^{81}Br and ^{127}I NQR and Phase Transitions in $CH_3NH_3HgBr_3$ and $CH_3NH_3HgI_3$ *

Hiromitsu Terao

Faculty of Integrated Arts and Sciences, Tokushima University, Minamijosanjima-cho,
Tokushima 770, Japan

Tsutomu Okuda

Department of Chemistry, Faculty of Science, Hiroshima University, Naka-ku,
Hiroshima 730, Japan

Z. Naturforsch. **45a**, 343–348 (1990); received August 26, 1989; in revised form November 15, 1989

The ^{81}Br and ^{127}I NQR spectra were recorded in $CH_3NH_3HgBr_3$ and $CH_3NH_3HgI_3$, respectively. In addition to a phase transition at 338 K, successive phase transitions take place at 127 ± 1, 184 ± 1, and 243 ± 5 K in $CH_3NH_3HgBr_3$. On heating, the resonance lines of $CH_3NH_3HgI_3$ disappear near a phase transition at 328 K and one line appears above this temperature. The temperature variations of the resonance frequencies of the terminal halogen atoms in both crystals are extraordinarily steep. This indicates the large amplitude molecular motions expected for the $CH_3NH_3^+$ cations which are linked to the terminal halogen atoms through $N-H \cdots X$ type H-bonding.

Introduction

Much information has recently been collected on the ferro- to paraelectric phase transition (at 335 K) in $CH_3NH_3HgCl_3$ [1–10]. A ^{35}Cl NQR study has further revealed that this crystal undergoes another phase transition in the range 108–121 K [7] which is closely related to the motion of $CH_3NH_3^+$ under the influence of $N-N \cdots Cl$ H-bonding.

$CH_3NH_3HgBr_3$ crystals have orthorhombic symmetry at room temperature with space group *CmCm* [11]. The environment of mercury is trigonal bipyramidal (Figure 1). Two chemically nonequivalent Br atoms exist in the unit cell. The terminal Br(1) atoms occupy two of three equatorial positions of a bipyramid. The (T-shaped bonding) bridging Br(2) atoms occupy the remaining equatorial position and also both apexes as axial ligands. Thus adjacent bipyramids share an edge and the bipyramids form double chains parallel to the *c*-axis. The equatorial Hg–Br distances (2.527 and 2.565 Å) are longer than the axial Hg–Br distances (3.192 Å). $CH_3NH_3HgI_3$ forms monoclinic crystals at room temperature belonging to the space group $P2_1/n$ with chains of corner sharing distorted tetrahedra (Fig. 2) [11]. Three chemically nonequivalent I atoms exist in the unit cell. Two terminal I atoms are linked to the Hg atom with the distances 2.708 Å for I (1) and 2.738 Å for I (2). The bridging atom I (3) is linked rather asymmetrically to two Hg atoms with the distances 2.777 and 2.976 Å. $CH_3NH_3HgBr_3$ undergoes a phase transition at 338 K which is not reproducible on cooling, while $CH_3NH_3HgI_3$ undergoes a reversible phase transition at 328 K [11]. Though the space groups exclude ferroelectricity for these crystals, the observed phase transition of $CH_3NH_3HgCl_3$ may be of ferro- to paraelectric nature. In this work we have observed ^{81}Br and ^{127}I NQR in order to investigate the chemical bondings and phase transitions in $CH_3NH_3HgBr_3$ and $CH_3NH_3HgI_3$, respectively.

Experimental

$CH_3NH_3HgX_3$ (X = Br, I) samples were prepared from the equivalent amounts of CH_3NH_3X and HgX_2 dissolved in methanol [11]. The C, H, and N elemental analyses were consistent with the stoichiometry of the compounds.

The ^{81}Br and ^{127}I NQR spectra were observed on superregenerative spectrometers with frequency modulation. The accuracy of measured frequencies was within ± 0.02 MHz and the measured temperatures was within ± 1 K.

---

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

Reprint requests to Dr. Hiromitsu Terao, Faculty of Integrated Arts and Sciences, Tokushima University, Minamijosanjima-cho, Tokushima 770, Japan.

