as nonstoichiometry and impurities (except maybe Cu) are nonmagnetic. While they modify drastically the residual ESR linewidth and resistivity they induce rather homogeneous changes in the magnetic behavior. In particular, our results suggest that the anomaly of M/H at high H is really due to a narrow detail of the band structure[8] which can be easily smoothed out by imperfections.

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Ferroelectric Phase Transition in Microcrystals

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The ferroelectric-paraelectric phase transformation in $NaNO_2$ microcrystals (size about 5 nm) has been investigated by differential thermal analysis. Single-domain particles exhibit spontaneous polarization irrespective of their microsize. The transformation temperature, T_c, of the interior of the particles remains unaffected by their dimension, whereas T_c of the surface monolayer is lowered by a few degrees.

PACS numbers: 77.30.+d, 77.80.Bh

The effect of a crystal's size on the temperature and/or type of a phase transition is of general interest as it illuminates the atomic interactions involved. Arguments based on energy considerations have been put forward proposing that the spontaneous polarization of isolated, freely suspended, ferroelectric crystals should cease below a certain crystal size.[1] Experimental tests of these ideas have been carried out by NMR studies of $NaNO_2$ crystals with sizes, d, ranging from 200 to 5000 nm.[2] Little effect on the phase transition has been observed. Clearly, the regime of crystal sizes well below 200 nm appears more promising for studies of size effects as surface effects become increasingly predominant. This Letter reports investigations of the phase transition of isolated $NaNO_2$ microcrystals with average sizes between 5 and 20 nm.

$NaNO_2$ has been selected because it is available in high-purity form and because of existing data from previous measurements. $NaNO_2$ undergoes a first-order ferroelectric-paraelectric phase transformation at $T_c = 165\,^\circ C$. This transformation is associated with a relatively large latent heat and can be readily detected by differential thermal analysis (DTA).

Small ($d \geqslant 5$ nm) particles of $NaNO_2$ were produced by several methods.

(1) Coprecipitation technique: An aqueous solution of about 0.5 wt.% $NaNO_2$ and 0.7 wt.% polyvinylalcohol (PVA) is splat quenched on a cold (77 K) Al plate. Subsequent freeze drying in high vacuum at 150 K leaves $NaNO_2$ microcrystals loosely suspended in a foamy PVA matrix.

(2) Noble-gas condensation technique: At about 400 °C, $NaNO_2$ is thermally evaporated into a low-pressure (20 to 100 Pa) He atmosphere where the excess kinetic energy of evaporated $NaNO_2$ is dissipated by collisions with He atoms. The condensing $NaNO_2$ particles are *in situ* embedded in silicon oil.

(3) Coevaporation technique: In a modified version of (2), $NaNO_2$ and a suitable metal (e.g., Cu) are evaporated from separate crucibles in a low-pressure He atmosphere and condense as a mixture of microcrystals onto a cooled Cu plate.

The size of the $NaNO_2$ microcrystals was determined by x-ray line broadening (Debye-Scherrer method) and by electron microscopy. The ferroelectric-paraelectric transformation was studied by DTA. Also, DTA provided a means of checking the stoichiometry of evaporated $NaNO_2$ by comparing the melting temperature with that of the bulk material (271 °C).

From the x-ray line broadening (Fig. 1) due to the microsize of the $NaNO_2$ crystals generated by the coprecipitation technique, an average crystal size of about 5 nm is obtained. The Debye-Scherrer diagram shown in Fig. 1 has been recorded after one DTA run of the $NaNO_2$-PVA specimen. The line broadening and, hence, the crystal sizes are found not to be affected by the heating cycle.

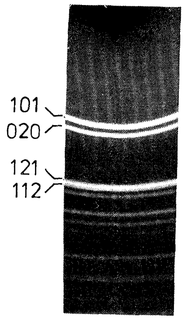

FIG. 1. X-ray line broadening due to microsize of $NaNO_2$ crystals embedded in PVA matrix by the coprecipitation technique.

Figure 2 compares DTA recordings of bulk $NaNO_2$ crystals and of 5-nm $NaNO_2$ microcrystals suspended in PVA. The two signals have identical peak temperatures but differ in width in the sense that the deviation of the DTA trace from the base line is shifted towards lower temperatures by about 10 °C for the microcrystalline $NaNO_2$.

The same result was found to be characteristic of any $NaNO_2$ microcrystals produced by the techniques listed above. "Recoarsening" the small crystals by adding water led again to a DTA signal identical to that of the bulk material.

