

Study of the temperature dependence of the elastic constants of natural and deuterated $(\text{NH}_4)_2\text{MCl}_6$ compounds

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 6879

(<http://iopscience.iop.org/0953-8984/4/33/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:24

Please note that [terms and conditions apply](#).

Study of the temperature dependence of the elastic constants of natural and deuterated $(\text{NH}_4)_2\text{MCl}_6$ compounds

B R K Gupta†§, U Kawald†, H Johannsmann†, J Pelzl† and Y C Xu‡

† Institut für Experimentalphysik AG VI, Ruhr-Universität Bochum, W-4630 Bochum, Federal Republic of Germany

‡ Pohl Institute, Tongji University, Shanghai 200092, People's Republic of China

Received 28 November 1991, in final form 11 May 1992

Abstract. Experimental and theoretical investigations of the temperature dependence of the elastic constants in the cubic phases of $(\text{NH}_4)_2\text{TeCl}_6$, $(\text{ND}_4)_2\text{TeCl}_6$, $(\text{NH}_4)_2\text{SnCl}_6$ and $(\text{ND}_4)_2\text{SnCl}_6$ have been made in the range of temperatures from 4.2 to 300 K. The temperature variation in the elastic constants has been measured by Brillouin scattering and an interionic potential model has been used to interpret the experimental results. It has been found that the three-body interaction considered in the potential model plays an important and significant role in explaining the characteristic behaviour of the crystals under study. Good agreement between the experimental and theoretical values of the temperature derivatives of the elastic constants at room temperature has been obtained.

1. Introduction

Studies of the lattice dynamics and the pressure derivatives of the elastic constants of hexahalometallate crystals have been quite useful in view of their phase transition properties [1–6]. These properties have been explained in terms of phonon anomalies arising from coupling between a soft optical phonon mode and the elastic strain. However, in the past no attempts seem to have been made to study theoretically the temperature dependence of the elastic constants of the hexahalometallates. Recently, Kawald *et al* [7] have performed Brillouin and Raman scattering experiments on natural and deuterated ammonium hexachlorotellurate, $(\text{NH}_4)_2\text{TeCl}_6$ and $(\text{ND}_4)_2\text{TeCl}_6$, respectively, and have investigated the temperature dependence of the elastic constants in the temperature range 70–300 K. Both compounds undergo a structural transformation from a cubic structure with the space group O_h^5 to a trigonal phase with the space group C_{3i}^2 at $T_c = 88$ K which is accompanied by a softening of the shear elastic constants C_E and C_{44} as the transition is approached from higher temperatures. The coupling to the homogeneous strain gives rise to the observed elastic anomaly [8]. The most intriguing feature observed is the effect of deuteration on the low-temperature phase. Although both the natural and the deuterated tellurium compound undergo the transition at the same temperature, the Raman results unambiguously give evidence for two further phase transitions of the deuterated crystals below 88 K [7, 9, 10, 11], whereas the natural compound stays trigonal down to 4.2 K. The physical origin of this experimental result remains unexplained. The

§ On leave from the Department of Physics, GB Pant University, Patnagar, India.

motive of the present work is to obtain further information on the anharmonicity in natural compared with deuterated ammonium hexahalometallates. We investigate the effect of deuteration on the normal temperature dependence and we interpret the experimental results of the temperature derivatives of the elastic constants within the framework of a quasi-harmonic theory based on an interionic potential model.

In the range from 140 K to room temperature the elastic constants of the tellurium compounds show the normal linear behaviour. In addition, natural and deuterated ammonium hexachlorostannate, $(\text{NH}_4)_2\text{SnCl}_6$ and $(\text{ND}_4)_2\text{SnCl}_6$, respectively, have been investigated in this work. Both tin compounds stay cubic down to temperatures as low as 4.2 K.

The theoretical model employed in the present investigation consists of long-range Coulomb and three-body interactions [12–14] and short-range overlap repulsion effective up to nearest-neighbour ions. The phonon–lattice interaction not used before in calculations for fluorite and antiferroite structure crystals has also been included in order to make the model more realistic. In view of phonon–lattice theory [15,16] it is found that the contribution due to three-body interactions to the total lattice potential of hexahalometallate compounds plays a significant role in explaining the temperature dependence of their elastic constants.

