Double nuclear magnetic resonance of point defects in $\beta$-PbF$_2$ + Na$^+$ single crystal

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The introduction of impurity ions into a crystal structure gives rise to the formation of point defects with a lowering of the symmetry of the crystal field below cubic both at the impurity ion site and at sites surrounding the impurity ion. Impurity or base-matrix nuclei with $I > 1/2$ will consequently experience static quadrupole interactions, and constitutes a probe characterizing the crystal chemistry of the resulting point defects.

The local state of the impurity and the associated point diamagnetic defects can be investigated down to concentrations of $\sim 2 \times 10^{-4}$ by the method of pulsed double nuclear magnetic resonance (DNMR),$^1$-4 It is important that DNMR permits the study of diamagnetic impurities in diamagnetic crystals. The indirect DNMR technique, in which the sparse nuclei are detected through their interaction with the base nuclei, the state of which is registered, has been noted in a number of papers (in Ref. 6 in particular) that the insertion of Na$^+$ or K$^+$ ions into the PbF$_2$ structure (space group $O_h$) that the insertion of Na$^+$ or K$^+$ ions into the PbF$_2$ structure (space group $O_h$) has been noted in a number of papers (in Ref. 6 in particular) that the insertion of Na$^+$ or K$^+$ ions into the PbF$_2$ structure (space group $O_h$).

The investigated crystal was grown by the Kyropoulos method with $\sim 0.1\%$ by weight of NaF added to the mix. The weak quadrupole interactions of $^{23}$Na nuclei were investigated by the DNMR technique. The quadrupole spectrum of the $^{23}$Na nuclei was registered with the aid of the $^{207}$Pb and $^{23}$Na for magnetic field orientation $B_0$ of the crystal. The measurements were made at $T = 77\, K$. The dipole–dipole reservoir was cooled by a Jeener pulse train at the 21.906 MHz frequency of the fluorine nuclei. The $^{23}$Na nuclear spin system was saturated by a high-frequency pulse with sinusoidal amplitude modulation at $\sim 1\, kHz$. The resultant dipole signal, the variation of which constitutes the DNMR signal, was registered in the intervals between the high-frequency pulses of duration $T_p = 45\, us$ using a multi-channel store based on an NTA-1024 analyzer, which carried out the preliminary processing of the signal with output of the results to a graph-plotted and a digital printer. The DNMR spectra were taken in the automatic-search and signal-record mode. The spin–lattice and dipole relaxation times at $77\, K$ where $T_{1L} = 3\, sec$ and $T_{1D} = 0.86\, sec$. The long spin–lattice relaxation time compared with the relaxation time of the dipole reservoir enabled the DNMR spectra to be recorded without using phase detection.

Figure 1 shows a sample of the recorded DNMR spectra of $^{23}$Na in the $\beta$-PbF$_2$ structure (space group $O_h$). A deficit of positive charge occurs at the site of the Na$^+$ ion, which can be compensated by an F$^-$ vacancy nearest the impurity ion. In this case, the $O_h$ symmetry of the positions of the Na nucleus is lowered to $C_{3v}$ with a distinct direction along the $[111]$ axis of the crystal. The reduction of the $O_h$ symmetry means that a non-zero static electric-field gradient will act on the $^{23}$Na nuclei. When the crystal is rotated along the axis $[011]$, the orientational dependence of the quadrupole splittings of the $^{23}$Na nuclei over the DNMR spectra for $C_{3v}$ positions in the first order of perturbation theory for the transition $-3/2$ $\rightarrow$ $-1/2$ is similar to that considered in Refs. 3, 8 and can be written in the form:

$$
\nu_1 = \nu_{+} + 3B_0^2 \cos^2 \theta \sin^2 \phi,
$$

$$
\nu_2 = \nu_{+} + 3B_0^2 \cos^2 \theta \sin^2 \phi,
$$

$$
\nu_3 = \nu_{+} - 3B_0^2 \cos^2 \theta \sin^2 \phi,
$$

where $B_0 = \frac{4 \pi Q Q_0}{4(21-1) + \nu h/6}$. The transition corresponding to Ref. 3 has double intensity.

