PHYSICAL REVIEW B VOLUME 9, NUMBER 10 15 MAY 1974

Thermal expansions of high-purity and OH^--doped NaCl at temperatures below 30 K

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(Received 26 December 1973)

A variable transformer dilatometer has been used to obtain linear thermal-expansion coefficients for temperatures from 2 to 30 K for single crystals of pure (OH^--free) NaCl and for NaCl crystals which contained 6.5 and 80 ppm of OH^- substitutional impurities. The thermal expansions of the pure sample are well behaved, with a Grüneisen parameter which agrees well with the elastic-constant value (1.06) below 6 K, and which shows a pronounced minimum near 15 K. A relatively large anomalous contribution to the thermal-expansion coefficient of the 80-ppm sample increases with decreasing temperature and has a magnitude which is ten times that of the pure sample at 2.25 K. These large excess thermal expansions are similar in form to heat-capacity contributions which can be calculated from published energy-level diagrams for OH^- in NaCl. The corresponding Grüneisen parameter for this impurity system is quite large (~ 40), and hence provides a direct confirmation that tunneling must be involved in any description of the thermodynamic properties of these impurity states.

INTRODUCTION

A high-purity dielectric solid such as NaCl is expected to obey the Grüneisen relation at low temperatures, with the temperature dependence of the thermal-expansion coefficient being similar to that of the specific heat. Preliminary measurements in this laboratory of the linear thermal-expansion coefficients of an NaCl single crystal (purchased from the Harshaw Chemical Co.) were found to be anomalously large below 10 K, however, and the present paper describes the results of experiments which demonstrate that these effects are due to small concentrations (6.5 ppm) of OH^- impurity. A preliminary account of these results and of similar data by White for KCl with Li^+ and CN^- impurities has been published elsewhere.[1] White's results for pure NaCl and pure KCl also have appeared more recently.[2]

A review article by Narayanamurti and Pohl[3] describes the properties of various substitutional impurities in alkali halides (including OH^-). The impurity ion in general can exist in a number of equivalent orientations along symmetry directions in the crystal; these correspond to the six $\langle 100 \rangle$ directions for OH^- in NaCl.[3,4] These stable configurations are separated by energy barriers, with tunneling through the barriers resulting for the simplest case in a completely delocalized ground state for $T = 0$. The actual ground state of this system is complex, with a breakdown of the sixfold degeneracy into three levels which can be described to first order by a tunnel-splitting parameter δ. Although δ is typically of the order of 0.3 K (0.2 cm^{-1}), it is believed to be somewhat higher (3 K or so, 2 cm^{-1}) for OH^- in NaCl.[3,4] As we will show, excited states also are of importance for this system.

The heat-capacity contribution due to these impurities, which is determined by δ and the thermal population of the available states, generally is small above 1 K. The thermal-expansion coefficient, however, is related to the volume dependence of the entropy and hence to the volume dependence of the occupation numbers of the various energy levels, and thus to the volume dependence of δ. Since a tunneling mechanism is involved, the magnitude of δ (and also of the energy of the first excited states) should be sensitive to the changes in barrier height which occur in a volume change, so it is not surprising that the impurity contributions to the thermal-expansion coefficients are large. Indeed, the existence of large thermal-expansion contributions which can be related directly to small OH^- concentrations can be used as a convincing demonstration that a tunneling mechanism must exist for the impurity states for OH^- in NaCl.

