

Quartic anisotropy of the recoilless fractions in NaCl

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Previously obtained data on the recoilless fractions in single crystals of sodium chloride have been reanalyzed in terms of the general formalism conforming to the crystal symmetry. The original data were obtained by using Rayleigh scattering of the Mössbauer radiation. It was found that above the quantum region and at a temperature high enough to neglect anisotropy of the ionic form factors there is some anisotropy of the thermal motion of the entirely quartic character. On the other hand, quadratic terms in the wave-vector transfer are completely quasiharmonic. A departure from the Gaussian thermal distribution is quite significant for both cations and anions. The anisotropy tends to diminish at high temperatures.

I. INTRODUCTION

Recoilless fractions are very good probes of the local atomic motions around the equilibrium positions in solids.¹⁻³ They could be measured either by using coherent methods, i.e., x-ray or neutron diffraction, or by incoherent methods like the Mössbauer spectroscopy. Incoherent methods do not suffer from the static disorder contributions, but they usually operate at the constant wave number. On the other hand, coherent methods have generally low-energy resolution resulting in the significant thermal diffusive contamination particularly at high temperatures. The exception is the Rayleigh scattering of the Mössbauer radiation either in the energy or time domain. It is characterized by the very good energy resolution.

Nuclear methods seem superior as the scatterers are truly pointlike. However, the standard nuclear neutron diffraction has generally poor energy resolution at the wave-number transfers required, while the Mössbauer spectroscopy operates at the constant wave number and for the limited range of scatterers. One has to realize that the nuclear (Mössbauer) forward or Bragg scattering of the synchrotron radiation is a two step process, and hence it suffers from the constant wave-number restriction as well.

The paper is aimed at the analysis of the recoilless fractions behavior in sodium chloride based on the data obtained by the Rayleigh scattering of the Mössbauer radiation from single crystals.^{4,5} Super sources of ¹⁸³W were used for the purpose.⁶

TABLE I. Coefficients of the lattice constant dependence upon temperature. Interpolation valid between 50 and 950 K. Note irrelevance of the linear term in agreement with the quantum-mechanical expectations.

a_0 [Å]	5.5870(4)
C_1 [Å/K]	$1.7 \times 10^{-7} (68 \times 10^{-7})$
C_2 [Å/K ²]	$7.8(4) \times 10^{-7}$
C_3 [Å/K ³]	$-1.34(9) \times 10^{-9}$
C_4 [Å/K ⁴]	$1.25(9) \times 10^{-12}$
C_5 [Å/K ⁵]	$-4.5(4) \times 10^{-16}$

II. RECOILLESS FRACTIONS IN NaCl

The recoilless fraction f can be approximated in the following way for an atom residing in a site having cubic symmetry with the inversion center:⁷

$$f = \exp(-\{q^2 \langle R^{(2)} \rangle + q^4 [\langle R^{(4)} \rangle - b_{40}^{(4)} (5(\sin \theta)^2 \times \{1 - (\sin \theta)^2 [1 - (\sin \phi)^2 + (\sin \phi)^4]\} - 1])\}), \quad (1)$$

provided all terms higher than quartic are neglected, and the isotropic part is described completely by the even terms. Here, q stands for the wave-number transfer to the system, θ and ϕ denote polar and azimuthal angles of the wave-vector transfer to the system in the main crystal coordinates ($\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$), respectively, while the parameters $\langle R^{(2)} \rangle$, $\langle R^{(4)} \rangle$, and $b_{40}^{(4)}$ describe vibrational dynamics. The latter parameters are temperature dependent. More details may be found in Ref. 7.

Recoilless fractions have been calculated versus temperature in the main axis and the chemical unit-cell diagonal directions for the average sodium cation and chlorine anion, respectively, based upon the results published in Ref. 4, and for various Bragg reflections. The latter results have been derived from the Rayleigh scattering of the Mössbauer radiation (RSMR) measurements performed upon single crystals at various temperatures and for various Bragg reflections having wave-vector transfer either along the main crystal axis or along the cell diagonal. The former reflections had even Miller indices, while the latter had either even or odd

TABLE II. Parameters describing recoilless fractions versus temperature. Temperature range covered: 300–950 K for Na and 220–950 K for Cl.

