Electron paramagnetic resonance of Mn^{4+} in $PbTiO_3$

1995 J. Phys.: Condens. Matter 7 6327

(http://iopscience.iop.org/0953-8984/7/31/015)

J. Phys.: Condens. Matter 7 (1995) 6327–6333. Printed in the UK

Electron paramagnetic resonance of Mn^{4+} in $PbTiO_3$

D J Keeble†‖, Z Li‡ and E H Poindexter§

† Department of Physics, Michigan Technological University, Houghton, MI 49931, USA
‡ Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA
§ Physics Division, US Army Research Laboratory, Fort Monmouth, NJ 07703, USA

Received 14 March 1995

Abstract. The electron paramagnetic resonance spectrum of Mn^{4+} in single-crystal lead titanate has been studied at 9.8 and 33.8 GHz. An axial sextet with $g_{\perp}^{eff} = 3.7742(1)$ to $g_{\parallel}^{eff} \approx 2.00$ was measured at 9.8 GHz and with $g_{\perp}^{eff} = 2.7048(15)$ at 33.8 GHz; a second sextet was observed at high field at 9.8 GHz. The spectrum was fitted using spin Hamiltonian parameters $S = \frac{3}{2}$, $I = \frac{5}{2}$, $g_{\parallel} = 1.99$, $g_{\perp} = 1.987$, $A_{\parallel} = 79.46 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 71.05 \times 10^{-4}$ cm^{-1} and $|D| = 0.3166$ cm^{-1}. The electronic spin value and the magnitude of the hyperfine constant, $|A| = 73.9$ cm^{-1}, confirm the Mn^{4+} assignment. A superposition model analysis using available $\bar{b}_2(R)$ functions for $3d^3$ configuration ions in oxide hosts was unable to reproduce the observed axial crystal field magnitude, $|D|$.

1. Introduction

The ferroelectric perovskite lead titanate has been extensively studied because of the technological importance of the material [1]; however, due to earlier problems in high-quality single-crystal growth fewer spectroscopic studies have been completed than in related perovskite oxides. Recent work on the development of nonvolatile semiconductor memory and pyroelectric detector devices has intensified interest in $PbTiO_3$. An important aspect of materials engineering is the ability to control physical properties through doping, for instance $PbTiO_3$ ceramics doped with Mn have been shown to produce materials with high mechanical quality factors and low dielectric losses [2]. Electron paramagnetic resonance (EPR) spectroscopy can unambiguously determine the configuration of an incorporated paramagnetic ion and yield information on the local site. At room temperature $PbTiO_3$ is tetragonal with $c = 415.2$ pm and $a = 390.4$ pm; the Ti ion is displaced with respect to the centre of the oxygen octahedron by 30 pm along [001] while the Pb ion is displaced 47 pm from the corner site with respect to the oxygen octahedron in the same direction [3].

Here room-temperature 9 and 35 GHz band EPR measurements of Mn^{4+} in $P4mm$ phase $PbTiO_3$ single crystals are reported. Computer simulations [4] of the spectra by exact diagonalization of the spin Hamiltonian

$$H = \beta \boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{A} \cdot \boldsymbol{I} + \boldsymbol{B} \cdot \boldsymbol{g}_n \cdot \boldsymbol{I}$$

have been performed. An alternative form for the second-order fine-structure term $\boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S}$ is $H_F = \sum_{m-2}^{M+2} b_2^m O_2^m$ where b_2^m are constants and O_2^m are normalized spin

---

‖ Permanent address: Department of Applied Physics and Electronic and Mechanical Engineering, University of Dundee, Dundee DD1 4HN, UK.

0953-8984/95/316327+07$19.50 © 1995 IOP Publishing Ltd

operators and can be transformed to axes where only O_2^0 and O_2^2 are non-zero yielding $H_F = b_2^0[S_z^2 - \frac{1}{3}S(S+1)] + \frac{1}{3}b_2^2(S_x^2 - S_y^2)$. Hence $b_2^0 \equiv \frac{3}{2}D_z$ and $b_2^2 \equiv \frac{3}{2}(D_x - D_y)$ and for tetragonal symmetry $b_2^0 \equiv D = \frac{3}{2}D_z$ is the only non-zero fine-structure or crystal field term.