0932-0784 / 90 / 0300-0343 $ 01.30/0. – Please order a reprint rather than making your own copy

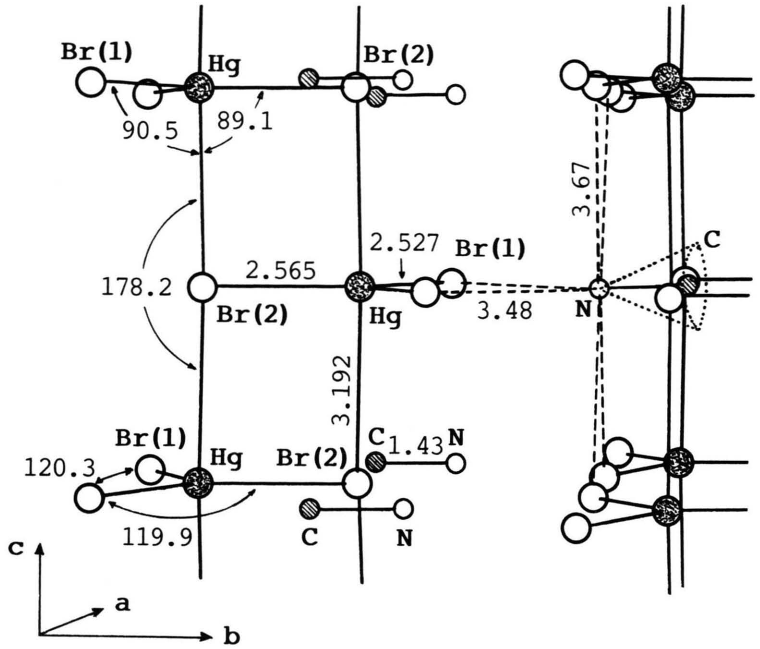


Fig. 1. The local environment of the Br atoms in the $CH_3NH_3HgBr_3$ crystal at room temperature (from [11]). A postulated cone on which the $CH_3NH_3^+$ group moves is schematically depicted by the dotted lines.

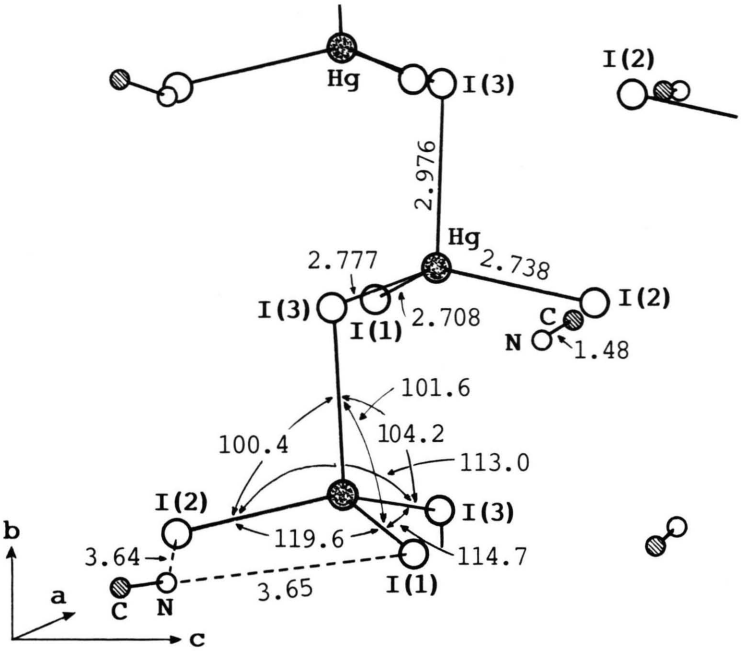


Fig. 2. The local environment of the I atoms in the $CH_3NH_3HgI_3$ crystal at room temperature (from [11]).

Results and Discussion

(A) ^{81}*Br NQR in* $CH_3NH_3HgBr_3$

The temperature dependence of the ^{81}Br NQR frequencies in $CH_3NH_3HgBr_3$ is shown in Fig. 3 and some frequencies are listed in Table 1. The phase transition at 338 K has already been reported. The newly found transition temperatures are 127±1, 184±1, and 243±5 K. At least four phases (I, II, III and IV) therefore exist between 77 and 338 K. In the room

Table 1. ^{81}Br NQR frequencies (ν) in $CH_3NH_3HgBr_3$.

T/K	ν/MHz				
77	111.05		98.37		91.04
298		101.75		87.05	

Table 2. ^{127}I NQR frequencies (ν), quadrupole coupling constants ($e^2 q_{zz} Q h^{-1}$), and asymmetry parameters (η) in $CH_3NH_3HgI_3$.