After the presentation of the experimental results in section 2 a brief model theory is given in section 3. The experimental and theoretical results are discussed in section 4.

2. Experimental details and results

Single crystals of $(\text{NH}_4)_2\text{TeCl}_6$, $(\text{ND}_4)_2\text{TeCl}_6$, $(\text{NH}_4)_2\text{SnCl}_6$ and $(\text{ND}_4)_2\text{SnCl}_6$ have been grown from aqueous solution and solutions of heavy water, respectively. The degree of deuteration was measured by Raman scattering from NH_4^+ and ND_4^+ internal vibrations. The deuterated crystals contained 15% hydrogen atoms at maximum. The size of good-quality crystals was typically in the range from 0.1 to 0.5 cm³. Brillouin scattering has been observed in back scattering from (111) and (100) crystal surfaces in the temperature range 4.2–300 K. The cubic elastic constants of the natural and the deuterated ammonium hexachlorostannate display a normal linear temperature behaviour above 30 K. Figure 1 shows the elastic constants corresponding to the longitudinal elastic waves propagating parallel to the [100] direction (C_{11}) and to the [111] direction (C_L). The variation at elevated temperatures has been adjusted to the quasi-harmonic linear relation

$$C_i(T) = C_i^0 + \bar{m}_i T. \quad (1)$$

The fitted parameters are collected in table 1. Room-temperature data on $(\text{NH}_4)_2\text{SnCl}_6$ are already available from ultrasonic investigations [4,5]. For $(\text{ND}_4)_2\text{SnCl}_6$ the elastic constants have been measured at 5 K by inelastic neutron scattering [17]. These data agree well with the results of the present measurements. At low temperatures there are deviations from the expected behaviour. On the basis of the Debye model the quasi-harmonic theory predicts a crossover from a linear to a T^4 -dependence as 0 K is approached [18]. Instead, the elastic constants rise above the extrapolated Debye curve. This deviation is most distinctly visible for C_{11} of $(\text{ND}_4)_2\text{SnCl}_6$ in figure 1 where the experimental results are displayed together with

a Debye function. We have computed the elastic Debye temperature Θ_D^{el} using the equations obtained by de Launay [21] from the extrapolated linear behaviour of the elastic constants at high temperatures ($T > 180$ K) to $T = 0$ K. At these low temperatures, all contributions from optical phonons to the Debye integral should be small; therefore only acoustic phonons have been included in the calculations. The results are shown in table 1. With these values of Θ_D^{el} the Debye functions displayed in figure 1 have been fitted to the experimental data above 180 K. The deviations from Debye behaviour at low temperatures are clearly larger than the experimental error. However, for the deuterated compound a mode-mode coupling contribution cannot be ruled out as a soft librational mode has been observed in the deuterated compound by inelastic neutron scattering [17]. On the other hand, investigations of the temperature dependence of the chlorine NQR show that the single-line spectrum of the cubic phase is retained in $(\text{NH}_4)_2\text{SnCl}_6$ and $(\text{ND}_4)_2\text{SnCl}_6$ down to temperatures as low as 4.2 K [19, 20].

Table 1. Experimental data obtained from Brillouin scattering in natural and deuterated ammonium hexahalometallates. The density ρ and the refractive index n were used to compute the elastic constants from the measured Brillouin shift. C_i^0 and m_i are the intercept value (at $T = 0$ K) and the slope of the linear part of the temperature dependence of the elastic constants, respectively, which were determined by adjusting equations (1) and (2) to the experimental data. The experimental error of C_i^0 and m_i is approximately 5%. The coupling parameter a_i is defined by equation (2). The Debye temperature Θ_D^{el} was calculated from the elastic data using the equations of de Launay [21].

