

ON THE OBSERVATION OF A CHEMICAL REACTION, BETWEEN DEFECTS IN
 $\text{ND}_4\text{D}_2\text{AsO}_4$, BEING REVERSIBLY TRIGGERED BY THE ANTIFERROELECTRIC-
 PARAELECTRIC PHASE TRANSITION.

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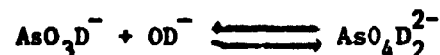
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ABSTRACT

Two distinct radical species $(\text{AsO}_4)^{4-}$ and $(\text{AsO}_3)^{2-}$ created by irradiation in crystals of $\text{ND}_4\text{D}_2\text{AsO}_4$ (DADA), clearly undergo (taking into account the deuterons) the following chemical reaction :

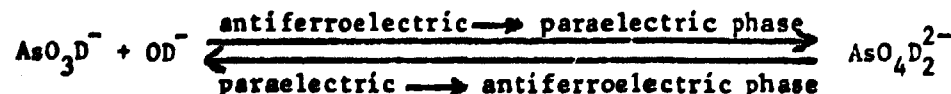


The effect occurs at the antiferroelectric-paraelectric phase transition of the compound. Its essential feature is that the reaction is completely reversible i.e. that it can be triggered by the phase transition. This phenomenon is also observed on the same radicals in $\text{NH}_4\text{H}_2\text{AsO}_4$ (ADA).

A curious phenomenon (1) has been clearly observed in single crystals of $\text{ND}_4\text{D}_2\text{AsO}_4$, a member of the KDP family, during EPR and ENDOR studies of radical defects created by irradiation in the arsenate salts of this family.

It corresponds to the fact that, between two types of distinct radicals identified by ESR, namely the $(\text{AsO}_4)^{4-}$ and the $(\text{AsO}_3)^{2-}$ radicals, there occurs a chemical reaction which happens in a reversible way (i.e. that its direction is determined by the direction of passage of the Curie point - $T_c = 32^\circ\text{C}$ -) at the phase transition between the antiferroelectric and paraelectric phases of the crystal.

The reaction is the following (taking into account the deuterons) :



that is, an hydroxyl ion OD^- can be detached from or reattached to the remaining $(\text{AsO}_3\text{D})^-$ radical ion.

The following table shows the relative concentration of the two types of radicals in the two phases of four different DADA crystals. These concentrations have been measured by double integration of the ESR lines corresponding to the different radicals.

	CRYSTAL 1		CRYSTAL 2		CRYSTAL 3		CRYSTAL 4	
	(a) A.F. phase	(a) P. phase	(a) A.F. phase	(a) P. phase	(a) A.F. phase	(a) P. phase	(a) A.F. phase	(a) P. phase
% $(AsO_4)^{4-}$ radicals	20 %	65 %	31 %	62 %	30 %	73,5 %	25 %	67 %
% $(AsO_3)^{2-}$ radicals	80 %	.35 %	69 %	38 %	70 %	26,5 %	75 %	33 %

(a) The measurement temperatures are 25°C (A.F. phase) and 38°C (P. phase), close to T_c but sufficiently far away to be out of the range of temperature where hysteresis of the Curie point occurs.

We must notice that this reaction is reversible in the sense that it can be reversibly triggered by the phase transition (and repeated indefinitely in both directions), but that it is different from what is called usually a reversible chemical reaction. In effect, in usual chemical reactions, the dissociation occurs when, at sufficient temperatures, the thermal energy of agitation of the two bonded atoms overcomes the internal binding energy of the two atoms, which is a relatively continuous process with temperature. In our case, the process is radically different : it is the entire crystalline network which, at the phase transition, drives away in a stepwise process the two atoms of the radical defect undergoing breakage. Thus, the dynamics of the chemical reaction is here completely determined by the physical process i.e. the local effects of the phase transition at the vicinity of the radical.

Several comments have to be made concerning this effect.

We have found ^{here} an effect corresponding to a somewhat unexpected connection between two types of phenomena which are unrelated a priori i.e. phase transitions and chemical reactions. However, there exists a common feature to the phenomena in our case : ferroelectric or antiferroelectric phase transitions must involve atomic displacements which are, of course, necessary in such a chemical reaction. But, at first sight, there seems to

exist a disproportion between the two types of phenomena, in particular concerning the magnitude of the atomic displacements expected in a chemical reaction and in a phase transition.

The fact that this does not appear to be the case here can receive several explanations :

- First, we must remark that the effect is observed on defects which are diluted in the crystal at concentrations of order of $10^{-3} - 10^{-4}$ M.
- Secondly, we think that favourable chemical conditions exist in these crystals which can facilitate the occurrence of such a reaction. Looking at the Periodic Table, we can observe in effect that the Arsenic atom represents in its column an intermediate situation where the coordination three and four with oxygen are both possible. This signifies that a fourth oxygen atom can be easily bound to, or released from, the AsO_3 entity.
- Thirdly, we think that relatively large atomic motions are less unexpected in hydrogen-bonded crystals than in other types of solids. Moreover we must point out that the large atomic displacements which must be involved in the course of the chemical reaction can be provided by the large amplitude fluctuations occurring in the critical temperature range of the transition. This is also supported by the fact that the chemical reaction is occurring essentially in the phase transition itself but that it begins to happen close to the transition, the graphs of concentration with temperature beginning to be curved in the approach of the transition, especially in the antiferroelectric phase.

Such an effect is also present in the other arsenate salts of the KDP family. It has been observed in KDA (2), where it happens only between certain particular varieties of the $(AsO_4)^{4-}$ and $(AsO_3)^{2-}$ radical. We have also observed that this reversible reaction exists also in ADA (3), where there is a marked increase of concentration of the $(AsO_4)^{4-}$ radicals when passing from the antiferroelectric to the paraelectric phase of the crystal, and a consequent decrease of the $(AsO_3)^{2-}$ radical. However, the effect seems not as clear and simple in this case than for the case reported above in DADA crystals.

- (1) B. LAMOTTE, Solid State Communications, in press
- (2) J. GAILLARD and P. GLOUX, Solid State Communications, in press
- (3) B. LAMOTTE, to be published.