The first study of $PbTiO_3$:Mn was performed by Ikushima and Hayakawa [5] and identified the spectrum of Mn^{2+}. The values of the spin Hamiltonian parameters reported for the tetragonal phase were $g_\perp = 2.084(2)$ with a hyperfine constant $A_\perp = -82.0(1.5) \times 10^{-4}$ cm^{-1} and an axial crystal field splitting $D = 502(4) \times 10^{-4}$ cm^{-1}. The Newman superposition model [6] was subsequently used to model the observed crystal field splitting from which it was concluded that the Mn^{2+} substituted for Ti^{4+} at a position intermediate between the Ti site displaced from the centre of the oxygen octahedron and the centred site [7]. A sextet spectrum with $g_\perp^{eff} \approx 4$ was first reported by Hennings and Pomplun [8] in Mn-doped ceramic tetragonal lead titanate and assigned to Mn^{4+} based on the magnitude of the hyperfine constant, $|A| = 74(1) \times 10^{-4}$ cm^{-1}. A further study of Mn-doped $PbTiO_3$ ceramic was completed by Windsch *et al* [9] and reported a resolved sextet at $g_\perp^{eff} \approx 4$ and two partially resolved sectets at higher field from which the spin Hamiltonian parameters $g = 1.987(2)$, $|A| = 72.0(1.5) \times 10^{-4}$ cm^{-1}, and axial crystal field splitting $|D| = 0.318(3)$ cm^{-1} were obtained. Superposition model analysis was also performed utilizing a power law form for the metal ion ligand function $\bar{b}_2(R)$ from which it was deduced that the Mn^{4+} ion was displaced 30 pm along [001] with respect to the oxygen octahedron, i.e. at the Ti site, the exact form of the function used was not given [9]. More recently Molak and Wöjcik [10] have reported 9 GHz band EPR experiments on a number of $PbTiO_3$:Mn single crystals; centres assigned to Mn^{2+} and to Mn^{4+} were observed. A sextet spectrum with $g_\parallel^{eff} = 2.01$, $g_\perp^{eff} = 4.79$, $A_\perp = 78.2 \times 10^{-4}$ cm^{-1} was assigned to Mn^{2+} while a similar spectrum with $g_\parallel^{eff} = 2.01$, $g_\perp^{eff} = 3.75$, $A_\parallel = 72.2 \times 10^{-4}$ cm^{-1}, $A_\perp = 69.7 \times 10^{-4}$ cm^{-1} was assigned to Mn^{4+}; variations in these parameters were found between different crystals. Following this work Klotzsche *et al* [11] have performed a 9 GHz band study on $PbTiO_3$:Mn single crystals and the spin Hamiltonian parameters $g = 1.983(2)$, $|A| = 72(1) \times 10^{-4}$ cm^{-1} and $|D| = 0.3045(15)$ cm^{-1} were obtained at room temperature.

Detailed EPR studies of manganese ion doping of related perovskite titanates $SrTiO_3$ and $BaTiO_3$ have been reported [5, 12–16]. In $SrTiO_3$ Mn^{4+} was identified in both the room-temperature cubic and low-temperature tetragonal phase and was determined to be substitute for Ti [15]. A study [16] of successive reduction of $SrTiO_3$:Mn cubic phase crystals identified three Mn-related centres assigned to Mn^{2+}, Mn^{2+}–V_O and Mn^{3+}–V_O. For $BaTiO_3$ Mn^{4+} has been observed only in the rhombohedral low-temperature ferroelectric phase [14]. From application of the superposition model it was concluded that the Mn^{4+} substituted for Ti^{4+} at the Ti site displaced from the centre of the oxygen octahedron. The absence of the Mn^{4+} spectrum from higher-temperature phases has been assigned to rapid reorientation yielding information on the character of the order–disorder $BaTiO_3$ phase transitions [14, 17]. Study of Cr^{3+}, isoelectronic with Mn^{4+}, in the three ferroelectric phases of $BaTiO_3$ has shown that Cr^{3+} substitutes for Ti^{4+} at the centre of the oxygen octahedron [18] in contrast to the Mn^{4+} case. The centred site is favoured as Cr^{3+} has one less positive charge than the Ti^{4+} it replaces and hence experiences a repulsion from the negatively charged oxygen ligands [14, 19]. The EPR of Mn^{2+} in tetragonal and cubic phase $BaTiO_3$ has been reported [5, 12, 13]; application of the superposition model showed Mn^{2+} substituted for Ti^{4+} at a site displaced from the centre of the oxygen octahedron toward the Ti site position, similar to Mn^{2+} in $PbTiO_3$ [7].