Parameter (units)	Value for the following compounds			
	$(\text{NH}_4)_2\text{TeCl}_6$	$(\text{ND}_4)_2\text{TeCl}_6$	$(\text{NH}_4)_2\text{SnCl}_6^a$	$(\text{ND}_4)_2\text{SnCl}_6^b$
ρ (kg m^{-3})	2350	2392	2410	2452
n	1.895	1.911	1.690	1.701
C_{11}^0 (GPa)	37.6	34.5	39.1	37.8
C_{12}^0 (GPa)	29.8	27.9	31.6	29.4 (29.0)
C_{13}^0 (GPa)	15.6	13.7	15.1	16.0 (14.8)
C_{44}^0 (GPa)	13.2	10.5	13.8	13.3 (11.2)
C_{AA}^0 (GPa)	20.1	18.0	20.3	20.3 (19.5)
C_{EE}^0 (GPa)	7.3	6.6	7.8	6.7 (7.1)
m_{11} (MPa K^{-1})	-22.7	-19.4	-33.7 (-27.3)	-26.2
m_L (MPa K^{-1})	-33.6	-29.2	-41.1	-38.7
m_{12} (MPa K^{-1})	-14.7	-11.6	-14.6 (-14.5)	-16.4
m_{44} (MPa K^{-1})	-12.2	-9.4	-14.8 (-11.6)	-15.3
m_A (MPa K^{-1})	-17.5	-14.9	-19.7 (-18.7)	-19.2
m_E (MPa K^{-1})	-4.4	-5.1	- 7.6 (-6.4)	-5.1
Θ_D^{el} (K)	106	100	112	105
a_{11} ($\text{MPa K}^{-1/2}$)	-101.1	-89.2		
a_L ($\text{MPa K}^{-1/2}$)	-143.0	-108.8		

^a The values in parentheses are from ultrasonic measurements [4].

^b The values in parentheses are from inelastic neutron scattering [17].

The natural $(\text{NH}_4)_2\text{TeCl}_6$ and deuterated $(\text{ND}_4)_2\text{TeCl}_6$ undergo a structural phase transition at $T_c = 88$ K which is driven by soft librational mode [7, 9–11]. The elastic softening, which already starts several tens of kelvins above T_c (figure 2) arises from the coupling of the homogeneous elastic strain to the fluctuations of the soft-mode