The above discussion can be framed more quantitatively in terms of a generalized Grüneisen relation. If only lattice-vibration effects are present, the volume thermal-expansion coefficient $\beta\,[=(\partial \ln V/\partial T)_P]$ is related to the constant-volume heat capacity C_V, the isothermal bulk modulus B_T, and the volume V by the relation

$$\beta = \gamma C_V / B_T V \ . \tag{1}$$

In the low-temperature continuum limit, γ approaches a constant value γ_0, which is rigorously related to the volume dependence of the Debye temperature, $\gamma_0 = -(d\ln\Theta_0/d\ln V)$, and which can be calculated from the low-temperature elastic constants and their volume derivatives. If two (or more) independent contributions to the free energy of a system exist, the individual thermal expansion or heat-capacity contributions are additive. As an example, Eq. (1) can be written for lattice and impurity contributions as

$$\beta = \beta^{1at} + \beta^{i} = (\gamma^{1at} C_V^{1at} + \gamma^{i} C_V^{i}) / B_T V \ . \tag{2}$$

Here, $\gamma^{\mathrm{lat}} = \gamma_0$ at low temperatures, and $\gamma^i = -(d\ln\delta/d\ln V)$ for the simplest model of OH^- in NaCl, although in general γ^1 reflects the volume dependence of the energy-level system. The Grüneisen parameters γ typically have values which can be understood qualitatively in terms of elementary models and which are close to 2 for most thermal phenomena. However, the value of γ^1 that we find for OH^--doped NaCl is large (close to 40), as would be expected from the qualitative discussion in the previous paragraph.

The results of the present experiments will be discussed in two parts. First, linear thermal-expansion-coefficient ($\alpha = \frac{1}{3}\beta$) data will be given for pure (OH^--free) NaCl for temperatures from 3 to 30 K, since these are necessary to provide the "lattice-only" values β^{lat} that must be subtracted from the data for the doped samples to obtain the impurity contributions. These data for pure NaCl also establish the temperature dependence of γ^{lat} [Eq. (1)] for comparison with theoretical calculations such as those of Achar and Barsch.[5] Next, results will be given for the linear-expansion coefficients of samples of NaCl which contain OH^- contributions of 6.5 and 80 ppm, respectively. A comparison will be made between the temperature dependence of the thermal-expansion coefficients that we observe and heat-capacity values that can be calculated from models for the energy levels of OH^- substitutional impurities in NaCl.

EXPERIMENTAL DETAILS

The variable transformer dilatometer used in these experiments is described in detail elsewhere.[6] This dilatometer is useful over the temperature range from 1.9 to 30 K, and has a sensitivity of ± 0.02 Å (2×10^{-10} cm) for the detection of length changes for 10-cm-long samples. This implies a relative precision of 0.1% for $\alpha \gtrsim 3\times10^{-8}$ K^{-1}. The absolute accuracy is limited by the calibration and is estimated to be from 0.5% to 1.0% from comparisons with other data for temperatures above 10 K.[6,7] The thermal-expansion coefficients obtained are absolute in the sense that only the sample changes length. Data generally are taken for relatively large (0.5 to 1 K) temperature increments, and subsequently are corrected to the true values of the expansion coefficient by an iterative process once the form of the expansion has been established. The sample thermometer has been calibrated in terms of the paramagnetic salt scale of Cetas and Swenson.[8,9]

The physical characteristics of the single-crystal samples are given in Table I. The commercial Harshaw crystal was described as of high purity, while the OH^--free (< 0.5 ppm) and 80-ppm OH^- samples were obtained through the assistance of Pohl.[10] The OH^- impurity concentrations were determined from far-ultraviolet absorption spectra[11] by Klein and Evans at the University of Illinois[12] from fragments of the original samples. The thermal-expansion samples were shaped by cleaving to obtain roughly square cross sections of dimensions from 0.6 to 1 cm, with rounded edges. They were handled as little as possible to avoid both contamination and cracking. The 4.2-K lengths were calculated from room-temperature measurements using the results of other investigators.[13]

RESULTS

The experimental data for the three samples are given in Table II, and are plotted in Fig. 1, where the anomalous behavior of the doped samples is shown clearly. The data for the 80-ppm sample are plotted only for temperatures down to 6 K, since these values relative to pure NaCl increase rapidly with decreasing temperature to roughly a factor of 10 at our lowest data point, 2.25 K, for which $\alpha T^{-3} = 64\times10^{-11}\ K^{-4}$. At and above 15 K, where the anomalous behavior presumably has disappeared, a systematic difference of roughly 0.5% exists between the data for the pure sample and for the two doped samples. Presumably, this effect is due to slight differences that occur in the experimental setup when samples are changed and that affect the calibration of the dilatometer. The dilatometer calibration constants that were used to analyze the individual data for the three samples were normalized to force the high-temperature data to agree when the anomalous contributions to the thermal expansion were calculated in the following. The data in Table II, however, were analyzed using a common dilatometer calibration constant and hence reflect these systematic differences.