Figure 2 shows a sample of the recorded DNMR spectra of $^{207}$Pb and $^{23}$Na for magnetic field orientation $B_0$ in $\beta$-PbF$_2$. The outermost lines in the $^{23}$Na spectrum correspond to positions $a$ (Fig. 3), while the sum of the contributions from positions $b$ and $c$ form the satellite about the central transition. The orientational dependence of the quadrupole splittings of the $^{23}$Na nuclei was taken at magnetic field orientations $B_0$ in $\beta$-PbF$_2$. The obtained experimental results are in complete agreement with the above model and are described by formulas (1), (2), and (3) for $B_0^2 = 48.8 \times 0.3\, kHz$. 

FIG. 1. Local environment of Na$^+$ ions in $\beta$-PbF$_2$. a, b, and c are three magnetically inequivalent positions of the impurity-vacancy dipole for motion of the crystal around the axis $[011]$. 

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The introduction of impurity atoms into a crystal structure is of great importance in searching for the formation of point defects with a lowering of the symmetry of the crystal field below cubic at the impurity ion site and at sites surrounding the impurity ion. Impurity or base-anion crystals with $\geq 1/2$ will consequently experience static quadrupole interactions, and constitute a probe characterizing the crystal chemistry of the resulting point defects.

The local state of the impurity and the associated point diamagnetic defects can be investigated down to concentrations of $\geq 10^{-6}$ by the method of pulsed double nuclear magnetic resonance (DNMR). It is important that DNMR permits the study of diamagnetic impurities in diamagnetic crystals. The indirect DSNM technique, in which the impurity nuclei are detected through their interaction with the base nucleus, the state of which is registered in the experiment, gives the greatest sensitivity (ca. $\sim 10^5$ spins/cm) and enables almost all nuclei possessing a magnetic moment to be investigated.

In the work reported here we studied a $\beta$-PbF$_2$ crystal by the DNMR technique. The $\beta$-PbF$_2$ crystal is a superionic conductor in which there is especial interest in view of the possibility of utilizing it as a solid electrolyte. It has a monoclinic crystal structure with space group $C2\overline{1}$. The introduction of Na$^+$ ions into the PbF$_2$ structure by the DNMR technique helps stabilize the $\beta$-phase of the crystal, in which the mobility of the F$^-$ ions is ten times greater. There is thus considerable practical interest in explaining the crystal-chemical features accompanying the introduction of Na$^+$ ions into the lattice of the PbF$_2$ crystal.

The investigated crystal was grown by the Kyropoulos method with $\geq 0.15$ weight of NaF added to the mix. The weak quadrupole interactions of Na$^+$ nuclei were investigated by the DNMR technique. The quadrupole spectrum of the $^{23}$Na nucleus was registered with the help of the inner nuclear magnetic resonance (INMR) signal. The outermost lines at $77^\circ K$ correspond to positions $a$ (Fig. 1), while the sum of the contributions from positions $b$ and $c$ forms the satellites about the central transition. The orientational dependence of the quadrupole splittings of the $^{23}$Na nuclei over the INMR spectra for $^{23}$Na positions in the first order of perturbation theory for the transition $3/2-1/2$ is similar to that considered in Refs. 3, 8 and can be written in the form

$$\Delta E = e^{2}Qq_{zz}/12(1 - \cos \theta) + \left(\frac{3}{2} + \frac{3}{2}\right)\Delta E_0.$$ 

The transition corresponding to Refs. 3, 8 has double intensity.

Investigation of the shift of the ferroelectric phase transition temperature in the PbSnTe crystal under the effect of external pressure has shown that this effect could be due to lattice anharmonicity.$^1$ In this work an explanation of the nonlinear pressure dependence of the phase transition temperature based on phenomenological theory is proposed.

The thermodynamic potential per unit mass of the ferroelectric is written in the form

$$\psi = -\frac{1}{2} \left(\frac{\partial T}{\partial P}\right)_H + P + f(p),$$

where $P$ is the pressure, $f(p)$ is the internal energy, $\psi$ is the critical temperature of the phase transition, $A$, $B$, and $C$ are coefficients, and $q$ is the external hydrostatic pressure.

Equation (1) differs from the thermodynamic potential usually used to describe first-order transitions in uniaxial ferroelectrics by the term $-\frac{1}{2}P\frac{\partial T}{\partial P}$ taken into account. We shall assume that $B + C = 0$ and $a, b, \text{ and } c k'G'(q) = 0$.

Using the equilibrium condition $\beta = 0$, we represent the initial thermodynamic potential (1) in the form of a series in powers of the polarization

$$\bar{\psi} = \bar{\psi}(q)(q)^{2}.$$