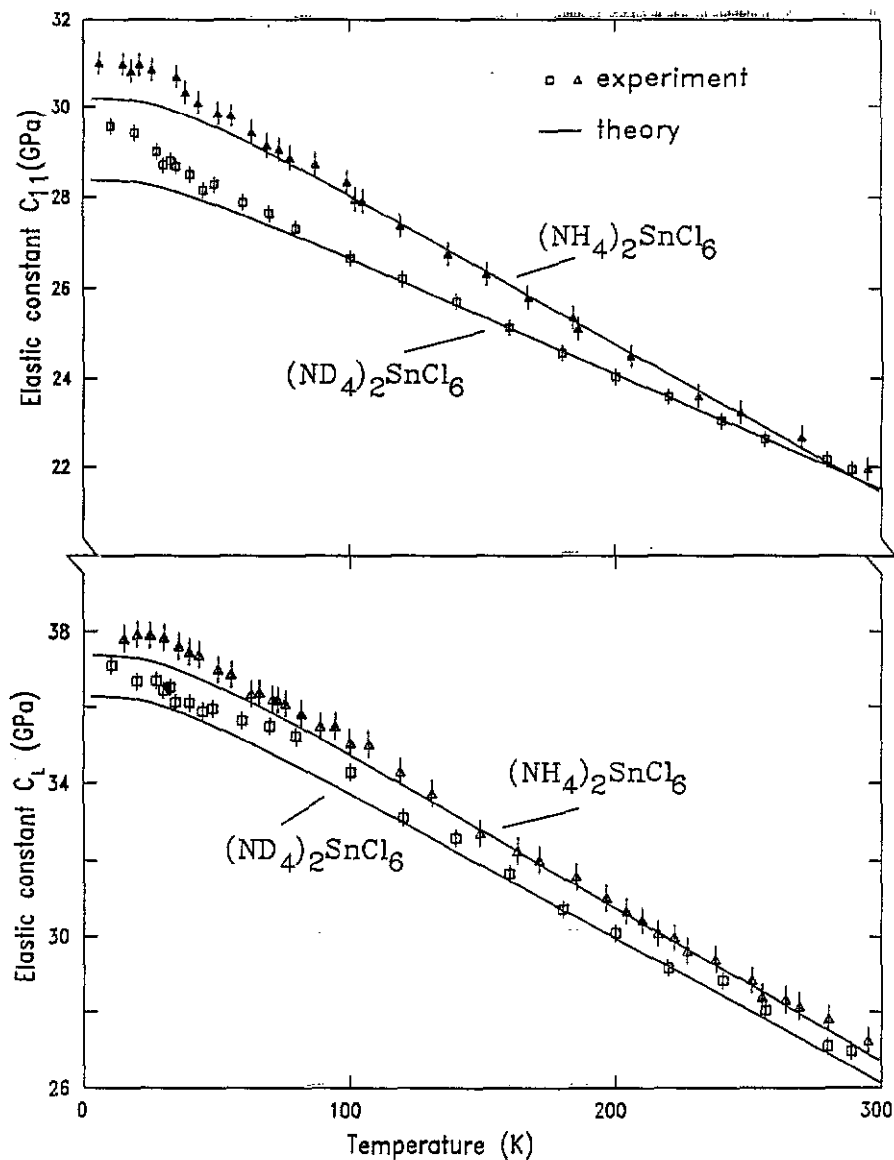


Figure 1. Temperature dependence of the elastic constants C_{11} and C_L corresponding to the longitudinal waves propagating in [100] and [111] direction in natural $(\text{NH}_4)_2\text{SnCl}_6$ and deuterated $(\text{ND}_4)_2\text{SnCl}_6$. The theoretical curve was obtained by fitting a Debye function to the experimental data above 180 K. The fitted parameters are collected in table 1.

coordinate. According to this model the temperature dependence of the elastic constants in the vicinity of T_c follows the relation (for $T > T_c$) [2,8]

$$C_i(T) = C_i^0 + m_i T + a_i T / \sqrt{T - T_c}. \quad (2)$$

As demonstrated for C_{11} and C_L in figure 2, the experimental results are in good accordance with the theoretically predicted behaviour. At room temperature the

temperature dependence of the elastic constants in the tellurium compounds is governed by the quasi-harmonic interaction which is taken into consideration by the first two terms of the above equation. The adjusted parameters are collected in table 1 where the indices A and E correspond to the symmetry-adapted elastic constant $C_E = \frac{1}{2}(C_{11} - C_{12})$ and to the bulk modulus $C_A = \frac{1}{3}(C_{11} + 2C_{12})$.