Pure NaCl

The data for the OH^--free NaCl sample can be represented from 3 to 30 K by the relationship

$$10^8\alpha = 5.7146\times10^{-3}T^3 + 2.857\times10^{-6}T^5 + 1.1757\times10^{-8}T^7 - 2.0163\times10^{-11}T^9 + 9.160\times10^{-15}T^{11}\ K^{-1}\ , \qquad (3)$$

TABLE I. Physical characteristics of NaCl samples used in these experiments.

OH^- Level (ppm mole fraction)	Source	4.2-K length (cm)
< 0.5 ("pure")	Cornell University[a] Ithaca, N. Y.	6.379
6.5	Harshaw Chemical Co. Cleveland, Ohio	10.011
80	Cornell University[a] Ithaca, N. Y.	8.090

[a] See the text.

TABLE II. Linear thermal-expansion coefficient data for the three samples described in Table I. Unless otherwise noted, the experimental precision is estimated to be better than 1%. The data are listed in the order in which they were taken, with individual runs (that is, data taken on different days) separated by spaces. The experimental procedure (Ref. 6) allowed the average temperature of a data point to be chosen exactly, and all corrections (such as those for finite temperature intervals) were applied to the values of α.

OH$^-$-free		6.5 ppm		80 ppm	
T (K)	α (10^{-8} K^{-1})	T (K)	α (10^{-8} K^{-1})	T (K)	α (10^{-8} K^{-1})
3.250	0.204 ± 5%[a]	4.500	0.583 ± 1.5%	12.300	12.264
8.500	3.658			15.500	25.857
9.500	5.190	4.500	0.577	19.500	56.852
6.500	1.608	3.750	0.342	11.200	9.217
13.000	14.108	3.000	0.190 ± 1.5%	5.000	1.411
		6.000	1.322	24.700	129.20
4.375	0.480 ± 1.5%	8.000	3.112	29.900	244.71
3.750	0.304 ± 2%	13.000	14.230		
3.000	0.153 ± 2.5%			6.500	2.265
5.500	0.973	7.000	2.086	5.500	1.639
7.500	2.501	5.200	0.864	4.500	1.190
		4.450	0.557 ± 1.5%	3.750	0.955
10.500	7.111	9.000	4.457	3.125	0.817
11.500	9.500	11.500	9.580	2.625	0.746 ± 1.5%
12.500	12.444	15.000	22.886	2.225	0.721 ± 2%
4.875	0.678			8.500	4.254
7.000	2.031	20.000	61.953		
18.000	42.564	25.000	134.76	6.000	1.916
		30.000	248.04	7.000	2.646
14.500	20.296	10.500	7.207	8.000	3.631
16.001	28.334	4.800	0.690	9.000	4.933
20.000	61.553	3.400	0.266	10.000	6.602
22.000	86.010	4.150	0.459	13.400	16.011
24.000	116.26	2.700	0.145 ± 2.5%		
26.000	152.96				
28.000	195.71				
30.000	246.39				

[a] This point was not used in the computer smoothing of the data.

with a root-mean-square deviation of 0.46%. These results agree to within 1.5% with those of White and Collins[2] at temperatures above 7 K, and to within the stated experimental uncertainties with the less precise results of Meinke and Graham.[14] The value of the leading or cubic term in this relation, which is the only parameter that has physical significance, does not appear to depend (to within 0.2%) on the upper limit of the temperature range used.