2. Experimental details

The polydomain $PbTiO_3$ single crystals used in this study were grown by a modified flux method detailed elsewhere [20]; none of them were intentionally doped with Mn. The crystals were light-yellow rectangular plates with [001] perpendicular to the major face. Electron paramagnetic resonance measurements were made with a Bruker ESP300 spectrometer. The 9 GHz band measurements were made with a cylindrical cavity and a rotating magnet while 35 GHz band measurements also used a cylindrical cavity but angular-dependent data required rotation of the sample. The microwave frequency was measured using an EIP 588 frequency meter and the magnetic field sweep calibrated at the sample position using a Micro-Now 515B NMR magnetometer.

3. Results and discussion

A sextet spectrum with a hyperfine constant typical of ^{55}Mn was observed from two of the crystals studied, ANL02PT and ANL03PT; the spectra presented were recorded from ANL03PT. Two sextets were observed for 9 GHz band measurements with the applied field B_0 perpendicular to [001] ($\theta = 90°$), one centred at 185 mT (see figure 1) and the second at 660 mT (see figure 2). The $g_{\perp eff}$ for the low-field group was found to be 3.7742(1); the variation of the line position with the angle θ between [001] and the applied field B_0 is shown in figure 3. The spectrum could not be resolved for $\theta < 30°$. The high-field sextet was located on the shoulder of a more intense transition which precluded study of the angular dependence. The 35 GHz band spectrum for $\theta \approx 90°$ is shown in figure 4 and yields $g_{\perp eff} = 2.7048(15)$. The experimental spectra were simulated [4] using the spin Hamiltonian parameters $g_{\parallel} = 1.99$, $g_{\perp} = 1.987$, $A_{\parallel} = 79.46 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 71.05 \times 10^{-4}$ cm^{-1} and $|D| = 0.3166$ cm^{-1}. The energy level diagram for B_0 perpendicular to [001] is shown in figure 5. The resulting simulations are shown in figures 1 to 4.

The observed angular dependence of the low-field hyperfine sextet is in agreement with that observed by Molak and Wöjcik [10]. Simulation of the observed spectra using $S = \frac{3}{2}$ resulted in close agreement allowing assignment of the Mn centre to Mn^{4+}. The magnitude observed for the hyperfine constant $A_{\perp}$, 71×10^{4} cm^{-1}, is less than that reported [5] for $PbTiO_3$:Mn^{2+}, 82×10^{4} cm^{-1}, consistent with this assignment. The axial crystal field splitting $|D| = 0.3166$ cm^{-1} obtained here is similar to that observed in ceramic and single-crystal $PbTiO_3$ by other workers [9, 11].

The Newman linear superposition model [6, 21] has been applied with considerable success to the determination of the local position of substituted transition metal ions in perovskite titanates [7, 14, 18]. The model assumes the spin Hamiltonian parameters may be calculated from a linear superposition of single ligand contributions of the form

$$b_n^m = \sum_i \bar{b}_n(R_i) K_n^m(\theta_i, \varphi_i)$$

where $K_n^m(\theta_i, \varphi_i)$ are spherical harmonic functions of rank n of the polar angles, e.g. $K_2^0(\theta) = \frac{1}{2}(3\cos^2\theta - 1)$. The $\bar{b}_2(R)$ are functions of the radial metal–ligand distance R and are intrinsic parameters dependent on the nature of the paramagnetic ion and on the ligand type. The form of $\bar{b}_2(R)$ can be expressed as a Lennard-Jones- (LJ-) type function

$$\bar{b}_2(R) = -A\left(\frac{R_0}{R}\right)^n + B\left(\frac{R_0}{R}\right)^m$$