T/K	ν/MHz		$e^2 q_{zz} Q h^{-1}$/ MHz	η
	$\Delta m = 1/2-3/2$	$\Delta m = 3/2-5/2$		
77	184.78	–	–	–
	138.28	262.40	882.0	0.206
	116.04	224.57	752.5	0.161
298	159.35	–	–	–
	127.24	250.92	838.3	0.105
	117.55	233.98	780.5	0.061

temperature phase IV two resonance lines exist in accordance with the crystal stucture. The more intense high-frequency line 1 (IV) is assigned to the terminal Br (1) and the low-frequency line 2 (IV) to the bridging Br (2). In I three lines exist. The line 3 (I) is somewhat broad and its intensity is about half that of the lines 1 (I) and 2 (I). On raising the temperature from 77 K, these lines suddenly disappeared at 127 K and the six new lines 1 (II) to 6 (II) immediately appeared. 1 (II) and 2 (II) are symmetrically frequency-shifted up and down, respectively, from 1 (I). Their intensities are half that of 1 (I). This shows that 1 (I) splits into 1 (II) and 2 (II). Similarly 2 (I) splits into 3 (II) and 4 (II), and 3 (I) splits into 5 (II) and 6 (II). On further raising the temperature, the six lines suddenly disappeared at 184 K and the three new lines 1 (III), 2 (III), and 3 (III) immediately appeared. Evidently the respective pairs formed at 127 K again coalesced. As the temperature is further raised, 1 (III) and 2 (III) approach each other and become unobservable near 243 K. Above this temperature 1 (III) and 2 (III) may coalesce into 1 (IV). On the other hand, 3 (III) exhibits no detectable change at this temperature and becomes 2 (IV). On further raising the temperature both 1 (IV) and 2 (IV) broaden, and their intensities diminished remarkably from ca. 320 K. The sample heated above $T_c = 338$ K did not show lines even on cooling.

(B) ^{127}I NQR in $CH_3NH_3HgI_3$

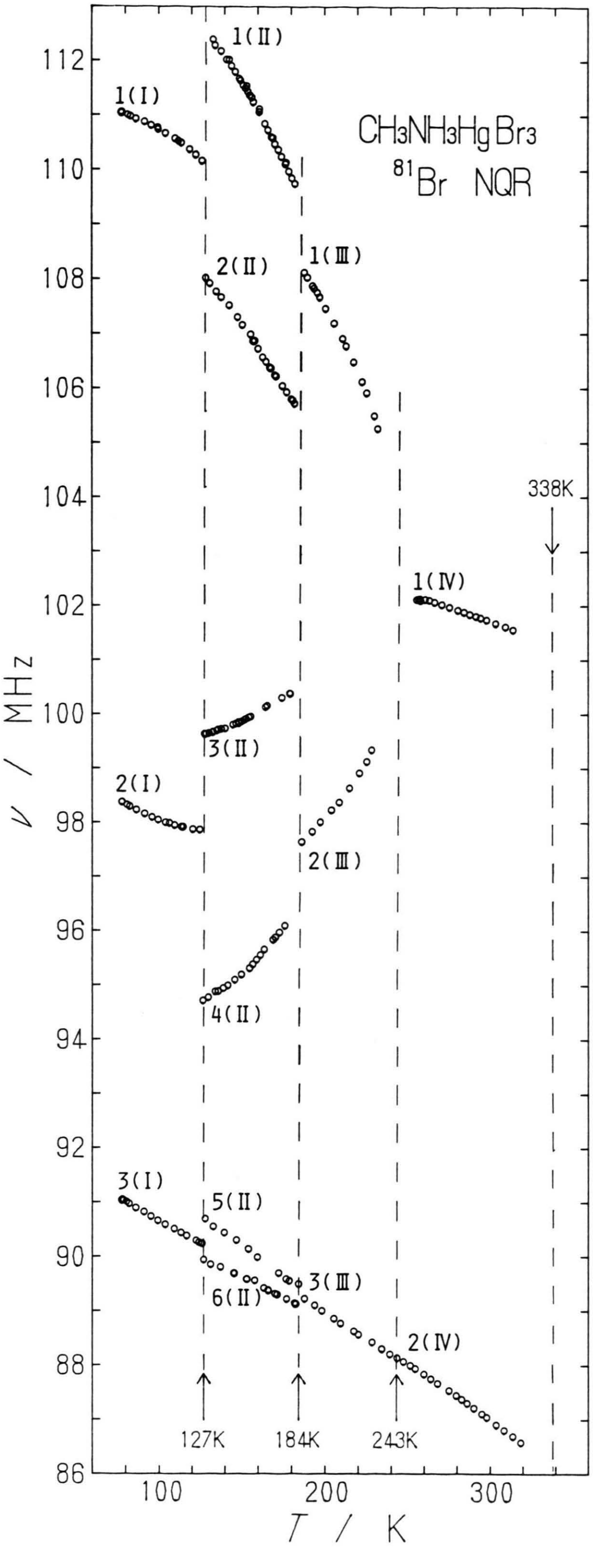
The ^{127}I NQR frequencies at 77 and 298 K are listed in Table 2. Five resonance lines were observed at both temperatures. The crystal structure indicates three nonequivalent I atoms. Therefore one line must be missing. The temperature dependence of the three low-frequency lines is shown in Figure 4. The high-frequency line 1 has an extraordinarily steep temperature dependence. The middle-frequency line 2 also has a steep temperature dependence, though not as steep as 1. The low-frequency line 3 shows a minimum frequency around 160 K and an increase with increasing temperature until 328 K. The intensity of 1 is more than five times smaller than that of 2 and 3, probably due to its abnormal temperature coefficient.