Equation (3) has been used to calculate the temperature dependence of the lattice Grüneisen parameter [Eq. (1)], which is given as the solid line in Fig. 2, using heat-capacity results from Morrison and Patterson[15,16] and temperature-independent 4.2-K values of the bulk modulus[17] $B_0 = 2.739 \times 10^{11}$ dyn/cm^2 and atomic volume $V_0 = 13.19$ cm^3.[13] This value of B_0 as given by Fugate and Schuele[17] is greater than that given by Lewis *et al.*[18] by roughly 3%, which is appreciably greater than the estimated experimental uncertainties in the Fugate and Schuele experiment. We have chosen arbitrarily to use the Fugate and Schuele value, since it is based on measurements taken on a single sample rather than on two independent samples.[18] No firm basis exists for the choice of either set of data, however.

Figure 2 also contains a representation of the

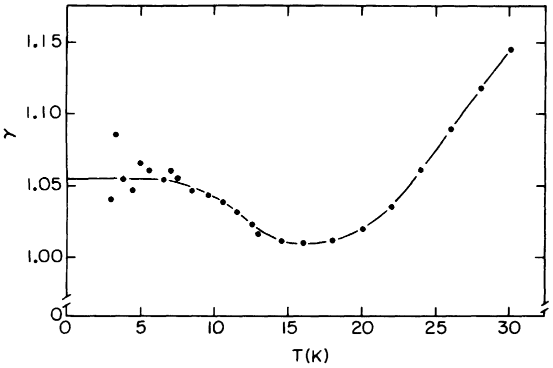

FIG. 1. Thermal-expansion results for the three samples. See the text for details.

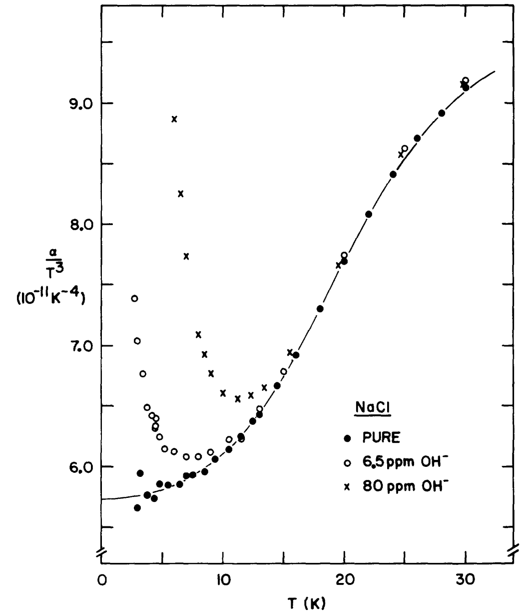

FIG. 2. Temperature dependence of the Grüneisen parameter for the pure (OH$^-$-free) sample of NaCl.

individual thermal-expansion data points that was obtained using the smoothed C_V results and the above values of B_0 and V_0. The data are smooth at the 0.2% level, except at the lowest temperatures where the sensitivity in the length-change determination is a limiting factor. The constancy of γ below 7 K suggests that the OH$^-$ contribution to α is effectively zero.

White and Collins[2] comment on the possible existence of the minimum in the γ-vs-T curve, which is shown clearly in Fig. 2. It was obscured somewhat in their results by scatter in the data and by a contribution below 7 K due to OH$^-$ impurities in their samples. A very similar behavior is suggested by a shell-model calculation by Achar and Barsch.[5] The depth of the minimum that they predict (0.06) is almost identical with that which we observe. The limiting value of γ that we obtain ($\gamma_0 = 1.054 \pm 0.01$) can be compared directly[2] with that calculated by Fugate and Schuele[17] (1.06) from the 4.2-K elastic moduli and their higher-temperature pressure derivatives. The agreement is quite good. The heat-capacity results are a limiting factor in the determination of the temperature dependence of γ, since the only available low-temperature data[15] are 20 years old. The low-temperature behavior of these data, however, is quite consistent with the elastic constant value[17,18] of the $T = 0$ Debye temperature ($\Theta_0 = 321$ K) used in our calculation of γ_0.