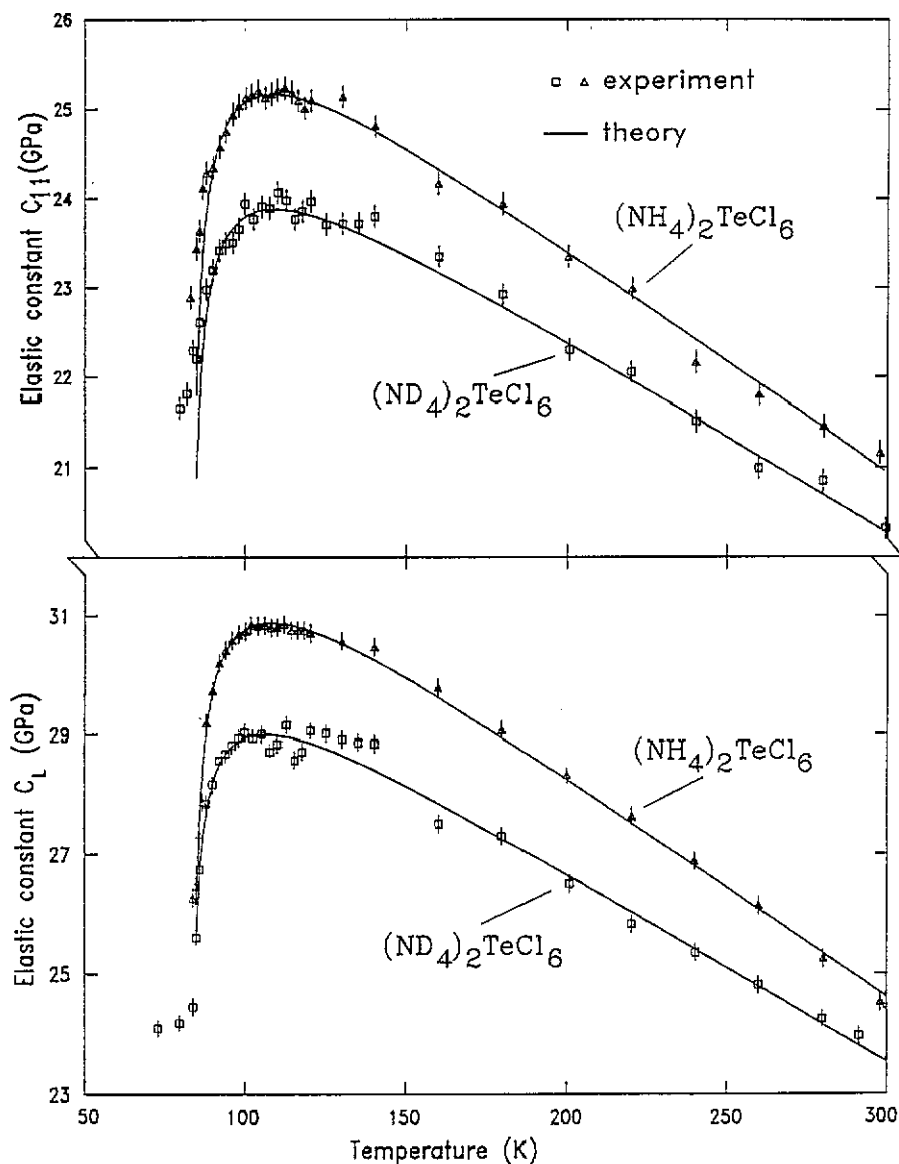


Figure 2. Temperature dependence of the elastic constants C_{11} and C_L corresponding to the longitudinal waves propagating in $\{100\}$ and $\{111\}$ direction in natural $(\text{NH}_4)_2\text{TeCl}_6$ and deuterated $(\text{ND}_4)_2\text{TeCl}_6$. The theoretical curve was obtained by adjusting equation (2). The fitted parameters are collected in table 1.

In the deuterated tellurium and tin compounds the elastic constants as well as

their temperature derivatives are mostly smaller than in the crystals containing natural ammonium groups. The differences, in particular between the temperature derivatives (table 1), are much larger than one would expect from the mass effect. These results provide evidence for a change in the vibrational anharmonicity as NH_4^+ is replaced by ND_4^+ . In order to quantify the anharmonicity the experimental data measured at room temperature are analysed on the basis of an ionic potential model.

3. Theory and method of calculation

For the hexahalometallates crystallizing in the cubic antiferite structure the expression for the potential energy can be written as follows [6]:

$$W(r) = W_C + W_R + W_T \quad (3)$$

where W_C , the Coulomb energy, is

$$W_C = -\frac{1}{2}e^2 \sum_{ll'kk'} \frac{Z(k)Z(k')}{r(ll',kk')} \quad (4)$$

$Z(k)$ is the valence of the k -type ion and $r(ll',kk')$ is the nearest-neighbour cation-anion separation. The second term in (3) represents the short-range overlap repulsion between nearest-neighbour ions and is of the Born-Mayer type:

$$W_R = \sum_{ll'kk'} Mb \exp\left[-\frac{r(ll',kk')}{\rho_{kk'}}\right] \quad (5)$$

M is the number of nearest-neighbour ions, b and $\rho_{kk'}$ are the strength and short-range overlap parameter, respectively, and can be determined using the equilibrium condition and compressibility data. The repulsive potential energy W_R is related to the short-range overlap parameters A and B :

$$e^2 A/4a^3 = \left(\partial^2 W_R / \partial r^2\right)_{r=a\sqrt{3}/4}$$

$$e^2 B/4a^3 = \left[(1/r)(\partial W_R / \partial r)\right]_{r=a\sqrt{3}/4}$$

The last term in equation (3) is due to the three-body interaction energy and can be written as follows:

$$W_T = e^2 \sum_{ll''kk'k''} f_k(r(ll',kk')) \frac{Z(k')}{r(ll',kk')} \quad (6)$$

where f_k is a function of the nearest-neighbour separation and measures the charge transfer on ion k . f is assumed to have the general functional form $f(r) = f_0 \exp(-r/\rho)$. Equations (3)–(6) as described above have been used previously by Gupta *et al* [6] and they have derived expressions for the elastic constants of crystals with the antiferite structure in terms of the model parameters. The model was then used to calculate the pressure derivatives of the elastic constants

of some hexahalometallate compounds. Good agreement between the theoretical [6] and experimental [4] results has been reported.

