ЖУРНАЛ ФІЗИЧНИХ ДОСЛІДЖЕНЬ
т. 15, № 3 (2011) 3401(4 с.)

JOURNAL OF PHYSICAL STUDIES
v. 15, No. 3 (2011) 3401(4 p.)

SOME PARAMETERS OF CRYSTAL LATTICE DYNAMICS IN CaF$_2$, LiF, NaCl AND KCl

M. D. Raransky[1], V. N. Balazyuk[1], V. M. Sergeev[2], M. I. Melnyk[1]
[1] *Yu. Fedkovych Chernivtsi National University, 2, Kotsyubynsky St., 58012, Chernivtsi, Ukraine*
[2] *H. Skovoroda Kharkiv National Pedagogical University, 29, Artem St., 61002, Kharkiv, Ukraine*

(Received February 2, 2011; received in final form June 3, 2011)

In this paper we propose a pendulum fringe method for measuring the basic parameters of crystal lattice dynamics that allows calculating with high precision the temperature and pressure dependence of structural amplitudes $F_H(T, P)$ without measuring the energy parameters of dispersion. It is shown that theoretical calculation of the Debye temperature dependence $\theta_D(T)$ should take into account the contribution of phonon ΔM and potential $\beta\Delta T$ components.

Key words: single crystals, pendulum fringes, X-ray interferometry, structural dispersion parameters.

PACS number(s): 41.50.+h, 65.00.00

The atoms in real crystals are in a state of continuous oscillatory motion, with its amplitudes linearly dependent on temperature. Some of the resulting anharmonic effects, such as a thermal expansion of solids, the temperature dependence of the specific heat and elastic moduli, etc. are readily found experimentally. The existing traditional methods of studying the anharmonic effects that are based on measuring the thermal dependence of specific heat, the velocity of supersonic waves propagation and the integral intensity of X-radiation dispersion [1] have different selective sensitivity to frequency characteristics of crystal photon spectrum $f(\omega)$ and to methods of choosing its averaging procedures. The basic parameters of crystal lattice dynamics, such as mean-square atomic thermal shifts $\langle \bar{U}_g^2 \rangle_i$, characteristic temperatures $\langle \theta \rangle_i$ and the Grüneisen parameters γ_i can be found from the absolute values of integral dispersion intensities $I_H(T)$. However, the measurement accuracy $I_H \sim 5 \div 7\%$ does not yield trustworthy results.

In this paper we propose a pendulum fringe method for measuring the basic parameters of crystal lattice dynamics that makes it possible to measure structural amplitudes as functions of temperature and pressure $F_H(T,P)$ with a high precision ($\sim$ 0.1–1 %) [2,3] without measuring the integral intensities. The pendulum fringe method is mainly used for highly perfect dislocation-free single crystals, such as Ge, Si and SiO$_2$. We have made an attempt to use this method for alkali-halide crystals, such as CaF$_2$, LiF, NaCl and KCl, which are traditionally referred to as ideally imperfect crystals in terms of X-ray diffraction.

THEORETICAL FUNDAMENTALS OF THE METHOD

A period of pendulum oscillations equals

$$\Lambda = \frac{\lambda \left(\gamma_0 \gamma_H\right)^{1/2}}{C \left|\Psi_H\right|}, \tag{1}$$

where λ is the wavelength of the radiation being used, γ_0, γ_H are the direction cosines of incident and diffracted waves, C is the polarization factor, $\Psi_H = \frac{e^2\lambda^2}{mc^2\pi V} F_H$ is the Fourier factorization coefficient of the crystal being used, V is the unit cell volume. In the symmetric case of the Laue diffraction over a wide temperature range the relationship (1) can be presented as

$$\Lambda = A \cdot V\left(T, P\right) \exp\left[M\left(T, P\right)\right], \tag{2}$$

where

$$M\left(T, P\right) = \frac{6h^2 T}{mk\theta_D^2}\left[\Phi\left(x\right) + \frac{x}{4}\right] \cdot \frac{\sin^2\theta}{\lambda^2}, \tag{3}$$

