phase of irradiated KH_2AsO_4 crystals

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New EPR investigations in the paraelectric phase of γ -irradiated KH_2AsO_4 crystals show the existence of a thermally reversible transformation between AsO_4^{4-} and AsO_3^{2-} free radicals. The transformation obeys a linear law, the parameters of which depend on the history of the crystal. We postulate that the phenomenon is allowed by interbond proton jumps between $\text{O}-\text{H}\cdots\text{O}$ bonds and that the AsO_3^{2-} radical is the consequence of the pairing of the AsO_4^{4-} radical with the D defect which is assumed in theories of the proton-conductivity mechanisms.

In crystals belonging to the family of the ferroelectric KDP (KH_2PO_4), NMR studies have shown that the protons of the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds connecting the XO_4^{3-} tetrahedra ($X = \text{P}, \text{As}$) play a prominent part in the lattice dynamics in the paraelectric phase.¹ Intrabond jumps occur above the Curie point corresponding to exchanges between proton configurations, principally the six Slater configurations, polar or lateral. At higher temperature interbond jumps appear, which accounts for the proton conduction.

In arsenate compounds of the family, α or γ irradiation creates a free radical of the AsO_4^{4-} type (electron capture) and several radicals of the AsO_3^{2-} type (breaking of an $\text{As}-\text{O}$ bond).² Since the AsO_4^{4-} radical retains the tetrahedral structure, it might seem possible to use this radical to examine the dynamics in the paraelectric phase. In various EPR studies, in particular of KDA (KH_2AsO_4), intrabond jumps at the radical have been observed.³ However, it is now well established that one is dealing here with local, slow dynamics where only the polar configurations are involved.⁴

The concentration of interest on the AsO_4^{4-} species in KDA probably explains why an important phenomenon has escaped notice. By avoiding temperatures where the free radicals, which are unstable species by nature, would be irremediably destroyed,

we have observed that the AsO_4^{4-} species is related by a thermally reversible equilibrium to an AsO_3^{2-} species (the K species of Ref. 2): the AsO_4^{4-} radical is transformed progressively into the AsO_3^{2-} radical as the temperature is raised in the paraelectric phase.

In the present article, we study this phenomenon, which is interesting for several reasons.

(a) Previously, transformations between AsO_4^{4-} and AsO_3^{2-} radicals have been observed in KDA (Ref. 5) and DADA ($\text{ND}_4\text{D}_2\text{AsO}_4$) (Ref. 6), taking place at fixed temperature, the Curie temperature. The present work constitutes the first observation of such a transformation occurring as a function of temperature, not produced by the phase transition.

(b) The phenomenon is quantitatively described by a linear law which has however the originality of depending on the crystal's history, i.e., on the crystal preparation and subsequent treatments (irradiation, annealing, . . .).

(c) The phenomena relating to the AsO_4^{4-} center have until now always been incompletely studied. The phenomenon described here leads to new and important developments in the understanding of the dynamics at the AsO_4^{4-} radical in the paraelectric phase. A difference in the number of protons surrounding the AsO_4^{4-} and AsO_3^{2-} radicals leads us to interpret the process $\text{AsO}_4^{4-} \leftrightarrow \text{AsO}_3^{2-}$ as the manifestation of an interbond proton exchange: in this in-

terpretation the AsO_3^{2-} radical then would be the result of the pairing of the AsO_4^{4-} radical and the D defect assumed in theories of the proton conductivity mechanisms⁷ and we should thus have obtained the first microscopic observation of this kind.

We did our EPR experiments on a Varian E3 spectrometer fitted with a variable temperature device using nitrogen as cold carrier gas. The EPR first derivative absorption spectra were obtained at low microwave power to avoid saturation. Double integration of the spectra gave the relative concentrations of the AsO_4^{4-} and AsO_3^{2-} species. For each radical it was sufficient to consider only one of the four EPR lines that arise from the hyperfine interaction of the electron with the arsenic ($I = \frac{3}{2}$), in practice the line at highest field.⁵ We have verified by comparison of the respective concentrations that no transformation between these two species and any other high-concentration species occurred to complicate the phenomenon.

Quantitative EPR study shows that the $\text{AsO}_4^{4-} \rightarrow \text{AsO}_3^{2-}$ transformation obeys a particularly simple law since we find that the logarithm of the ratio of the concentrations $[\text{AsO}_3^{2-}]/[\text{AsO}_4^{4-}]$ depends linearly on $1/T$ when $T >$ about 160–170 K. Below this temperature we found that the concentrations no longer varied within the precision of our measurements, which suggests that the transformation is then frozen.

The phenomenon cannot of course be classed as a thermodynamic equilibrium like those governing the concentrations of the intrinsic defects in a crystal in

equilibrium. Free radicals are by nature unstable defects: a warmup sufficient to restore the equilibrium of the crystal destroys them in an irreversible way. However, although to our knowledge it is the first time that such an observation has been made in the solid state, there is nothing strange in finding an equilibrium between such defects given that it occurs in a temperature range where the destruction process is much slower than the kinetics of the phenomenon.