In order to calculate the temperature derivatives of the elastic constants of the ammonium hexachlorometallates, we have also included the phonon-lattice interaction arising from the thermal vibrations at temperature T . In view of this, the Hildebrand equation of state at temperature T can be written as

$$P = -dW/dV + \alpha_V B_S T \quad (7)$$

where p is the pressure and the second term on the RHS is the phonon pressure developed in the lattice at temperature T . α_V and B_S are the volume thermal expansion coefficient and the adiabatic bulk modulus, respectively. Using equations (3)–(7) and following Brugger's theory of elastic constants based on homogeneous deformation [15, 16, 22], one can easily obtain the following expressions for the temperature derivatives of the elastic constants at constant pressure:

$$(dC_{11}/dT)_p = \frac{1}{3}(C_{111} + 2C_{112} + C_{11})\alpha_V \quad (8)$$

$$(dC_{12}/dT)_p = \frac{1}{3}(C_{123} + 2C_{112} + C_{11} + 3C_{12})\alpha_V \quad (9)$$

$$(dC_{44}/dT)_p = \frac{1}{3}(C_{144} + 2C_{166} - C_{11} + C_{12} + 3C_{44})\alpha_V. \quad (10)$$

C_{ij} and C_{ijk} represent the second-order and third-order elastic constants, respectively. The values of the C_{ijk} are determined following the procedure of Gupta *et al* [6]. α_V , the volume thermal expansion coefficient, has been evaluated using the following expression based on the thermodynamic theory as described by Wallace [15]:

$$\alpha_V = -(C_V/2r_0) \left[W'''(r_0)/W''(r_0)^2 \right]. \quad (11)$$

Here, C_V is the specific heat at constant volume, $W''(r)$ and $W'''(r)$ are the second and third spatial derivatives of the total lattice energy and r_0 is the equilibrium distance of nearest-neighbour ions. The values of the model parameters determined using the input data of [7] are given in table 2, and the values of the temperature derivatives of C_{11} , C_{12} and C_{44} calculated from equations (8)–(10) are also shown there. The experimentally determined values of $(dC_{ij}/dT)_p$ are also given in table 2 for comparison with the theoretical results.

4. Results and discussion

A look at table 2 clearly indicates that the calculated values of the temperature derivatives of the elastic constants are in good agreement with the experimental values. A general observation is that on deuteration all elastic constants become smaller in the linear temperature regime. The amount of reduction is different for the different elastic constants and also varies with composition. In the frame of the applied microscopic model the decrease in C_{ij} must be accounted for by the change in the short-range force parameters A and B as only these parameters exhibit the same trend on deuteration for both the tellurium and the tin compound (table 2). The conclusion seems to be reasonable also on physical grounds. In the

Table 2. Values of the model parameters A , B and $f(r_0)$ calculated using the input data (at room temperature) C_{11} , C_{12} , C_{44} and a (lattice constant) and calculated values of the temperature derivatives of the elastic constants at room temperature compared with experimental results in parentheses. The elastic constants used as input data could be determined to within an error margin of 2.5%. This leads to an error of about 10% for the computed temperature derivatives.