In spite of our extensive search of the missing resonance line, no other signal was observed. Our spectrometers are highly sensitive in the low-frequency region (< 200 MHz) compared to the high-frequency region. Therefore the missed line may exist at probably > 270 MHz. Thus the three lines in Fig. 4 were assigned to the $\Delta m = \pm 1/2 - \pm 3/2$ transitions as shown in Table 2, and the remaining two lines to the $\Delta m = \pm 3/2 - \pm 5/2$ transitions and paired up with the lines due to the $\Delta m = \pm 1/2 - \pm 3/2$ transitions by considering their signal-to-noise ratios and also the temperature dependences. The obtained quadrupole coupling constants ($e^2 q_{zz} Q/h$) and asymmetry parameters (η) are also listed in Table 2. Further we assign the line 3 to the bridging I (3) atoms considering that this line has the lowest frequency and a different temperature coefficient from 1 and 2.

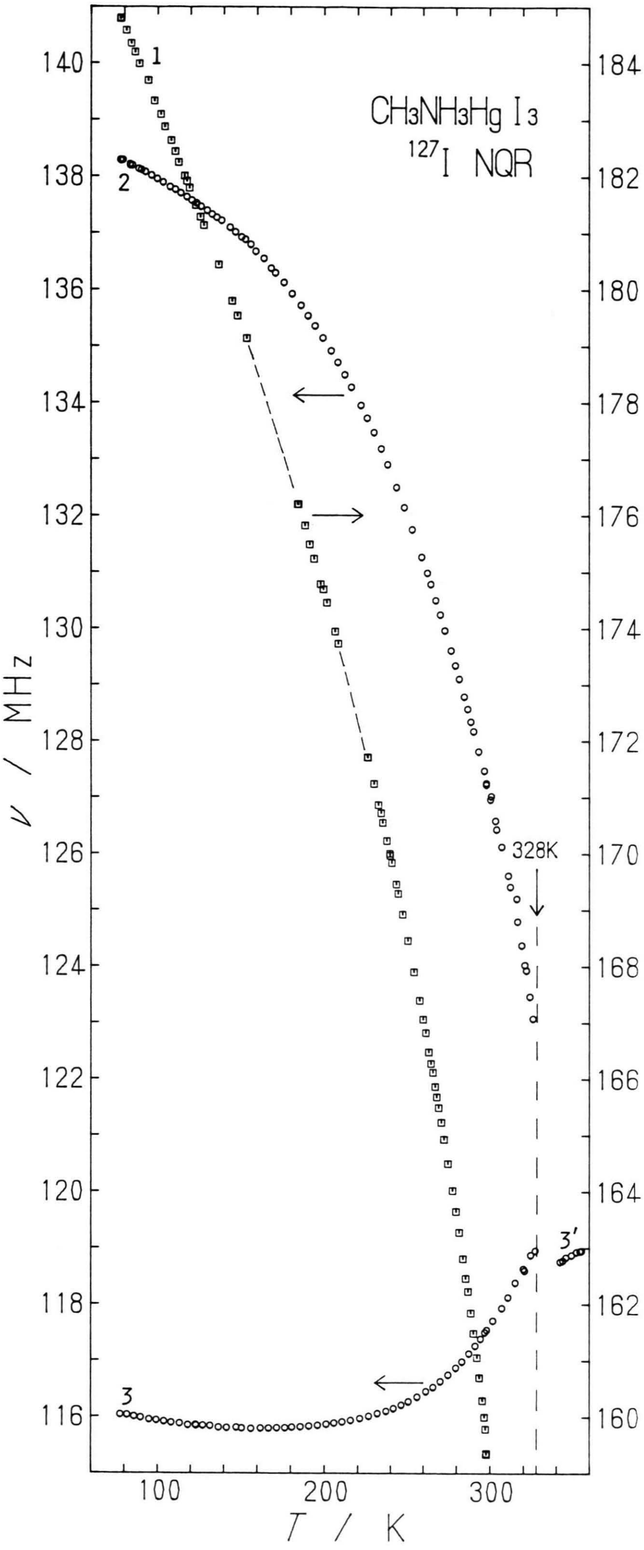
On heating, all three resonance lines exhibited line-broadening and disappeared near $T_c = 328$ K (1 was practically unobservable from ca. 300 K). After keeping the sample temperature about 20 K above T_c for a while, a new one line 3′ was observed (118.95 MHz at 353 K). This line become gradually more intense, exhibiting a positive temperature coefficient. No other line was detected until 355 K. The line 3′ is broad and may possibly be assigned to the bridging I atoms.