and $x = \frac{\theta}{T}$, $\Phi(x)$ is the Debye function, and variable in close approximation can be considered as constant. For temperatures $T \geq \theta$ in the Debye–Grüneisen approximation and with account of

$$\left(\frac{d\left(\ln\theta\right)}{dT}\right) = -\gamma\beta \tag{4}$$

a relationship is easily obtained

$$\Lambda_T = \Lambda_0 \exp\left(\Delta M\right) \exp\left\{\beta\Delta T\left[1 + \Delta M\left(\gamma - \frac{1}{3}\right)\right]\right\}, \tag{5}$$

where γ is the Grüneisen parameter, β is the coefficient of crystal volume expansion; $\Delta M = M_{T_2} - M_{T_1}$, and $T_2 > T_1$, Λ_0 is the period of pendulum fringes at low temperatures.

The relationship (5) was obtained [2] with an allowance for the fact that the Debye–Waller factor is $\left[\Phi\left(x\right) + \frac{x}{4}\right] = 1$. For the crystals where β value is negligibly small, the temperature dependence $\Lambda(T)$ can be represented as

$$\Lambda_T = \Lambda_0 \exp(\Delta M). \tag{6}$$

Precisely this dependence was used in the work by N. Kato [4] for the estimation of Ge and Si characteristic temperatures. As is shown in paper [3], the neglect of factor $\exp\left\{\beta\Delta T\left[1 + \Delta M\left(\gamma - \frac{1}{3}\right)\right]\right\}$ already at room temperature leads to an error of the Λ_T calculation of 0.5–1.5 %, even for such crystals as Ge, GaAs, SiO_2, where $\beta \approx 10^{-6}$ K^{-1}. Such changes of Λ_T can be readily detected experimentally, particularly at high temperatures [3].

At isothermal compression and $T > \theta$, from (1) we can derive

$$\left(\frac{d\ln\Lambda}{dP}\right)_T = \left(\frac{d\ln V}{dP}\right)_T + \left(\frac{dM}{dP}\right)_T . \qquad (7)$$

Factor M in the Debye–Waller factor can be represented as $M = B\cdot\theta_D^{-2}\cdot V^{-2/3}$, where B is a P-independent constant. In the Debye–Grüneisen approximation

$$\left(\frac{d\theta}{dP}\right)_T = \left(\frac{d\theta}{dV}\right)_T \cdot \left(\frac{dV}{dP}\right)_T , \qquad (8)$$

and

$$\left(\frac{d\theta}{dV}\right)_T = \frac{\gamma_P\,\theta}{V}; \quad \left(\frac{dV}{dP}\right)_T = -\chi V. \qquad (9)$$

Then from (7) we can derive

$$\left(\frac{d\ln\Lambda}{dP}\right)_T = -\chi\,P\left[1+2M\left(\gamma_P-\frac{1}{3}\right)\right]. \qquad (10)$$

Integrating (10) within $P_0 \to P$ we obtain

$$\Lambda_P = \Lambda_0 \exp\left\{-\chi\,P\left[1+2M\left(\gamma_P-\frac{1}{3}\right)\right]\right\}, \qquad (11)$$

where Λ_0 is a period of pendulum fringes at the atmospheric pressure, χ is the isothermal compressibility, γ_P is the isothermal Grüneisen parameter.

Variation of Λ_P quantities for Ge and Si single crystals ($\chi_{\mathrm{Ge}} = 1.33\cdot10^{-11}$ m^2/H, $\chi_{\mathrm{Si}} = 1.022\cdot10^{-11}$ m^2/H) was determined experimentally in the pressure range of $10\div30$ kbar [2].

