

Critical Behaviors Near the Antiferroelectric Phase Transition Temperature of NaNO_2

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This is a review of the experiments performed recently on the antiferroelectric phase transition of NaNO_2 by our group (K. Hamano, I. Hatta, T. Yamaguchi and K. Ema of Tokyo Institute of Technology, and M. Tanaka of the Institute for Solid State Physics, the University of Tokyo).

NaNO_2 undergoes a paraelectric-to-sinusoidal-antiferroelectric phase transition at about 165°C (T_N) followed by an antiferroelectric-to-ferroelectric phase transition at about 163.5°C (T_C). The former transition is of the second order. The dielectric constant shows a maximum around T_N . It has been considered that this maximum corresponds to T_N .

Recently careful measurements were carried out of the temperature dependence of the dielectric constant, ϵ_2 , in the vicinity of T_N . It was found that ϵ_2 versus temperature curve is remarkably asymmetric about T_N : ϵ_2 drops from its maximum more rapidly toward the low temperature side than toward the high temperature side. The simultaneous measurements of ϵ_2 and the specific heat, C_p , revealed that the maximum of ϵ_2 does occur, not at T_N , but at about 0.1°C above T_N , and that the slope of $\epsilon_2(T)$ becomes maximum at T_N . This temperature dependence of ϵ_2 around T_N is very similar to that of the magnetic susceptibility of an antiferromagnet around its Néel temperature. Perhaps this is the first observation of such a critical behavior of the dielectric constant in the vicinity of an antiferroelectric phase transition temperature.

Another aspect of the antiferroelectric phase transition in NaNO_2 should be noted here. It has been found that the specific heat at constant pressure, C_p , the thermal expansion coefficients, β_i ($i = 1, 2, 3$), and the isothermal elastic compliances, s_{ij}^T ($i, j = 1, 2, 3$), show divergence at T_N with the same critical exponents ($\alpha = 0.38$, $\hat{\alpha} = 0.18$).

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Such temperature dependences of C_p , β_i and s_{ij}^T can be understood phenomenologically by "Pippard's relations". The important result of the phenomenological theory is that the specific heat at constant volume, C_V , and the adiabatic elastic compliances, s_{ij}^S , remain finite through the phase transition. In fact s_{ij}^S 's have been found to show a finite cusp at T_N , and C_V calculated from the value of C_p using a thermodynamic relation appears to show a very small anomaly. These facts must be taken into account in constructing a microscopic theory of the antiferroelectric phase transition in NaNO_2 .

Anomalous temperature dependences of the electrostrictive constants, Q_{2i} ($i = 1, 2, 3$), and the interpretation of them in connection with the critical behavior of ϵ_2 will be mentioned also.

On Mechanism of Anomalous Polarization Reversal in NaNO_2

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Polarization reversal in NaNO_2 is carried out through rotation of NO_2 -radical. Such phenomena of ferroelectric polarization reversal caused by the rotation of radicals seem uncommon. In this paper attention is paid to the fact that there is the relation $a_c > a_b > a_a$ among the electronic polarizabilities of the NO_2 -radical, where they are given as $a_a = 2.336\text{\AA}^3$, $a_b = 3.128\text{\AA}^3$ and $a_c = 4.909\text{\AA}^3$ (Kinase, Ohi and Ishikawa: J. Phys. Soc. Japan 24 (1968) 431). It is noticed that the electronic polarizability of NO_2 in the direction of P_s becomes maximum by the 90° -rotation of NO_2 round the a-axis, which is caused by the relation $a_c > a_b$. The fact that dipole interaction becomes strong in the region near the point of the 90° -rotation of NO_2 round the a-axis is thought to make the polarization reversal easy. From this point of view the polarization reversal is explained in this paper by using a *complex Ising model* taking account