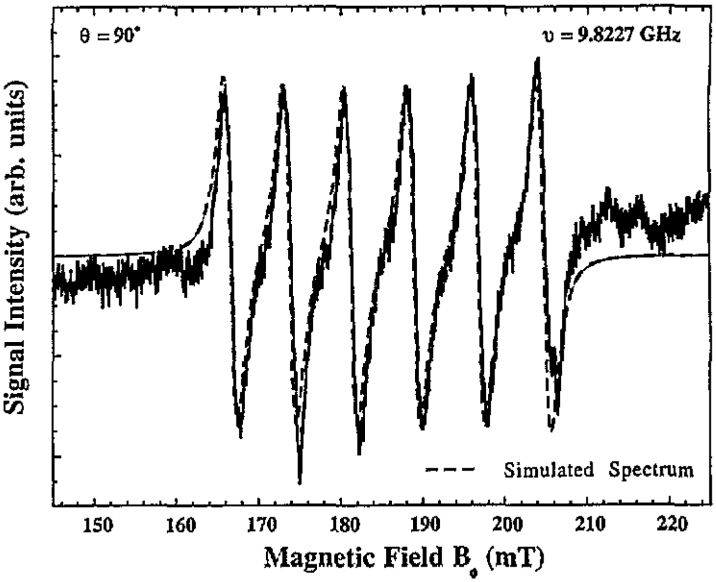

Figure 1. The room-temperature 9 GHz band experimental EPR spectrum for B_0 perpendicular to [001] and the simulated spectrum showing the low-field sextet.

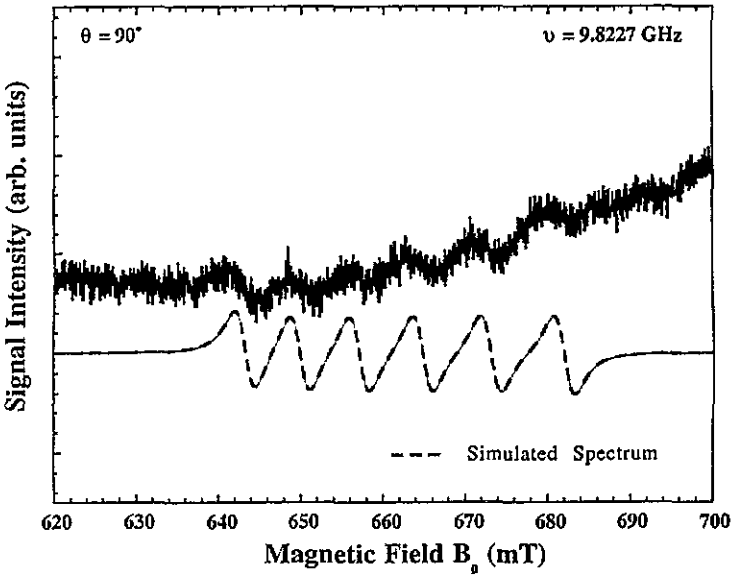

Figure 2. The room-temperature 9 GHz band experimental EPR spectrum for B_0 perpendicular to [001] and the simulated spectrum showing the high-field sextet.

which has been shown to be applicable to Cr^{3+} in $SrTiO_3$ and to Mn^{4+} in $SrTiO_3$ based on experimental unaxial stress EPR experiments [14, 22]. The function is obtained, in part, by matching the value and derivative to those obtained from the experimental strain coupling parameters, G_{11} and G_{22}. Over a more limited range of R a power law expression of the

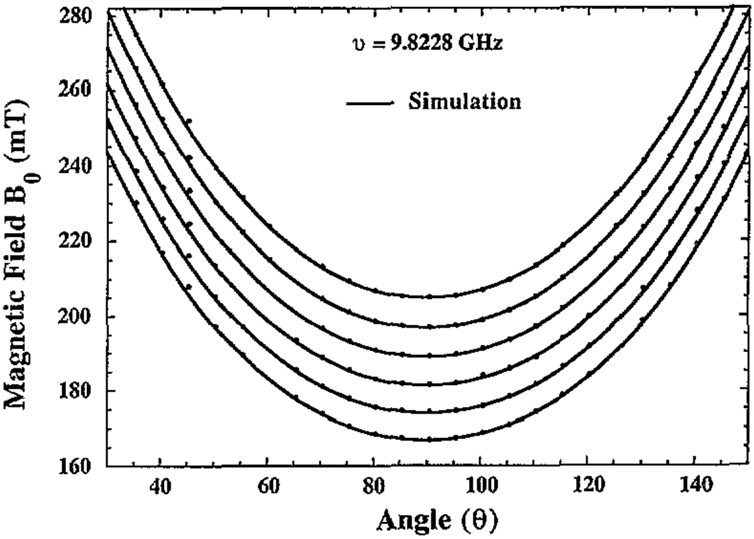

Figure 3. Experimental and simulated line positions for the low-field sextet as a function of angle, θ, between the applied magnetic field B_0 and [001].