(C) Phase transitions in $CH_3NH_3HgBr_3$ and $CH_3NH_3HgI_3$

The X-ray measurement on $CH_3NH_3HgCl_3$ [6] shows that the $CH_3NH_3^+$ cations are almost completely disordered in the paraelectric phase, while or-


CH3NH3HgBr3
81Br NQR
1(I)
1(II)
2(II)
1(III)
1(IV)
3(II)
2(I)
2(III)
4(II)
3(I)
5(II)
6(II)
3(III)
2(IV)
338K
127K
184K
243K
ν / MHz
T / K
86
88
90
92
94
96
98
100
102
104
106
108
110
112
100
200
300

3


CH3NH3Hg I3
127I NQR
1
2
3
3'
328K
ν / MHz
T / K
116
118
120
122
124
126
128
130
132
134
136
138
140
160
162
164
166
168
170
172
174
176
178
180
182
184
100
200
300

4

dered with pronounced thermal motion in the ferroelectric phase. Many other investigations are also compatible with the order-disorder type phase transition. Below the ferroelectric phase transition temperature (T_c'), the cations move on the surface of a cone and the cone vertex angle increases on approaching T_c' [9, 12]. Above T_c' the cations are flipping between two equivalent equilibrium sites with local orientation rotated by 90° [6, 9]. The proton-^{14}N double resonance [9] and the spectroscopic (INS, FIR) [10] experiments show that a significant amount of molecular motion and disorder is still present in $CH_3NH_3HgCl_3$ even at rather low temperatures.

A similar motion of $CH_3NH_3^+$ may also exist in $CH_3NH_3HgBr_3$ and $CH_3NH_3HgI_3$. It is thus thought that above 328 K the cations are completely disordered in $CH_3NH_3HgI_3$ crystals like in $CH_3NH_3HgCl_3$. In $CH_3NH_3HgI_3$ crystals the terminal I(1) and I(2) atoms have the possibility of H-bonding with the $N \cdots I$ distances 3.65 and 3.64 Å, respectively. Therefore the effect of the motion of $CH_3NH_3^+$ is more pronounced on the terminal I(1) and I (2) atoms than on the bridging I(3) atom which does not participate in H-bonding. Thus only the resonance line of the bridging I(3) may be observed above T_c. The discontinuity between the lines 3 and 3′ is consistent with a first-order type phase transition where the Hg–I chain probably suffers a rearrangement. Further, H-bonding may also be responsible for the abnormal temperature variations of the NQR frequencies of 1 and 2. That is, the cationic motion, such as a tumbling motion, will additionally induce the large amplitude of torsional oscillations in the Hg–$I_{terminal}$ bonds which are linked to the cations through $I \cdots H–N$ type H-bonds. Thus, the resonance frequencies of 1 and 2 may drastically decrease with the excitation of the motion of the cations as the temperature increased. The relatively large η values for the terminal I may indicate the existence of H-bonding. And also a large decrease in η from 77 to 298 K is compatible with the pronounced motion of $CH_3NH_3^+$ at high temperatures.