ANALYSIS OF THE EXPERIMENTAL RESULTS

The measurement of pendulum oscillation periods Λ_T was carried out in the temperature range of 100–700 K. Single crystals with the dislocation density $\rho \le 10^2$ cm^{-2} were made wedge-shaped with the angle of 1.5–3 °. CuK_α- and MoK_α-radiations were used. The effect of different factors on the pendulum fringe location and the accuracy of measuring Λ periods is discussed in paper [5]. Temperature dependences $\ln\frac{\Lambda_T}{\Lambda_0}$ for CaF_2, LiF, NaCl and KCl single crystals are shown in Fig. 1. Unlike integrated intensity, we can observe the growth of $\ln\frac{\Lambda_T}{\Lambda_0}$ values with a rise in temperature. It is significant that the functional dependence $\ln\frac{\Lambda_T}{\Lambda_0}$ on T is nonlinear. Let us analyze the previously derived relationship (5) and rewrite it as

$$\ln\frac{\Lambda_T}{\Lambda_0} = \Delta M + \beta\Delta T\left[1+\Delta M\left(\gamma-\frac{1}{3}\right)\right]. \qquad (12)$$

Such a representation allows to separate the contribution of phonon ΔM and potential $\beta\Delta T$ summands to dependence Λ_T. Theoretical calculations show that for CaF_2, LiF, NaCl and KCl single crystals the prevailing summand takes into account thermal expansion $\beta\Delta T$, whereas for Si, Ge, GaAs single crystals — ΔM [2]. Relationship (5) was obtained on the assumption of a volume dependence of the characteristic temperature θ_D. However, the experimental determination of $\theta_D(T)$ in the temperature range of 100–700 K for given single crystals shows that characteristic temperature is a function of temperature (Fig. 2), and its dependence in the form of (4) proves to be underrated compared with the experimental one. Similar conclusions were obtained while measuring the temperature dependences of the integral intensities for many materials (see, for example, [6]). Taking into account the volume and temperature dependence of characteristic temperature, we can write:

$$\frac{d\ln\theta}{dT} = \left(\frac{\partial\ln\theta}{\partial V}\right)_T dV + \left(\frac{\partial\ln\theta}{\partial T}\right)_V dT, \qquad (13)$$

or

$$\frac{d\ln\theta}{dT} = -\gamma\beta + \left(\frac{\partial\ln\theta}{\partial T}\right)_V dT. \qquad (14)$$

As there is no explicit dependence $\theta(T)$, the addend in equation (14) can be estimated only experimentally. In Mikhalchenko's paper [6], estimation is made of the quantity

$$\left(\frac{d\ln\theta}{dT}\right)_V \approx \tau\gamma\beta, \qquad (15)$$

where factor τ=1÷2. Integrating (15) within the limits ΔT=$T_2 - T_1$, we get

$$\theta_T = \theta_0\left(1-\tau\gamma\beta\Delta T\right). \qquad (16)$$

Taking into account the semi-empirical dependence (16), it seems possible to determine the Grüneisen parameter γ from the experimental values $\theta(T)$, which at T=293 K for the referred single crystals proved to be: $\gamma_{\mathrm{CaF_2}} = 0.9$; $\gamma_{\mathrm{LiF}} = 1.5$; $\gamma_{\mathrm{NaCl}} = \gamma_{\mathrm{KCl}} = 1.6$. In papers [7, 8] the Grüneisen parameters γ were calculated for some metals and alkaline-halide compounds based on the experimental values of averaged elastic moduli and the velocity of acoustic wave propagation. The Grüneisen parameters given in those papers are: $\gamma_{\mathrm{CaF_2}} = 1.38$; $\gamma_{\mathrm{LiF}} = 1.34$; $\gamma_{\mathrm{NaCl}} = 1.6$; $\gamma_{\mathrm{KCl}} = 1.47$.

The authors have analyzed the effect of lateral and longitudinal strain on the anharmonicity of atomic oscillations in the crystal lattice. With regard to velocity averaging of the acoustic wave propagation for polycrystals made by the authors of papers [7, 8] one can state a satisfactory agreement between the γ values that we established for single crystals under study. In the general case, it must be also taken into account that the Grüneisen parameters γ for the anisotropic materials are tensor quantities.