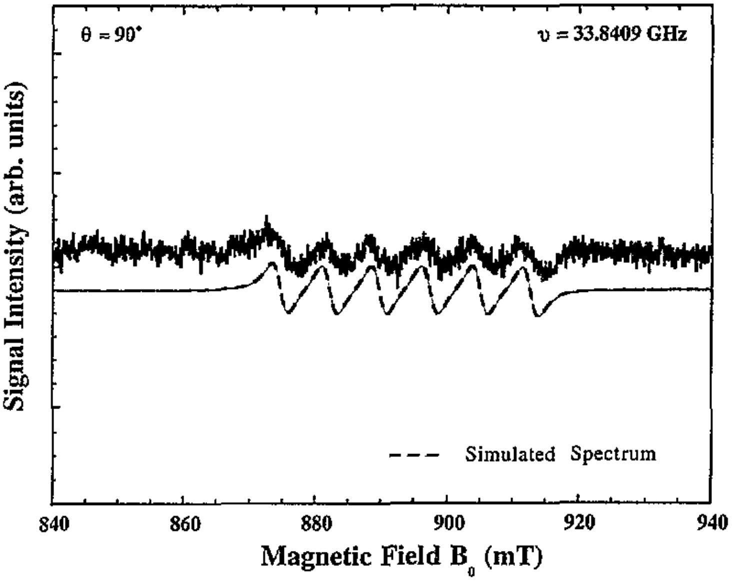

Figure 4. The room-temperature 35 GHz band experimental EPR spectrum for B_0 perpendicular to [001] and the simulated spectrum.

form

$$\bar{b}_2(R) = \bar{b}_2(R_0)\left(\frac{R_0}{R}\right)^{t_2}$$

may be applicable where $t_2\bar{b}_2 = -\frac{3}{4}G_{11}$ and $\bar{b}_2 = \frac{1}{2}G_{22}$. The LJ form of $\bar{b}_2(R)$ for

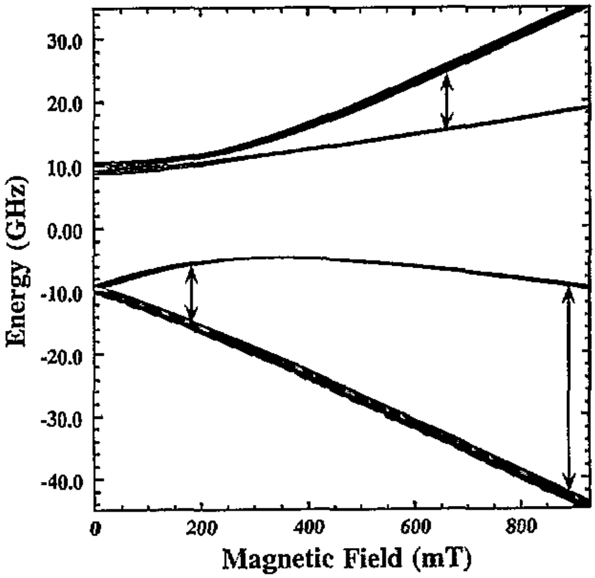

Figure 5. The calculated energy level diagram for B_0 perpendicular to [001] showing observed 9.5 and 33.8 GHz band transitions.

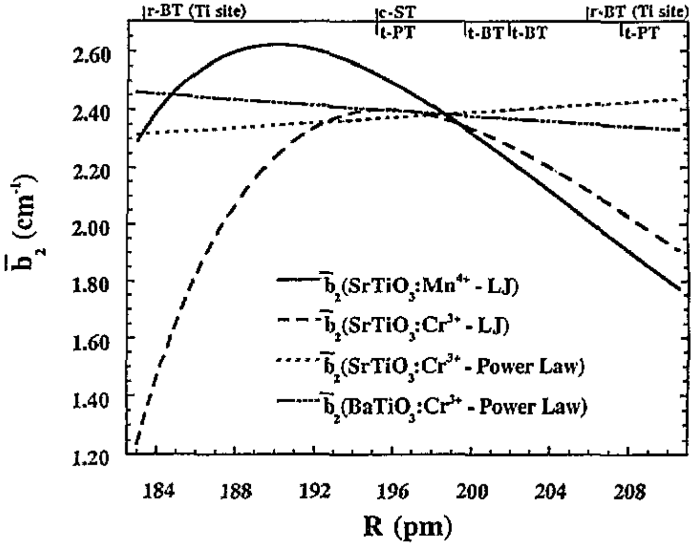

Figure 6. Superposition model functions $\bar{b}_2(R)$ for $SrTiO_3:Mn^{4+}$ [14] and $SrTiO_3:Cr^{3+}$ [22] in Lennard-Jones form and power law functions for $SrTiO_3:Cr^{3+}$ [22] and $BaTiO_3:Cr^{3+}$ [18]. The characteristic lengths for cubic (c) $SrTiO_3$ (ST), tetragonal (t) $BaTiO_3$ (BT) and $PbTiO_3$ (PT) and rhombohedral (r) $BaTiO_3$ are also shown.

