

High-Temperature Thermoconductivity of Nitrogen-Type Crystals

V.B. Kokshenev^{1,2*}, I.N. Krupskii² and Yu.G. Kravchenko²

¹ *Departamento de Física, Universidade Federal de Minas Gerais*

ICEx, C.P. 702, CEP 30161-970, Belo Horizonte, MG, Brazil

² *Institute for Low Temperature Physics and Engineering of the Academy of Science of Ukraine, Kharkov 310 164, Ukraine*

Received May 15, 1997

We firstly report on the leading scattering mechanism responsible for the heat resistivity in simple molecular crystals. The analysis is given in the terms the phonon and libron three-particle-scattering processes in crystals formed by linear molecules (N_2 , CO, CO_2 , N_2O , etc.) On the basis of a comparison of heat resistivity estimations with known experimental data the dominated microscopic scattering mechanism is established, namely, the process of absorption (and emission) of the one libron by the two acoustic phonons.

I. Introduction

The fact of the presence of molecular rotation in molecular crystals besides to vibration motion, leads to formation of additional libron branches in the crystal spectrum which in a way can be treated as an analog of optical phonon modes. In the general case, because of a narrow width of the libron zones their contribution to the whole heat flow is rather small, except in a few special cases, when certain conditions of a libron heat transfer are hold [1]. On the other hand, the role of librions in a α - N_2 , α -CO, N_2O and CO_2 crystals as a scattering subsystem is very important [2].

The family of N_2 -type crystals is formed by linear molecules, the molecular centers of mass of which occupy *fcc* sites, and their axes are directed along the four spatial diagonals of the cube. In the case of solid N_2 and CO the angular vibrations of molecules are highly anharmonic even at the lowest temperatures [3] and the barriers preventing the molecule rotation are comparatively small. As a consequence, both crystals undergo phase orientational transitions with increasing temperature into orientationally disordered phase. By contrast, in the specific case of N_2O and CO_2 molecular crystals the anisotropic molecular interaction is too strong so that they conserve the orientational order structure up to their triple points temperatures. By

the same reason in the whole region of existence of solid state phase their libration anharmonicity is rather weak comparatively to that of N_2 and CO crystals.

For a long period N_2 -type crystals have been a subject of intensive experimental and theoretical investigations and a lot of data on their thermal properties have been carefully selected and analyzed in a review book [3]. Later, the data on thermoconductivity (reversed to heat resistivity) of N_2O and CO have been obtained [4] at temperatures above 140 K. They give clear evidence that phonon-phonon contribution to heat resistivity of both crystals is much larger than those earlier derived [2] from experiment. From the facts at hand we came to conclusion that the role of the phonon scattering mechanisms should be revised. We propose a new analysis of the thermal conductivity data [4-6] in the high temperature range, where three-particle scattering processes cause the linear temperature dependence of heat resistivity.

For α -phase of N_2 crystal this range takes place up to the lowest temperatures (23 K) achieved in the experiment [5]. In cases of α -CO, N_2O and CO_2 these correspond to temperatures above 26K, 50K and 70K, respectively [4-6]. Therefore, the temperature behavior of thermal resistivity can be represented by usual way, namely, $W = A + BT$. The coefficient A differs from zero only for case of CO and N_2O crystals formed

*E-mail: VALERY@oraculo.lcc.ufmg.br

by the asymmetrical molecules with a small dipole moment. As it was mentioned in Refs. 4 and 6, this part (A) of heat resistivity is caused by head-to-tail disorder

effect of asymmetrical molecules. The values of coefficients A and B derived from experimental data for all four crystals are given in Table 1.

Table 1. Parameters for the heat resistivity components.

