Critical Behaviors Near the Antiferroelectric Phase Transition Temperature of $NaNO_2$

Katsumi Hamano

Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro, Tokyo

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 (a = 0.38, $\acute{a}$ = 0.18).

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 $NaNO_2$

Wataru KINASE

Department of Physics, School of Science and Engineering, Waseda University, Nishiokubo, Shinjuku, Tokyo

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 $\alpha_c > \alpha_b > \alpha_a$ among the electronic polarizabilities of the NO_2-radical, where they are given as $\alpha_a = 2.336A^3$, $\alpha_b = 3.128A^3$ and $\alpha_c = 4.909A^3$ (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 $\alpha_c > \alpha_b$ 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