Fig. 3. The temperature dependence of ^{81}Br NQR frequencies in $CH_3NH_3HgBr_3$.

Fig. 4. The temperature dependence of the ^{127}I NQR three low-frequency lines in $CH_3NH_3HgI_3$. These lines are assigned to the $\Delta m = \pm 1/2 - \pm 3/2$ transitions.

On the other hand, at temperatures just below and above the high temperature transition in $CH_3NH_3HgBr_3$, the cations may undergo a more drastic motion such as a liquid-like diffusion; the original symmetry of the crystal may not consequently be recovered on cooling. In $CH_3NH_3HgBr_3$ the terminal Br has also the possibility of H-bonding with the $N \cdots Br$ (1) distance 3.48 Å. It is, however, noted that 1 (IV) exhibits a very mild temperature dependence in spite of the pronounced motion of the cations, whereas the respective lines of the terminal Br are subject to drastic temperature variations below 243 K.

This situation is realized if we suppose the existence of the cone motion of the cations [12] in the room temperature phase, in which N atoms occupy the vertexes of the cones and the cone axes are parallel to the *b*-axis (A cone is schematically depicted by the dotted lines in Figure 1). Below 243 K the time-averaged directions of the C–N axes may be no longer bisectors of two differently directed Hg–$Br_{terminal}$ bonds but make different angles for these bonds with the different $N \cdots Br$ distances. Probably, on going from the high temperature phase to the low temperature phase, the $HgBr_3^-$ groups (being originally in the *a*–*b* plane) may rotate around the *b*-axis by small angles. On this phase transition, the resonance lines of terminal Br underwent considerable broadening and were practically unobservable at ca. 234–252 K. This may be connected with the fluctuations of the time-averaged C–N directions between two terminal Br.

In Fig. 3, the curves in I quasi continue in III after having been split in II. This may indicate that I and III belong to the same space group. The low temperature phase I has higher symmetry than the high temperature phase II where two formula units exist. This peculiarity is also observed for the ferroelectric transition in $CH_3NH_3HgCl_3$. The discontinuities in the temperature dependence curves may show that the transitions at 127 and 184 K are first-order. On the other hand, a second-order phase transition occurs at 243 K.

In concluding, the present results indicate that the $CH_3NH_3^+$ cations more significantly in both $CH_3NH_3HgBr_3$ and $CH_3NH_3HgI_3$ even at rather low temperatures, and an interplay of this motion with H-bonding is present at the phase transitions.

[1] A. Ben Salah, J. W. Bats, R. Kalus, H. Fuess, and A. Daoud, Z. Anorg. Allg. Chem. **493,** 178 (1982).
[2] F. Milia, Solid State Commun. **51,** 625 (1984).
[3] A. Ben Salah, A. Daoud, J.-L. Miane, and J. Ravez, Rev. Chim. Min. **21,** 34 (1984).
[4] J.-L. Miane, R. Chastanet, A. Ben Salah, and A. Daoud, Phys. Stat. Sol. (a) **88,** 325 (1985).
[5] F. Milia and E. Giannacopoulos, Japan J. Appl. Phys. Suppl. [**24-2**], 637 (1985).
[6] H. Fuess, M. Körfer, H. Arend, and R. Kind, Solid State Commun. **56,** 137 (1985).
[7] F. Milia and M. Voudouris, Solid State Commun. **60,** 261 (1986).
[8] F. Milia and M. Voudouris, Phys. Lett. A **116,** 292 (1986).
[9] J. Seliger, V. Žagar, R. Blinc, J. Milia, S. Giannacopoulos, and R. Kind, Solid State Commun. **59,** 877 (1986).
[10] M. Körfer, H. Fuess, M. Prager, and E.-J. Zehnder, Ber. Bunsenges. Phys. Chem. **92,** 68 (1988).
[11] M. Körfer, H. Fuess, J. W. Bats, and G. Klebe, Z. Anorg. Allg. Chem. **525,** 23 (1985).
[12] R. Kind and J. Roos, Phys. Rev. B **13,** 45 (1976).