Parameter	Equation	α -N ₂	CO	N ₂ O	CO ₂
A , cm K/Watt	in text	-	30	50	-
B , cm /Watt	in text	11.76	6.00	1.27	1.07
B_0 cm K/Watt	(4)	2.95	2.09	0.57	0.49
W_1/W_0	(1a)	2.88	1.48	1.18	1.13
W_2/W_0	(2a)	0.11	0.39	0.06	0.04
mr^2/I	(1a)	53.0	51.1	17.4	15.8

II. Analysis of the thermoresistivity

To analyze the part of resistivity caused by orientational subsystem of molecular crystals we need to derive the contribution of pure *phonon-phonon* scattering. In case of Ref.2 this has been analyzed through Leibfried and Schlömann formula [7], given by Eq.(4) below. Due to the model simplifications employed to obtain this formula it leads to some numerical errors. Additionally, it does not take into account non-acoustic branches of the crystal spectrum. Here we derive the *phonon-phonon* scattering contribution effectively from experimental data avoiding the theoretical estimations of A and B values. For this purpose these contributions have been plotted in reduced coordinates in Fig. 1. The dashed-dotted line corresponds to the pure phonon-phonon contribution which, within the reduced coordinates, is approximated by a universal constant for all the family of *fcc* crystals. The reduced molecular coordinates [8] are introduced through the temperature $T^* = T/T_{mol}$ where $T_{mol} = \epsilon/K$, and the heat resistivity $W^* = W/W_{mol}$, where $W_{mol} = (r^2/K)(m/\epsilon)^{1/2}$. Here ϵ stands for the effective molecular binding energy, m is the molecular mass and r is the intermolecular distance in the lattice at zero temperature. As it follows from Fig. 1 reduced heat resistivities of N₂O and CO solids nearly coincide in the linear dependence range. At the same time the reduced heat resistivities of light representatives of the crystals under discussion are systematically higher. Thus, we conclude that at least for the ordered phases of N₂ and CO the contribution of libron scattering mechanisms to the heat resistivity

is rather large. Also, the relative position of curves suggests that this contribution does not decrease but, instead, increases with lowering of rotational barriers, preventing the rotation of molecules in the lattice. This contradiction to the result [2] will find his explanation in the current analysis.

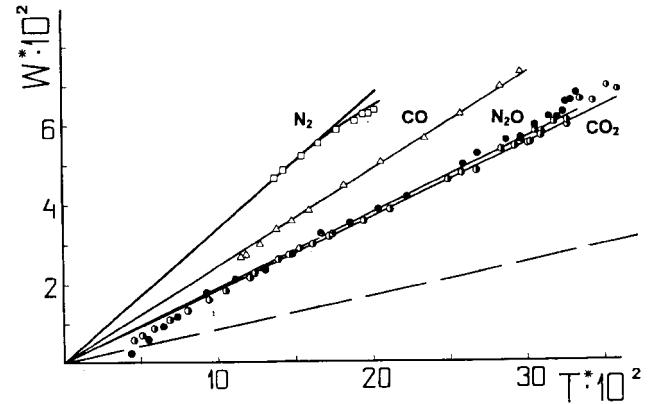
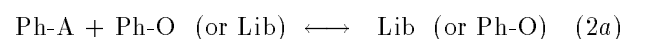
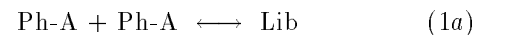


Figure 1. Temperature dependence of heat resistivity in reduced coordinates for α -N₂ (\square) [5,6], α -CO (Δ) [5,6], N₂O (\bullet) [4] and CO₂ (\bullet) [4]. (For the cases of α -CO and N₂O the data displayed after a subtraction of the component caused by head-tail disorder). The solid straight lines show the best fitting results to find universal parameters of the theory and the dashed-dotted line shows the contribution of generalized phonon-phonon scattering processes (4). For the case of α -CO the departure of linear behavior is calculated by taking into account the softening of libron modes near the $\alpha - \beta$ transition.