Parameter (units)	Value for the following compounds			
	$(\text{NH}_4)_2\text{TeCl}_6$	$(\text{ND}_4)_2\text{TeCl}_6$	$(\text{NH}_4)_2\text{SnCl}_6$	$(\text{ND}_4)_2\text{SnCl}_6$
a (nm)	1.0220	1.0204	1.0060	1.0054
C_{11} (GPa)	21.2	20.3	22.0	21.9
C_{12} (GPa)	10.6	10.3	10.6	11.4
C_{44} (GPa)	7.8	7.7	9.5	9.0
A	71.85	76.39	104.92	108.97
B	-5.31	-4.97	-5.37	-4.98
$f(r_0)$	0.0927	0.0709	0.0817	0.1213
$[dC_{11}/dT]_p$ (MPa K ⁻¹)	-19.28 (-22.7)	-17.30 (-19.4)	-28.70 (-33.7)	-25.58 (-26.2)
$[dC_{12}/dT]_p$ (MPa K ⁻¹)	-14.02 (-14.7)	-13.25 (-11.6)	-17.49 (-14.6)	-20.62 (-16.4)
$[dC_{44}/dT]_p$ (MPa K ⁻¹)	-12.94 (-12.2)	-11.35 (-9.4)	-16.43 (-14.0)	-18.48 (-15.3)
$[dC_E/dT]_p$ (MPa K ⁻¹) ^a	-2.63 (-4.4)	-2.03 (-5.1)	-5.61 (-7.6)	-2.48 (-5.1)
$[dB_3/dT]_p$ (MPa K ⁻¹) ^b	-15.77 (-17.5)	-14.60 (-14.9)	-21.23 (-19.7)	-22.27 (-19.2)
α_V (10 ⁻⁵ K ⁻¹)	17.50 (17.7)	17.05	16.80 (14.9)	16.50

$$^a C_E = (C_{11} - C_{12})/2.$$

$$^b B_3 = (C_{11} + 2C_{12})/3.$$

deuterated salt because of the heavier mass the local motion of ND_4^+ will become slower. In consequence the time-averaged overlap repulsion should be diminished, leading to a smaller force constant. A more complex behaviour is displayed by the temperature coefficients of the elastic constants, indicating a more pronounced influence of the three-body interaction contributions which show different trends in the tin and the tellurium salts (table 2). The calculated as well as the experimental values of $[dC_{11}/dT]_p$ for $(\text{ND}_4)_2\text{TeCl}_6$ and $(\text{ND}_4)_2\text{SnCl}_6$ are both smaller than those of their respective $(\text{NH}_4)_2$ compounds. On the other hand, the calculated and the experimental values of $[dC_{12}/dT]_p$ and $[dC_{44}/dT]_p$ for $(\text{ND}_4)_2\text{TeCl}_6$ are smaller than those of $(\text{NH}_4)_2\text{TeCl}_6$ whereas in $(\text{ND}_4)_2\text{SnCl}_6$ they are larger than in $(\text{NH}_4)_2\text{SnCl}_6$.

This unusual behaviour of the deuterated compounds may be ascribed to the fact that the difference between the Cauchy discrepancies $C_{12} - C_{44}$ of $(\text{ND}_4)_2\text{SnCl}_6$ and $(\text{NH}_4)_2\text{SnCl}_6$ is much larger than that of $(\text{ND}_4)_2\text{TeCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$. This results in a large difference of the calculated three-body parameters $f'(r)$ and $f''(r)$, the space derivatives of the charge transfer function $f(r)$, between $(\text{ND}_4)_2\text{SnCl}_6$ and $(\text{NH}_4)_2\text{SnCl}_6$. For $(\text{ND}_4)_2\text{TeCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ the calculated values of the same parameters do not differ much in magnitude. It is well established microscopically [12, 13] that the three-body interaction explains Cauchy breakdown satisfactorily in ionic solids.

It is obvious from equations (8)–(10) that higher negative values of C_{123} , C_{144} and C_{166} as determined here by using the repulsive and three-body interaction parameters produce larger magnitudes of $(dC_{12}/dT)_p$ and $(dC_{44}/dT)_p$. Therefore, the calculated values for $(\text{ND}_4)_2\text{SnCl}_6$ are higher than those calculated for $(\text{NH}_4)_2\text{SnCl}_6$ whereas they are smaller for $(\text{ND}_4)_2\text{TeCl}_6$ than for $(\text{NH}_4)_2\text{TeCl}_6$. However, the val-

ues of $|\text{d}C_{11}/\text{d}T|_p$ for both deuterated compounds are found to be smaller than in the respective natural compounds as the predicted values of C_{11} and C_{12} used to calculate $(\text{d}C_{11}/\text{d}T)_p$ for the deuterated crystals are smaller in magnitude than those of the undeuterated crystals.