	Na	Cl
A [-]	$1.14(9) \times 10^{-4}$	$5.6(4) \times 10^{-5}$
B [1/K]	$2.01(2) \times 10^{-6}$	$1.33(1) \times 10^{-6}$
α [-]	$-2.0(4) \times 10^{-9}$	0.0
β [1/K ³]	$6.51(5) \times 10^{-16}$	$6.46(3) \times 10^{-16}$
a [-]	$2.2(2) \times 10^{-8}$	$1.41(7) \times 10^{-8}$
b [1/K]	$-1.38(9) \times 10^{-10}$	$-1.06(4) \times 10^{-10}$
c [1/K ²]	$4.2(1) \times 10^{-13}$	$3.50(5) \times 10^{-13}$

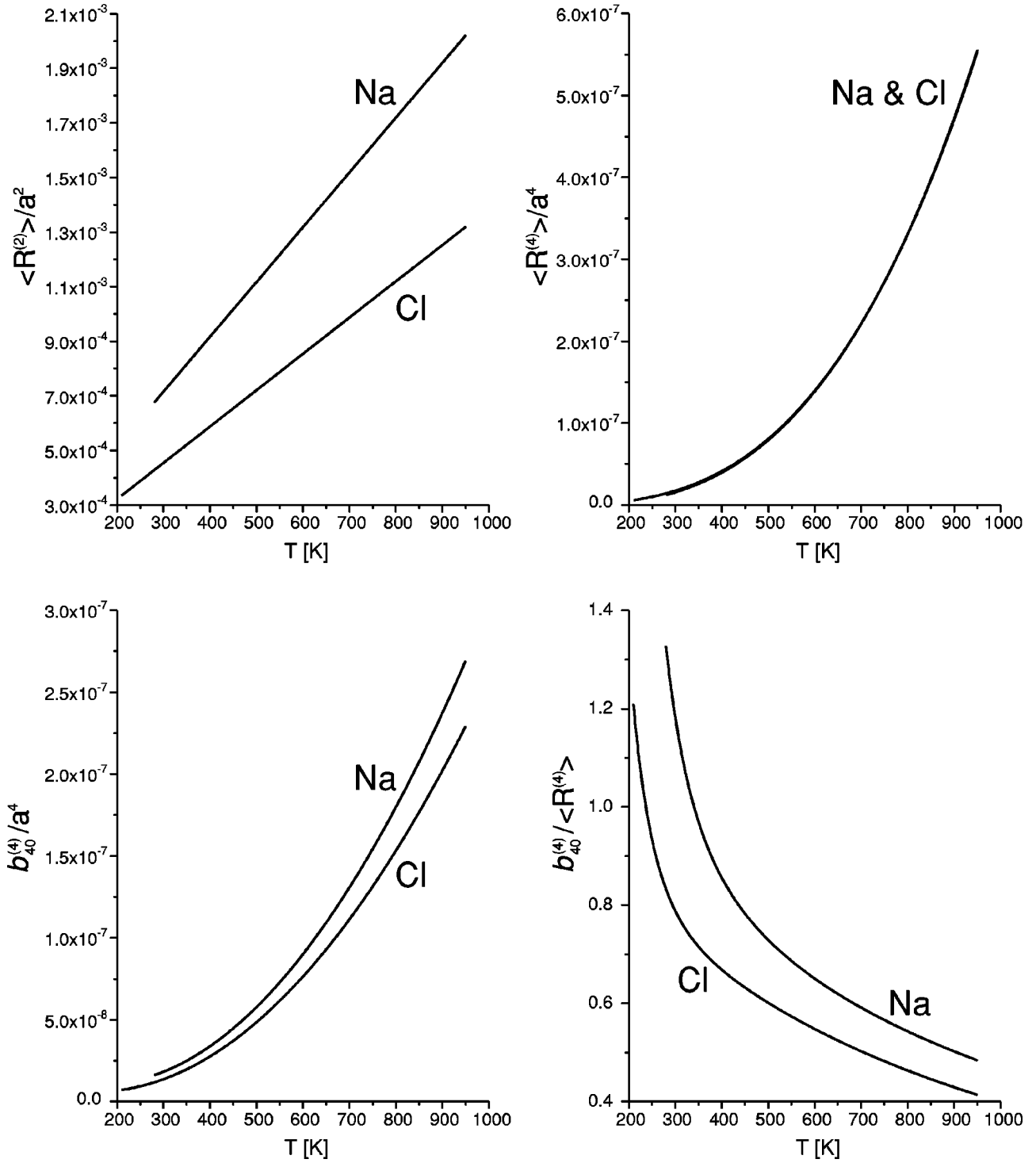


FIG. 1. Parameters of the recoilless fractions plotted as functions of the temperature at “zero” pressure.

indices. The 46.5-keV γ -ray line of ^{183}W was used as the radiation source. Experimental details are described in Ref. 4. The energy resolution of the RSMR method assures that the intensity under the Bragg reflection is entirely due to the elastic component with the negligible thermal diffusive contribution.