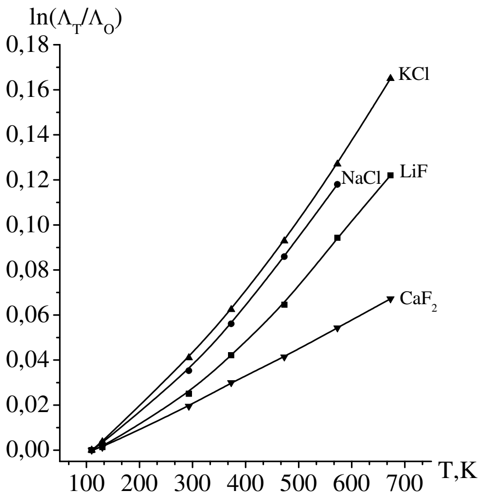

Fig. 1. Temperature dependences $\ln\frac{\Lambda_T}{\Lambda_0}$ for CaF_2, LiF, NaCl and KCl single crystals.

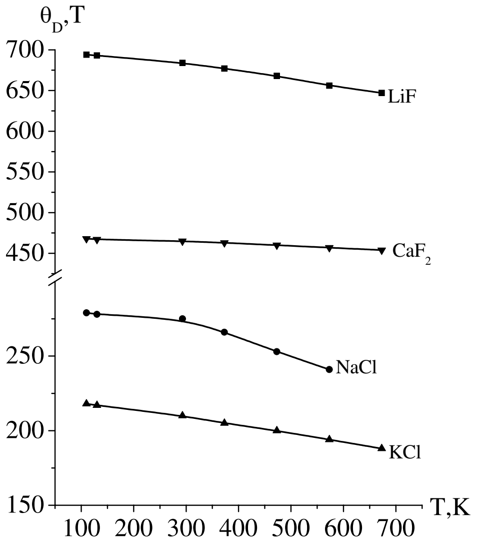

Fig. 2. Temperature dependences $\theta_D(T)$ for CaF_2, LiF, NaCl and KCl single crystals.

It must be also noted that there is a marked difference between the theoretically calculated $\theta_T(T)$ and the experimental $\theta_e(T)$. This is due to the fact that the temperature dependence Λ_T (5) for these single crystals is mainly determined by the factor $\exp(\beta\Delta T)$, whereas the factor $\exp(\Delta M)$ is of importance and makes 20–30 % of the general contribution to dependence Λ_T. Therefore, the account of thermal expansion alone does not provide full agreement between the theory and the experiment. Secondly, these single crystals have diatomic lattices, where the anion and cation masses are different. Therefore, one should also expect their different frequency contribution to the total crystal phonon spectrum.

In paper [6] it is shown that product $\gamma\cdot\beta$, rather than γ or β separately, should be considered a generalized measure of anharmonicity. As follows from the experimental result analysis, these crystals can be arranged as the "anharmonicity row" KCl, NaCl, LiF and CaF_2, followed by SiO_2, GaAs, Ge and Si single crystals [2].

Table 1 shows characteristic temperatures of these crystals measured by a calorimetric method θ_C [9,10], elastic constant method θ_y [11], integrated intensity method θ_P [12] and pendulum fringe method θ_Λ.

Single crystals	θ_y	θ_C	θ_P	θ_Λ
KCl	224	224	230	210
NaCl	306	306	280	275
LiF	700	700	—	684
CaF_2	515	514	—	465

Table 1. Values of characteristic temperatures at $T = 273$ K.

It should be noted that $\theta_C \approx \theta_y > \theta_P \approx \theta_\Lambda$. Such inequality is determined by different selective sensitivity of experimental methods to the frequency characteristic of phonon spectra. More specifically, the values θ_C and θ_y are insensitive to a specific form of the phonon spectrum and are determined by its long-wave part alone, whereas θ_P is determined by averaging over the entire range of the phonon frequency spectrum. For the same reason, the pendulum fringe method gives the values $\theta_\Lambda \approx \theta_P < \theta_C$. In conclusion, it should be noted that for low-symmetry crystals the basic parameters of the crystal lattice dynamics are tensor quantities.