The values of the temperature derivatives of the shear modulus and the bulk modulus have also been estimated using the calculated results of $(\text{d}C_{11}/\text{d}T)_p$ and $(\text{d}C_{12}/\text{d}T)_p$. Fairly good agreement between the calculated values and the experimental results has been achieved. The present explanation is based on the assumption that the mode-mode coupling does not provide a prominent contribution to the linear temperature dependence of the elastic constants above the phase transition in the tellurium compounds.

In the scope of the fluctuation model [2, 5] the renormalization of the elastic constants due to the coupling of the homogeneous strain to the optical soft mode leads to a critical temperature dependence near the transition temperature and a contribution linear in T which is superimposed on the quasi-harmonic behaviour (equation (2)). Most remarkably the critical coupling coefficients a deduced from the experiments are considerably smaller in the deuterated compound (table 1). This result indicates a smaller critical fluctuation amplitude in the deuterated crystal in agreement with the conclusions drawn from the observations in the linear temperature regime.

5. Conclusion

On the basis of the overall description obtained from the present interionic-force model it is shown that this model, by taking into account three different interaction fields, is capable of predicting fairly well the temperature-dependent properties of the elastic constants of natural and deuterated ammonium hexachlorometallate crystals. On the basis of the observed systematic trends it has been concluded that deuteration mainly affects the short-range interaction potentials, leading to a reduction in the elastic force constants in the linear temperature regime. The same mechanism has also been adopted to explain the deuteration effects on the elastic anomalies near the structural phase transition in the ammonium hexachlorotellurates.

Acknowledgment

This work is supported by the Bundesminister für Forschung und Technologie (project 03-PE1BOC8) and the Volkswagenstiftung.

References

- [1] Sutton M, Armstrong R L, Powell B M and Buyers W L 1983 *Phys. Rev. B* **27** 380
- [2] Wruk N, Pelzl J, Höck K-H and Saunders G A 1990 *Phil. Mag.* **B 61** 67
- [3] Armstrong R L, Mintz D, Powell B M and Buyers W L 1979 *Phys. Rev. B* **19** 448
- [4] Wruk N, Pelzl J, Saunders G A and Hailing T 1985 *J. Phys. Chem. Solids* **46** 1235
- [5] Pelzl J, Höck K-H, Miller A J, Ford P J and Saunders G A 1981 *Z. Phys.* **B 40** 321
- [6] Gupta B R K, Adhikari R S, Gupta O P and Goyal R P 1988 *J. Phys. C: Solid State Phys.* **21** L353
- [7] Kawald U, Müller S, Pelzl J and Dimitropoulos C 1988 *Solid State Commun.* **67** 239

- [8] Henkel W, Pelzl J, Höck K-H and Thomas H 1980 *Z. Phys.* B **37** 321
- [9] Müller S, Kawald U and Pelzl J 1990 *Phonons* 89 ed S Hunklinger, W Ludwig and G Weiss (Singapore: World Scientific) p 1120
- [10] Dimitropoulos C, Pelzl J and Borsa F 1990 *Phys. Rev.* B **41** 3914
- [11] Pelzl J, Müller S and Dimitropoulos C 1990 *Proc. Int. Conf. on Raman Spectroscopy* ed J R Durig and J F Sullivan (Chichester: Wiley) p 490
- [12] Lowdin P O 1947 *Ark. Mat. Astra Fys.* A **35** 30
- [13] Lundqvist S O 1961 *Ark. Fys.* **6** 113; **19** 113
- [14] Verma M P and Singh R K 1969 *Phys. Status Solidi* **33** 769
- [15] Wallace D C 1970 *Solid State Physics* vol 25 (New York: Academic) p 301; 1972 *Thermodynamics of Crystals* (New York: Wiley)
- [16] Shrivasta U C 1980 *Phys. Status Solidi* b **100** 641
- [17] Powell B M, Press W and Dolling G 1985 *Phys. Rev.* B **32** 3118
- [18] Johannsmann H 1982 *Master's Thesis* Ruhr-Universität Bochum
- [19] Dimitropoulos C and Pelzl J 1980 *J. Mol. Struct.* **58** 107
- [20] Dimitropoulos C, Pelzl J, Kawald U and Svare I 1988 *Europhys. Conf. Abstr.* A **12** 240
- [21] de Launay J 1959 *J. Chem. Phys.* **30** 91
- [22] Brugger K 1964 *Phys. Rev.* **133** A1611