The unusual feature of the present phenomenon comes from the fact that the parameters found for the linear law depend on the history of the crystal, that is on its origin and on various treatments (irradiation, annealing, . . .). Figure 1 shows a sampling of the variations of the phenomenon as observed between 170 K and room temperature. The transformation $\text{AsO}_4^{4-} \rightarrow \text{AsO}_3^{2-}$ continues its progression at higher temperature but temperatures are soon reached where the irreversible process of annealing of radicals would generate errors in the measurements of relative concentrations. We note that at low temperature the residual relative concentration of the AsO_3^{2-} radical varied considerably, being occasionally almost zero but attaining sometimes some tens of percent, in correlation with the value of its concentration at room temperature. The persistence of a linear effect in the various situations encountered is undeniable: we note the reliability with which the experimental points lie on a straight line, which at the same time shows the accuracy of the measurements. Paradoxically this confirms that the simple concentration ratio has a physical sense, but it allows one also

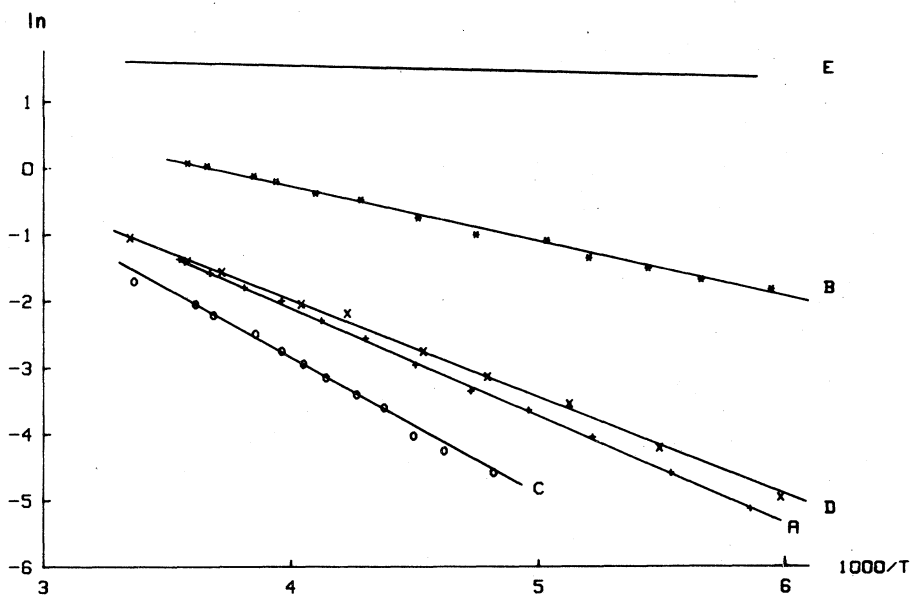


FIG. 1. Various examples of the linear dependence of $\ln([\text{AsO}_3^{2-}]/[\text{AsO}_4^{4-}])$ vs $1000/T$. A, B, C: crystals of different origins after various treatments; D: crystal C after a new annealing and a new irradiation; E: In population ratio of lateral to polar configurations (following Slater theory).

to assert that the differences, even small, which appear from one experiment to another are meaningful.

The nature of the reversible transformation $\text{AsO}_4^{4-} \leftrightarrow \text{AsO}_3^{2-}$ has to be determined. ENDOR (electron-nuclear double resonance) studies of the radical structures in the ferroelectric phase have revealed the existence of hyperfine couplings with four protons for the AsO_4^{4-} radical⁸ and with five protons for the nontransformed fraction of the AsO_3^{2-} radical.^{5(b)} This difference in number of couplings observed evidently poses an important question: does it reflect a real inequality in the number of protons neighboring the AsO_4^{4-} and AsO_3^{2-} species connected by the reversible transformation?

The presence of a fifth proton close to the AsO_4^{4-} radical, with coupling too weak to be measured, can be excluded. Indeed the C_2 symmetry of the tetrahedron about the \bar{c} axis, which leads to the two-by-two chemical equivalence of the four protons of the $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, could not then be maintained at the radical: there would be a general splitting of all the ENDOR lines and we have found no trace of this in spite of the high degree of resolution achieved. Therefore the AsO_4^{4-} radical must be considered as the simple result of electron capture by a lattice AsO_4^{3-} tetrahedron that has no special peculiarities.