$SrTiO_3:Mn^{4+}$ [14] and $SrTiO_3:Cr^{3+}$ [22] is shown in figure 6 along with the power law function for the latter [22]. The parameters for $SrTiO_3:Mn^{4+}$ are $A = -11.1$ cm^{-1}, $B = -8.48$ cm^{-1}, $R_0 = 190.5$ pm, $n = 10$ and $m = 13$. These values were used along with available crystallographic data [3] for $PbTiO_3$ to calculate Mn^{4+} b_2^0 values. The experimental magnitude was not reproduced for any position along [001] from the centred site to the Ti site. The minimum magnitude was found for the position halfway between the two sites where $b_2^0 = -1.1$ cm^{-1}. The studies of Mn^{4+} in perovskite titanates show that substitution for Ti takes place [14]. The neutral charge state of Mn^{4+} with respect to the lattice would be expected to favour the off-centre Ti site specifically [19].

4. Conclusions

The electron paramagnetic resonance spectrum of Mn^{4+} in single-crystal $PbTiO_3$ has been identified and shown to be consistent with the spin Hamiltonian parameters $g_\parallel = 1.99$, $g_\perp = 1.987$, $A_\parallel = 79.46 \times 10^{-4}$ cm^{-1}, $A_\perp = 71.05 \times 10^{-4}$ cm^{-1} and $|D| = 0.3166$ cm^{-1}. These values are in agreement with previous studies [9, 11]. The available superposition model functions $\bar{b}_2(R)$ for $3d^3$ ions in oxide hosts were found not to be sufficiently accurate to reproduce the observed crystal field magnitude for $PbTiO_3$:Mn^{4+}.

References

[1] Xu Y 1991 *Ferroelectric Materials and Their Applications* (New York: North-Holland)
[2] Ikegami S, Ueda I and Nagata T 1971 *J. Acoust. Soc. Am.* **5** 1060
[3] Shirane G, Pepinsky R and Frazer B C 1956 *Acta Crystallogr.* **9** 131
[4] McGavin D G, Mombourquette M J and Weil J A 1993 *Computer Program EPR* (Department of Chemistry, University of Saskatchewan, Canada)
[5] Ikushima H and Hayakawa S 1969 *J. Phys. Soc. Japan* **27** 414
[6] Newman D J and Siegel E 1976 *J. Phys. C: Solid State Phys.* **9** 4285
[7] Siegel E and Muller K A 1979 *Phys. Rev.* B **20** 3587
[8] Hennings D and Pomplun H 1974 *J. Am. Ceram. Soc.* **57** 527
[9] Windsch W, Chien T Q and Milsch B 1988 *Ferroelectrics* **80** 51
[10] Molak A and Wöjcik K 1992 *Ferroelectrics* **125** 349
[11] Klotzsche G, Windsch W and Wöjcik W 1993 *Ferroelectri. Lett.* **15** 115
[12] Odehnal M 1963 *Czech. J. Phys.* B **13** 566
[13] Ikushima H 1966 *J. Phys. Soc. Japan* **21** 1866
[14] Muller K A, Berlinger W, Blazey K W and Albers J 1987 *Solid State Commun.* **61** 21
[15] Muller K A 1959 *Phys. Rev. Lett.* **2** 341
[16] Serway R A, Berlinger W, Muller K A and Collins R W 1977 *Phys. Rev.* B **16** 4761
[17] Muller K A 1986 *Helv. Phys. Acta* **59** 874
[18] Muller K A, Berlinger W and Albers J 1986 *Phys. Rev.* B **32** 5837
[19] Sangester M J L 1981 *J. Phys. C: Solid State Phys.* **14** 2889
[20] Li Z, Grimsditch M, Xu X and Chan S-K 1993 *Ferroelectrics* **141** 313
[21] Yeung Y Y and Newman D J 1986 *Phys. Rev.* B **34** 2258
[22] Muller K A and Berlinger W 1983 *J. Phys. C: Solid State Phys.* **16** 6861