PHYSICAL PROPERTIES OF SOLID ADA-ADP SOLUTIONS*

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Abstract

The variation of the Curie-Weiss temperature and the maximal dielectric permeability (in the direction perpendicular to the polarization axis) of the solid ADA-ADP solution with concentration of the components are measured. The linear dependences observed and their simple interpretation in the frame of the pseudospin model enable one to estimate the physical parameters of a given mixed antiferroelectric compound as well as to predict its behaviour in the critical temperature region.

As it is very well known[1,2], some optimal physical properties can be realized by composing the solid ferro and antiferroelectric solutions.It is of interest that such compounds possess both the chemical stability and optimal physical properties in a wide (working) temperature interval. With this aim chemically stable ADP is dopped by ADA component thus obtaining some intermediate transition temperature and improved dielectric properties. The perpendicular dielectric permeability of a free solid ADA-ADP solution as a function of temperature and concentration (x) of components, say As, has been measured by making use of a capacitive bridge (General Radio Company, Type 1615-A) at 1 kcps. Temperature has been measured in a close vicinity of the crystal by a Fe-Constantan or NiCr-NiAlloy thermopair with accuracy of $\pm$ 0,25 ^{o}K. The experimental results are given at Fig. 1. The observed linear behaviour of $T_o(x)$

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(the Curie-Weiss temperature) and $\varepsilon^{11}_{max}(x)$ can be simply interpreted in the frame of the pseudospin model[3,4] (and its extension to the photon-photon coupling[5,6]) which is widely used in the theory of order-disorder ferroelectrics[7,8]

In the molecular field approximation[5-11] the Curie-Weiss temperature, associated with antiferroelectric instability of the proton subsystem (see Ref. 7), can be simply expressed in terms of the proton tunnelling energy (2Ω) and the Fourier transformed (taken at the edge of the Brilloin-zone, q_o) proton coupling constant (J_{q_o}),

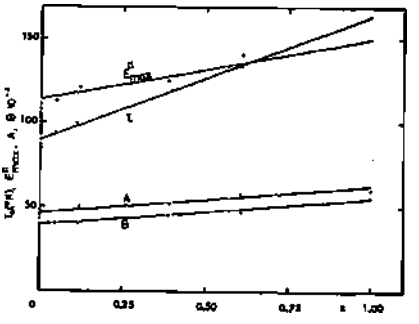

Fig. 1.

$$k_B T_o(x) = \frac{\Omega(x)}{\operatorname{arth}[2\Omega(x)/J_{q_o}(x)]} = \frac{J_{q_o}(x)}{2} \quad . \qquad (1)$$

Now taking as an appropriate approximation[4,9]

$$J_{q_o}(x) = J^{P}_{q_p}(1-x) + J^{As}_{qAs}x \quad , \qquad (2)$$

the indecies P and As being related to ADP and ADA, respectively, one easily reproduce

$$T_o(x) \simeq \frac{1}{2k_B}\left[J^{P}_{q_p}(1-x) + J^{As}_{q_{As}}x\right] \simeq T^{P}_{o} - (T^{As}_{o}-T^{P}_{o})x \quad , \qquad (3)$$

(where the observed Curie-Weiss temperatures were $T^{P}_{o}=91.86^{o}K$ and $T^{As}_{o}=164.96^{o}K$), while using simple derivations[6,10,11] one also finds

$$\varepsilon^{11}_{max}(x) \simeq A + \frac{B(x)}{\Delta} \quad , \qquad (4)$$

Here A is the static dielectric constant of the lattice and being already of small value is nearly independent of x; the Curie constant is defined by

$$B(x) = \frac{16\pi k_B N(2\mu)^2}{[2\Omega(x)]^2}\, b(x) \ , \qquad (5)$$

where

$$b(x) = \{T_o^P T_c^P + [T_o^P(T_c^{As}-T_c^P) + T_c^P(T_o^{As}-T_o^P)]x\} \ ; \qquad (6)$$

$T_c = T_o + \Delta T = J_{q_o}/2k_B$ is the critical temperature of the total (proton and heavy-ion) system but $J_{q_o} = J_{q_o} + J'_{q_o}$, J'_{q_o} being and indirect proton coupling constant through heavy-ion complecies); $\Delta T = J'_{q_o}/2k_B$, as estimated theoretically, should be about ~ 40^oK (see Refs. 6,10), while experimentally, it is found to be ~ 54^oK; $N = 10^{-21}$ is the total number of proton pseudo-dipole electric moments (μ) per unit volume, μ being of the order 10^{-18}esu.

For all antiferroelectrics considered

$$J_q = 2J[\cos(q_x - q_{x_o})a + \cos(q_y - q_{y_o})a + \cos(q_z - q_{z_o})a] \ , \qquad (7)$$

where a is an effective lattice constant of proton sites. As the assumption (2) actually holds for an arbitrary q, for a mixed antiferroelectric one obtains

$$a(x) = \frac{\pi + D(x)}{\bar{q}} \ ; \quad \bar{q} \neq 0, \ q_o(x), \qquad (8)$$

where

$$D(x) = \arccos\left[\frac{J_{\bar{q}}(x)}{J_{q_o}(x)}\right] \qquad (9)$$

and

$$q_o(x) = \frac{\pi\bar{q}}{\pi + D(x)} \qquad (10)$$

Having defined $J_{q_o}(x)$, $J'_{q_o}(x)$ as well as $T_o(x)$ and $T_c(x)$, we now have to find the effective tunnelling energy of the proton. It can be obtained from the Curie constant (Eq.(5)) which as measured varries with x from 4000^oK to $5650\ ^oK$.

$$2\Omega(x) = 4\mu\left[\frac{N\pi k_B b(x)}{B(x)}\right]^{1/2}$$

Finally, by a straightforward calculation on can predict the critical behaviour of the soft mode in the paraelectri phase of the solid ADA-ADP solution[8,12]:

$$\omega_q^2(x) = \lambda(x)\frac{T-T_c(x)}{T_c(x)} + \rho(x)\sum_{i=1}^{3}\left[q_i - q_{io}(x)\right]^2 ; \quad (12)$$

$$\lambda(x) = \frac{\Omega^2(x)}{k_B T_c(x)} , \qquad \rho(x) = \frac{2\Omega(x) J_{q_o}(x)}{6}$$

Concluding this paper it should be pointed out that in the present experimental analysis the solid ADA-ADPsolutions have manifested both features of order-disorder type and displacive type antiferroelectrics, whereas the phase transition at T_o has been assigned as one of the first order.

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