The lattice constant $a(T)$ evolution with the temperature T has been approximated by the relationship

$$a(T) = a_0 + \sum_{k=1}^5 C_k T^k, \quad (2)$$

where the parameters a_0 and C_k have been fitted to the data of Refs. 8–10. The numerical results are summarized in Table I. The function $a(T)$ is further abbreviated by the symbol a . Hence the “natural” units of length were used in further calculations, i.e., fractions of the lattice constant at a given temperature. Such an approach is possible in the cubic systems with the unique length scale.

Calculated recoilless fractions have been fitted to the parameters: $\langle R^{(2)} \rangle / a^2$, $\langle R^{(4)} \rangle / a^4$, and $b_{40}^{(4)} / a^4$ separately for the average sodium cation and chlorine anion versus temperature. The following temperature dependencies were found

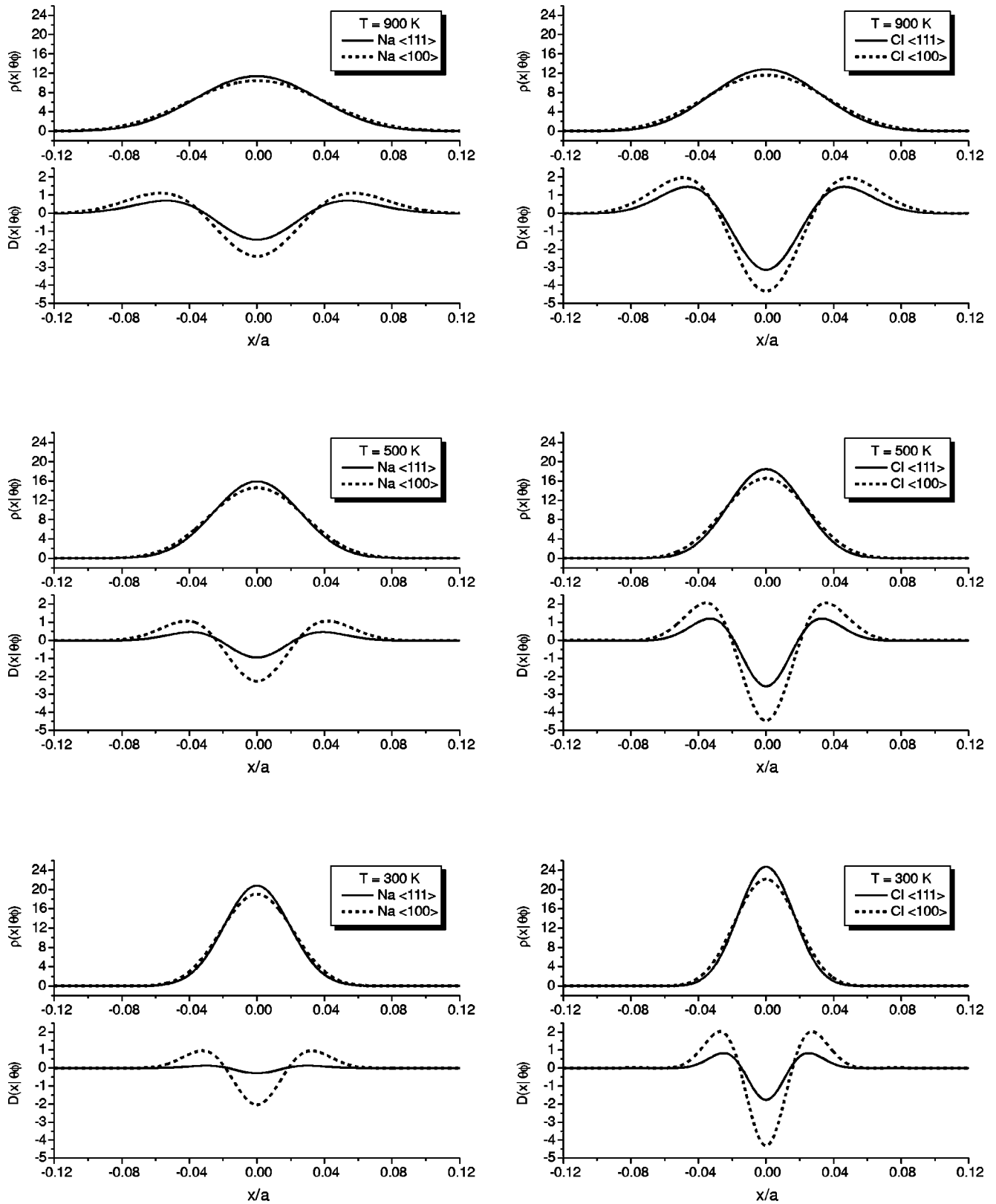


FIG. 2. Functions $\rho(x|\theta\phi)$ and $D(x|\theta\phi)$ plotted versus x/a for sodium and chlorine at various temperatures and for the angles ($\theta\phi$) corresponding either to the $\langle 100 \rangle$ or $\langle 111 \rangle$ crystal directions. One has to note that the above functions are dimensionless in the x/a coordinates.

applying polynomial fits with the minimum number of parameters:

$$\langle R^{(2)} \rangle / a^2 = A + BT,$$

$$\langle R^{(4)} \rangle / a^4 = \alpha + \beta T^3,$$

$$b_{40}^{(4)} / a^4 = a + bT + cT^2. \quad (3)$$

The numerical values of the parameters are listed in Table II. Additionally, the ratio $b_{40}^{(4)}/\langle R^{(4)} \rangle$ was calculated versus temperature for sodium and chlorine. The functions $\langle R^{(2)} \rangle/a^2$, $\langle R^{(4)} \rangle/a^4$, $b_{40}^{(4)}/a^4$, and $b_{40}^{(4)}/\langle R^{(4)} \rangle$ are plotted versus temperature in Fig. 1 for sodium and chlorine both.

The biggest sources of the systematic experimental errors are the following: (i) extinction, (ii) static disorder, and (iii) nonlocal character of the scattering ionic amplitudes. It seems that neither extinction nor the static disorder have any meaning for the samples investigated.⁴ Isotropic contributions to the nonlocal scattering amplitudes have been accounted for during the original data evaluation.⁴ However, the anisotropic contributions due to the solid-state effects cannot be accounted for reliably leading to the mixing between genuine recoilless fractions and the ionic scattering amplitudes (distributions of scattering electrons). This effect becomes stronger at low temperatures where the “thermal” motion is small, while the electronic distribution remains practically unaffected for the sodium chloride. It is particularly strong for light atoms with few almost unperturbed core electrons contributing to the scattering. Hence the data could be treated as reliable above 220 K for chlorine and above 300 K for sodium.