---

[1] G. Leibfried, V. Ludwig, *Theory of anharmonic effects in crystals. Translation from English*, edited by V. L. Bonch-Bruyevich (Inostrannaya Literatura, Moscow, 1963).

[2] G. S. Boyadzhan, I. P. Mikhailyuk, M. D. Raransky, Ukr. J. Phys. **18**, 327 (1973).

[3] M. D. Raransky, G. S. Boyadzhan, Solid State Phys. **25**, 298 (1983).

[4] H. Hattori, H. Kuriyama, T. Katagawa, N. Kato, J. Phys. Soc. Jpn **20**, 988 (1965).

[5] I. P. Mikhailyuk, M. D. Raransky, S. A. Kshevetsky, Ukr. J. Phys. **10**, 1742 (1970).

[6] V. P. Mikhalchenko, G. P. Kooshta, Ukr. J. Phys. **9**, 799 (1964).

[7] V. N. Belomestnikh, E. P. Tesleva, Theor. J. Phys. **74**, 140 (2004).

[8] D. S. Sanditov, V. V. Mandatov, B. D. Sanditov, Solid State Phys. **51**, 947 (2009).

[9] S. A. Novikova, *Thermal expansion of solids* (Nauka, Moscow, 1974).

[10] *Acoustical crystals*, edited by M. P. Shaskolskaya (Nauka, Moscow, 1982).

[11] *Physical acoustics — Principles and Methods, Vol. III, Part B: Lattice dynamics*, edited by W. P. Mason , (Academic Press, New York, London, 1965).

[12] E. I. Geshko, V. P. Mikhalchenko, Ukr. J. Phys. **15**, 635 (1971).

ДЕЯКІ ПАРАМЕТРИ ДИНАМІКИ КРИСТАЛІЧНОЇ ҐРАТКИ $\mathbf{CaF_2}$, LiF, NaCl I KCl

М. Д. Раранський[1], В. Н. Балазюк[1], В. М. Сергєєв[2], М. І. Мельник[1]
[1] *Чернівецький національний університет ім. Ю.Федьковича*
вул. Коцюбинського, 2, Чернівці, 58012, Україна
[2] *Харківський національний педагогічний університет ім. Г. Сковороди*
вул. Артема, 29, Харків, 61002, Україна

У статті запропоновано метод маятникових смуг для визначення залежностей структурних амплітуд від температури й тиску $F_{hkl}(T, P)$ без вимірювання інтеґральних інтенсивностей. Досліджено температурні залежності періодів маятникових осциляцій Λ_T в інтервалі температур 100–700 K лужногалоїдних монокристалів $\mathrm{CaF_2}$, LiF, NaCl, KCl та досконалих монокристалів Ge, GaAs, SiOв Cu та MoK_α — випромінюваннях. Проаналізовано розбіжності числових значень температур Дебая $\theta_{\mathrm{D}}()$, розрахованих із температурних залежностей $\Lambda_T(T)$ і пружних модулів C_{ijkl}. Установлено, що максимальний внесок в $\Lambda_T(T)$ робить доданок, який враховує термічне розширення — $\beta\Delta T$. Фонний доданок Δ становить 20–30%. Тому врахування тільки теплового розширення не забезпечує повного узгодження теорії з експериментом.

Із експериментальних температурних залежностей $\theta_{\mathrm{D}}(T)$ визначено параметри Ґрюнайзена γ лужногалоїдних монокристалів $\mathrm{CaF_2}$, LiF, NaCl, KCl, числові значення яких відповідно рівні: $\gamma_{\mathrm{CaF_2}} = 0.9$ і 1.38; $\gamma_{\mathrm{LiF}} = 1.5$ і 1.34; $\gamma_{\mathrm{NaCl}} = 1.6$ і 1.6; $\gamma_{\mathrm{KCl}} = 1.6$ і 1.47.