By the observed phase transitions, the $NaNO_2$ microparticles prove to be spontaneously polarized up to $T_c = 165\,^\circ C$ irrespective of their size. As the 5-nm particles investigated are smaller than the known thickness of ferroelectric domain walls,[3] they must be regarded as polarized single-domain particles. This fact disagrees with the idea that single-domain particles undergo no spontaneous polarization in order to minimize their free energy.[1] The discrepancy may be associated with the screening of the electric stray

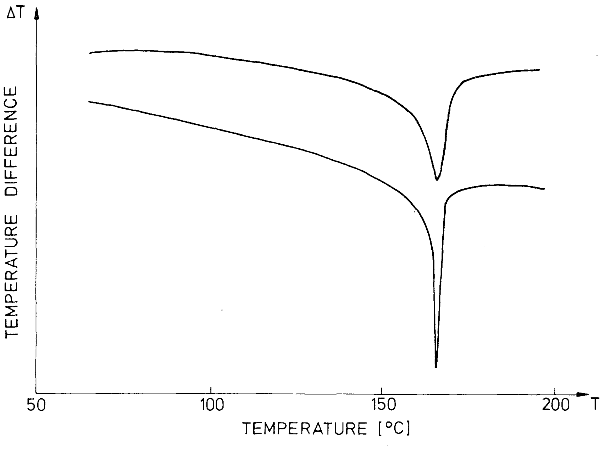

FIG. 2. Endothermal DTA signal of microcrystalline $NaNO_2$ in PVA matrix (upper curve) as compared to the signal of bulk $NaNO_2$ crystals. The temperature difference ΔT is given in arbitrary units. For better visibility, the curves have been displaced along the ΔT axis.

field by surface charges. If the experimental results are interpreted in terms of surface effects, the broadening if the DTA signal towards lower temperatures indicates a lower disordering temperature of the dipoles in the surface region as compared to the dipoles in the interior. The number of dipoles in the surface region may be taken from the area under the broadened shoulder of the endothermal signal. Provided the latent heat of disordering is identical to that of the bulk, the fraction of "surface dipoles" is estimated to be about 30% to 50%. This value coincides with the number of $NaNO_2$ molecules located at the free surface of a 5-nm crystal. In other words, surface effects are restricted to about one monolayer. There is little evidence for the existence of "dead layers"[2] at the surface and for particle-size effects on the disordering of the "volume dipoles" as concluded from the unshifted peak temperature.

The interpretation of the experimental data by analogy to superparamagnetism appears unlikely as it requires the "surface" and "volume" dipoles to disorder simultaneously. Simultaneous disorder of both types of dipoles implies an enhanced dipole coupling in the surface region[4] which appears implausible in view of the reduced coordination number. In addition, it would be hard to understand in terms of this model why the DTA peak is broadened but not shifted.

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Efficacious Form for Model Pseudopotentials

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A simple way has been discovered to put model pseudopotentials, $V(\vec{r}) = \sum_{lm} |Y_{lm}\rangle V_l(r) \times \langle Y_{lm}|$, into a form which reduces the number of integrals of $V(\vec{r})$ required for an energy-band calculation from $mn(n+1)/2$ to mn for each l in the sum (where n is the number of plane waves used in the expansion and m the number of points in the Brillouin zone at which the calculation is performed). The new form may be chosen to improve the accuracy of the pseudopotential when used in other chemical environments.

PACS numbers: 71.10.+x, 31.15.+q, 71.25.Cx

Pseudopotentials may be divided into three classes, of which one is empirical[1] and the other two are based on first prinicples. One of the first-principles pseudopotentials is obtained by adding some core functions ψ_c to the wave function ψ to obtain a smooth pseudo wave function,

$$|\varphi\rangle = |\psi\rangle + \sum_c \alpha_c |\psi_c\rangle, \tag{1}$$

and in its most general (non-Hermitian) form is [see Austin, Heine, and Sham[2] (AHS)]

$$V_{\mathrm{Ps}}{}^{\mathrm{AHS}} = V + \sum_c |\psi_c\rangle\langle F_c|, \tag{2}$$

where $F_c(\vec{r})$ is an arbitrary function. By substituting Eq. (1) into the Schrödinger equation, the relation

$$\alpha_c = \langle F_c|\varphi\rangle/(E - E_c) \tag{3}$$

is obtained. Zwicker[3] has shown that in general the AHS pseudopotential is nonvariational, i.e., first-order errors in a trial pseudofunction φ_t cause first-order errors of either sign in the energy E_t. The original Phillips-Kleinman (PK) pseudopotential[4,5]

$$V_{\mathrm{Ps}}{}^{\mathrm{PK}} = V + \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c| \tag{4}$$

has a nonunique φ because $\alpha_c{}^{\mathrm{PK}} = \langle\psi_c|\varphi\rangle$ makes $\varphi' = \varphi + \sum_c \beta_c \psi_c$ a solution of Eq. (1). Zwicker[3] was able to show that $V_{\mathrm{Ps}}{}^{\mathrm{PK}}$ is variational and

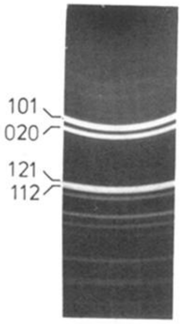

FIG. 1. X-ray line broadening due to microsize of $NaNO_2$ crystals embedded in PVA matrix by the coprecipitation technique.