OH$^-$-doped NaCl

The anomalous contributions to the thermal expansions of the impure samples were calculated by subtracting the normalized "pure" values from the experimental data. The results for the 6.5- and the 80-ppm samples scale with concentration, except possibly at the lowest temperatures, so the following discussion will concentrate on the much larger effects found for the 80-ppm sample, which are plotted at the top of Fig. 3. The impurity contributions to the data for this sample can be represented satisfactorily at "high temperatures" ($T \gtrsim 11$ K, where the Schottky function varies as T^{-2}) as $\alpha^{\mathrm{OH}^-} = 6 \times 10^{-7} T^{-2}$ K^{-1}, with a leveling off at 6.5×10^{-9} K^{-1} at lower temperatures. No other data exist for this system that could be used to compare with these results.

Equation (2), however, suggests that the temperature dependence of α^{OH^-} should be similar to that for the corresponding impurity heat-capacity contribution. These contributions to C_V are small, and no heat-capacity data are available from which even their orders of magnitude could be estimated. The energy-level diagrams for OH$^-$ in NaCl that have been derived from both microwave-spectroscopy[19] and thermal-conductivity[20] experiments can be used to estimate the heat-capacity contribution of the OH$^-$ impurity, however, and the results of such calculations are shown for our 80-ppm sample in the lower part of Fig. 3. Similar calculations have been used to interpret heat-capacity anomalies that have been observed in the system Li$^+$ in KCl.[3,21]

The actual energy-level diagrams used for these calculations are shown in Fig. 4. The splitting in

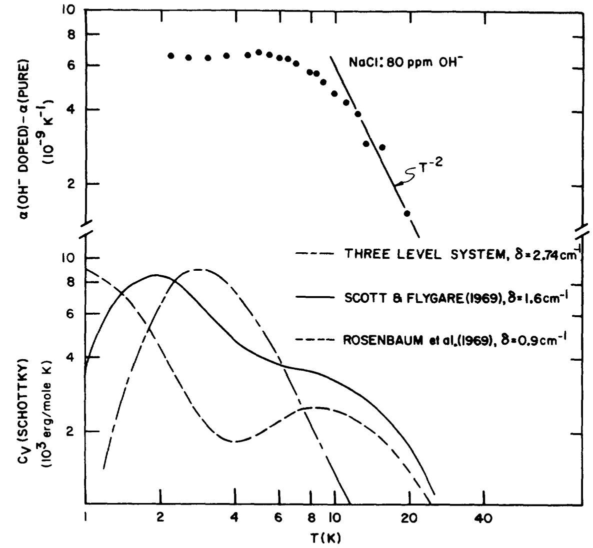

FIG. 3. Comparison of the excess thermal-expansion contribution and various calculated heat-capacity contributions for the 80-ppm sample. The C_V calculation is for one mole of NaCl containing 80 ppm (mole-fraction) of OH$^-$ as a substitutional impurity. The energy-level schemes used are described in Fig. 4.