In the crystals under discussion the participation of librons in the process of heat flow scattering can be described at least by three type of interactions:



where the notations Ph-A, Lib and Ph-O stand for acoustic phonons, librions and optical phonons, respectively. Which of the processes shown above yields the most important contribution to heat resistivity? This question has been firstly discussed through a comparison of phonon scattering amplitudes [2,9] in the scope of molecular field approximation (MFA). In other words, the angular potential energy part has been considered as a function of angle departures of molecules from their equilibrium positions given by self-consistent molecular field. In this case the third partial derivative of the energy by double translation and single angle-deviation

coordinates of molecules equals zero. It results to the one-libron scattering processes (1a) which do not contribute at all to the total heat resistivity of the crystals. Other estimations, realized beyond the scope of MFA restore this term and involve a large factor mr^2/l (m and l stand for mass and moment inertia of a linear molecule) instead of that for the squared rotational barrier. Taking this into account we have reestimated the heat resistivity terms for *libron-phonon* processes (1a) and (2a) and the final result can be represented in the following form [2]:

$$W_1(T) = C_1 T \left(\frac{h}{k_B} \right)^3 \frac{\gamma_{lib}^2}{mr\Theta^3} \frac{mr^2}{l} S_1 \quad S_1 = \sum_{\nu\nu'} g_\nu \phi_\nu \quad (1b)$$

$$W_2(T) = C_2 T \left(\frac{h}{k_B} \right)^3 \frac{\gamma_{lib}^2}{mr\Theta^3} \frac{mr^2}{l} S_2 \quad S_2 = \sum_{\nu} g_\nu g_{\nu'} f_{\nu\nu'} \quad (2b)$$

The direct estimation shows that the two-libron process (3a) contribution to W_3 is negligible. The results can be physically understood as a generalization of the known expressions in the theory the heat resistivity due to the pure *phonon-phonon* scattering processes obtained by Leibfried and Schlömann [7]:

$$W_0(T) = C_0 T \left(\frac{h}{k_B} \right)^3 \frac{\gamma_{lib}^2}{mr\Theta^3} \quad (4)$$

Here C_1 , C_2 (and C_0) are adjustable parameters which are defined by the geometry of the crystal and, therefore, are common for all the family of *fcc* crystals under discussion; γ_{lib} and γ_{Ph} are the libron and phonon Grüneisen parameters averaged over their spectra; (Θ) stands for characteristic temperature of the acoustic spectrum part; ϕ_ν and g_ν are the degeneracies of libron and optical phonon branches. The estimations for constant energy surfaces S_1 and S_2 have been given in the framework of the simplest Debye-Einstein model for the process (1) [2,10]:

$$\phi_\nu = (\alpha\nu - 1)^2(-\alpha\nu + 6\alpha\nu^3 - 1) ; \alpha_\nu = \Theta_\nu/\Theta \quad (1c)$$

and that for the process (2) [1]:

$$f_{\nu\nu'} = \sigma_{\nu\nu'}^3(12 - \sigma_{\nu\nu'}^2) ; \sigma_{\nu\nu'} = |\Theta_\nu - \Theta_{\nu'}|/\Theta \quad (2c)$$

where Θ_ν and $\Theta_{\nu'}$, are libron and optical phonon frequencies. The magnitudes of these values, those of Debye characteristic temperature Θ_0 (for $T = 0$), Θ_∞ (high temperatures) and $\Theta = \Theta(4)^{1/3}$ (averaged over four sublattices) are summarized in Table 2 as well as summations (1b) and (2b). By rearranging we obtain the heat resistivity of a molecular crystal in the following form, for case of pure *phonon-phonon* (4) and two *libron-phonon* scattering mechanisms (1) and (2), namely:

$$W(T) = BT ; B = B_0[1 + (mr^2/l)(\alpha S_1 + \beta S_2)] , \quad (5)$$

where the sums S_1 and S_2 are given by (1b) and (2b). The values of γ_{lib} are included into universal coefficients α and β because of their closeness for all crystals under discussion [3]. These coefficients have been derived from the best fitting (5) to the data [4-6] in the reduced coordinates described above. Here we used suggestion

that all the reduced values of W_0 (4) has the same value for the crystals under discussion as it was firstly proved for the case of solidificated inert gases [8]. As a result, the best fitting values of B_0^* , α and β : 0.085, $7.19 \cdot 10^{-3}$

and $3.49 \cdot 10^{-5}$ have been achieved, respectively. These in turn permitted us to make a numerical analysis of all kind of scattering mechanisms introduced above which form the heat resistivity of N_2 -type crystals.