We might also consider the opposite case where the two AsO_4^{4-} and AsO_3^{2-} radicals connected by the equilibrium would both involve four protons. The residual fraction of the AsO_3^{2-} radical would then have formed another species with five protons not taking part in the equilibrium. But, at temperatures where the two AsO_3^{2-} species would be present simultaneously, we find no trace of an EPR line splitting of the kind that would support this possibility. On the other hand, a splitting of the EPR line that we observed for some orientations where the resolution is best is very representative of the coupling of the fifth proton of a single radical. There is a final important argument. If an independent AsO_3^{2-} species exists, the corresponding residual concentration would have to be subtracted from the $\text{AsO}_4^{4-} \leftrightarrow \text{AsO}_3^{2-}$ equilibrium in the quantitative description, which would show up as a deviation from linearity, the deviation increasing with the size of the fraction removed. We conclude therefore in favor of the uniqueness of the AsO_3^{2-} species having five near protons.

Thus, the reversible transformation appears on warmup as the result of the capture of a proton by a radical of AsO_4^{4-} type which, except for the additional electron, is not distinguished from a normal tetrahedron by any anomaly in the immediate environment. We note that the charge excess of the AsO_4^{4-} radical can only help the proton capture. Without making any deduction at present concerning the origin of this proton, it must be supposed that its

attachment to an oxygen breaks the corresponding As—O bond. The result of this is the transformation of the species into a radical of AsO_3^{2-} type, which preserves three of the As—O bonds, and we may reasonably complete it by a water molecule which would come from the bonding of the proton with the broken OH^- fragment, the whole unit forming the species with five protons that is observed by ENDOR spectroscopy.

The transformation involves a configuration change: the AsO_4^{4-} species is associated with high and low polar Slater configurations,⁴ the AsO_3^{2-} species is associated with lateral Slater configurations.^{5(b)} Thus, intrabond jumps of some protons occur in this case, as in the exchange observed between the polar configurations of the AsO_4^{4-} radical. However, given the presence of the additional proton and of an AsO_3^{2-} lateral form that has a very deformed structure relative to a tetrahedral lateral form, we cannot assimilate this equilibrium to the one which is assumed to exist between the tetrahedral lateral and polar forms of the lattice. We note moreover that the concentration ratio estimated by the simple Slater theory⁹ gives a straight line, shown in Fig. 1, which has nothing in common with the lines describing our radical equilibria, and it is not the introduction of more sophisticated theories that would be capable of reducing the disagreement. Nevertheless, the increase of the percentage of lateral configurations in the environment can only promote the appearance of radical configurations of the lateral type, even if it is more appropriate to attribute the change of the radical configuration to the respective self-stability of each one of the species.

The question of the origin of the additional proton remains outstanding. We have ruled out the possibility that there exists, close to and associated with the AsO_4^{4-} radical, an anomaly of the lattice which is the subject of a local reorganization. Therefore, there remains the assumption that the proton comes from a hydrogen bond of the neighboring tetrahedra which is not bridged to the radical. In this hypothesis, the existence of interbond jumps at the radical would be revealed; the mechanism would be sufficiently fast above 160–170 K since, if we change the temperature, we observe that the equilibrium is already attained when the temperature has stabilized. The observation of the AsO_3^{2-} radical would represent the first microscopic observation of a defect associated with proton mobility in the crystal.

The theories of the mechanisms of the proton conductivity introduce D and L defects, respectively, doubly occupied and vacant hydrogen bonds, which moreover agree well with one of the two adjacent tetrahedra associated with a configuration of the lateral type.⁷ Within the framework of the preceding hypothesis, owing to the local charge excess, we must conceive the pairing of the AsO_4^{4-} radical with a D

defect. A reorganization within the (AsO_4^{4-}, D) pair gives the AsO_3^{2-} defect and then we can write the quasichemical reaction $\text{AsO}_4^{4-} + D \rightleftharpoons \text{AsO}_3^{2-}$. In the temperature range investigated, extrinsic conductivity is expected.⁷ To explain the linearity of $\ln([\text{AsO}_3^{2-}]/[\text{AsO}_4^{4-}])$ versus $1/T$, we must suppose that in each crystal studied impurities have introduced a concentration of D defects which remains practically constant, and which also requires that $[D] \gg [\text{AsO}_3^{2-}]$. We recall that we had found previously a correlation between the AsO_3^{2-} concentration and the silicon content.^{5(b)} After the present discussion we cannot continue to state as in^{5(b)} that a SiO_4H_3^- unit substitutes for an AsO_4H_2^- unit next to the AsO_3^{2-} radical, but we may rightfully suppose that such an impurity brings its contribution for giving a concentration of D defects which leads to the

presence of the AsO_3^{2-} species. The concentration $[D]$ will depend on the impurity content which is present in the crystal, leading to various parallel lines for the $\text{AsO}_4^{4-} \leftrightarrow \text{AsO}_3^{2-}$ equilibrium. In Fig. 1 the line slopes also vary from one experiment to another in non-negligible proportions, changing from 0.08 to 0.18 eV for the outer lines if we take the slope as the effective energy term of a law of mass action. Though it is quite conceivable for an equilibrium between unstable species to be reproducible, it appears that this is not the case here. After the various treatments and in particular after irradiation, the crystal is in a nonequilibrium state. We can only suppose that the relative stabilities of the species depend on the physical state of the crystal.

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