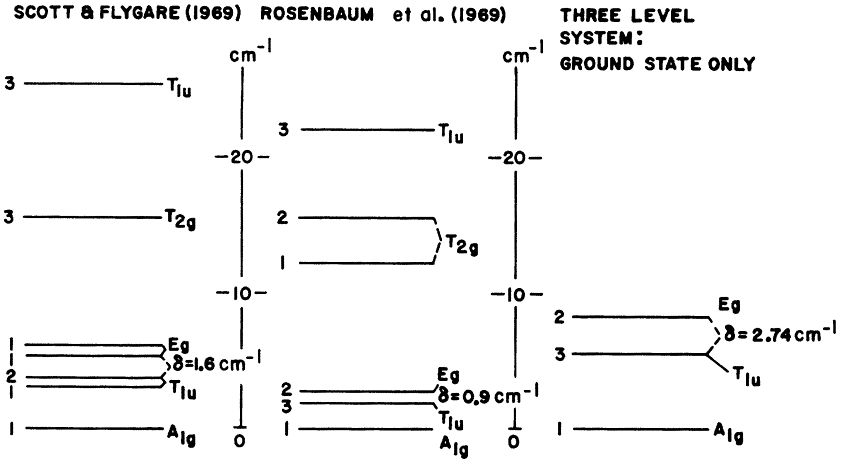

FIG. 4. Energy-level diagrams used to calculate the various C_V contributions in Fig. 3. The sources are (from left to right) Refs. 19, 20, and (for the value $\delta = 2.74$ cm^{-1}) 22.

the sixfold degeneracy of the ground state is characterized by the tunnel-splitting parameter δ, and is represented by the ground-state-only levels at the right-hand side of Fig. 4. If only these levels were important in determining the impurity contribution to the thermodynamic properties, together with the relatively large value of δ suggested by Pandey and Shukla[22] (which perhaps is used inaccurately here), the shape of the thermal-expansion anomaly would be quite different from what is observed. The other two energy-level diagrams include the six levels associated with the first excited state. While these two diagrams differ in detail, both result in a Schottky heat-capacity contribution that extends over a wider range of temperature than is found for the ground-state-only (three-level) scheme.

The form of the thermal-expansion data appears to be in best agreement with the level scheme suggested by Rosenbaum *et al.*,[20] although it is unfortunate that we do not have data for the lower temperatures, where a factor-of-two (or larger) increase in α^{OH^-} could have been expected to occur due to the ground-state level splitting. The thermal-expansion results do suggest, however, that the excited-state levels in both schemes should be reduced somewhat in energy to give a T^{-2} dependence for C_V down to 11 K or so. In any event, these C_V calculations can be used to estimate a value for the Grüneisen parameter $\gamma^i \approx 40$ [Eq. (1)] for the OH⁻-doped samples.

CONCLUSIONS

The present experiments have shown that high-purity (OH⁻-free) single crystals of NaCl have a well-behaved thermal-expansion versus temperature relation at temperatures below 30 K. The form for the γ-vs-T relations can indeed be understood quantitatively in terms of a lattice-dynamical shell-model calculation.[5] Measurements on a single crystal of NaCl that contains 80 ppm of OH⁻ substitutional impurity show an anomalous thermal-expansion behavior that appears to be closely related to heat capacities that can be calculated from published energy-level diagrams for OH⁻ in NaCl. The rather large magnitudes of the resulting Grüneisen parameter (~40) can be used as a confirmation of the current picture that tunneling is an important factor in any description of the state of these impurities. The anomalous thermal-expansion results found for our original Harshaw crystal can be understood quantitatively in terms of the 6.5 ppm of OH⁻ that exist in it, using the results for the deliberately doped sample.

The results which were presented in Fig. 3 clearly suggest that these thermal-expansion data should be extended to lower temperatures. The magnitude of the impurity contribution to C_V for the 80-ppm sample is also relatively large, and at 2 K, for instance, it is roughly 20% of that for the pure sample. Hence considerable information about these impurity states in NaCl could be obtained from low-temperature heat-capacity measurements which extend to temperatures below 1 K. The contribution of the first excited states to the properties of OH⁻ in NaCl, however, make it difficult to interpret data such as these. White[1] has shown that similar thermal-expansion anomalies occur for the simpler case of Li⁺ in KCl, for which considerably more data exist than for NaCl and for which an energy-level diagram exists that is consistent with the data.[3,21] White's continuing investigation of this system may possibly turn out to be more profitable than an extension of the present work on NaCl.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Dr. Robert O. Pohl, who first confirmed the possibility that these anomalies could be due to OH⁻ impurities, and who assisted in the acquisition of the high-purity and highly doped samples. They also are indebted to Dr. D. W. Lynch for a number of conversations, to Dr. M. V. Klein for arranging for the analysis of the OH$^-$ content in the samples, and to Dr. G. K. White for keeping them informed of his results.

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