The recoilless fraction could be used to calculate a spatial distribution $\rho(x|\theta\phi)$ of the scattering center along some crystal direction ($\theta\phi$) with x being a departure from the equilibrium position. Such a distribution is Gaussian $G(x|\theta\phi)$ provided all terms higher than quadratic in the wave-vector transfer to the system are neglected. Hence it is useful to define a function $D(x|\theta\phi) = \rho(x|\theta\phi) - G(x|\theta\phi)$, the latter function being a good measure of anharmonicity.

Figure 2 shows reconstructed functions $\rho(x|\theta\phi)$ and $D(x|\theta\phi)$ plotted in the “natural” coordinates x/a for various temperatures and two crystal directions, i.e., $\langle 100 \rangle$ and $\langle 111 \rangle$, both for sodium and chlorine.

III. CONCLUSIONS

One can conclude that quadratic terms are isotropic as expected in the cubic environment. They are linear versus

temperature above the quantum region and maybe the vicinity of the melting point provided they are plotted in the natural coordinates. Hence they represent quasiharmonic motion. Residua at zero temperature are small indicating a small static disorder at all temperatures within the range investigated. The crystal is strongly ionic, and hence the static disorder is expected to be small.

Isotropic quartic terms are practically the same for sodium and chlorine within the whole temperature range considered. Such a behavior indicates that these terms are due to collective motions, i.e., interaction between acoustic phonons.

The anisotropy of the motion has the same character for both ions leading to bigger displacements along the main crystal axes in comparison with the displacements along the cell diagonals. However, lighter ions exhibit bigger anisotropy. It seems that all phonons contribute to the anisotropy as it depends upon temperature in a more complex way than quartic isotropic terms. It has to be stressed that the entire anisotropy is of the quartic character. The motion becomes more isotropic at high temperatures. The data at very low temperatures cannot be reliably evaluated due to the admixture of the scattering amplitudes anisotropy.

Departures from the Gaussian thermal distributions are quite significant at all temperatures accessible to the data evaluation. Distributions are flatter than Gaussians. This is an indication that bottoms of the potential wells are flatter than parabolic. The above flatness depends upon direction being the biggest in the main axes directions.

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