Table 2. Characteristic temperatures (or energies) [3] for acoustic phonons (Ph-A), optical phonons (Ph-O) and librons (Lib).

Energy, Kr	Mode	α -N ₂	CO	N ₂ O	CO ₂
Θ_0	Ph-A	83.5	103	141	152
Θ_∞	Ph-A	76.2	89.00	119.9	128.3
Θ	Ph-A	48.0	56.10	75.5	80.8
Θ_0	Ph-O Au	67.34	92.80	149.6	151.2
	Ph-O Eu	77.69	83.45	134.8	136.3
	Ph-O Tu	69.92	71.65	95.68	97.12
	Ph-O Tu	99.85	123.02	162.6	163.73
Θ_{lib}	Lib Eg	46.19	64.03	100.7	108.48
	Lib Tg	52.37	75.54	119.1	134.38
	Lib Tg	86.33	130.93	181.6	191.93
S_1	Eq. (1b)	7.56	4.03	9.41	9.92
S_2	Eq. (2b)	58.8	217.4	95.1	75.1

III. Results and discussion

As it follows from Table 1 the process (1) is the major contribution to the heat conductivity of N_2 -type crystals and its intensity grows with anharmonicity of librons. For the case of α -N₂ this component is three times larger than that for the phonon-phonon scattering processes (4). At the same time the contribution of the process (2), which includes a participation of one libron and one optical phonon, to the total heat resistivity was found to be small. Thus, for crystals α -N₂, N₂O and CO₂ this contribution is not larger than 2 or 3% of their whole heat resistivity and only for the case of α -CO it reaches 13.5 % because of a large value of factor S_2 (2b).

Taking into account the magnitude of the factor mr^2/l (see Table 1), one can conclude that the role of two-libron scattering processes (3) is negligible. A similar conclusion can be arrived to with respect to the processes of a resonant absorption of acoustic phonons during their interaction with two optical phonons. In addition, it follows from the result obtained above that the contribution of the scattering process of two acoustic and one optical phonons to heat resistivity W_0 (4) is also comparatively small. At last, we argue that the phonon component of heat resistivity of these crystals is

almost entirely driven by interactions limited to acoustic phonons.

The analysis presented here shows that the libron component of the α -N₂ heat resistivity is related, in general to the highest energy libron branch Tg. Indeed, at low temperatures this provides a maximum for the function ϕ_ν (1c). For the case of α -CO the energy of this branch is higher than 2Θ , so that because of the energy conservation law, the librons of this branch do not take part in the process (1). That is the reason why the resulting contribution of these librons is approximately half lower less for this case than that for the case of α -N₂. On the other hand, the effect of softening of the libron modes with temperature leads to the gradually bringing into the scattering type (2) of these librons, which are on the bottom edge of high frequency zone. The growing of the crystal heat resistivity evidently only compensates its fast decrease which is due to the softening of other libron modes. As a result in the case the of α -CO the linear dependence of $W^*(T^*)$ extends up to the highest temperatures. In the case of α -N₂ both effects have the same sign and as a result the increase of heat resistivity gradually slows down as one gets closer the to $\alpha - \beta$ temperature transition where the temperature dependence of resistivity W deviates from the linear one appreciably. Our estimation for this

deviation taking into account the temperature dependence of libron modes[3] is also displayed in Fig. 1.

In the case of the other couple of crystals, namely N_2O and CO_2 , the molecule binding energy is almost completely determined by the anisotropic part of the interactions. This leads to the fact that the frequency ratio of libron to phonon modes conserves with increasing temperature and the linear behavior W^* should take place up to the highest temperatures. This gives a reason to suggest that multi-particle scattering processes play an important role at the temperature region near the triple points, where a tendency for growing of the heat resistivity of N_2 -type crystals was observed.

One of the authors (V.B.K.) is thankful to the Brazilian agencies FAPEMIG, CAPES and CNPq for their financial support provided for the completion of this work and also to D.N. Domingues for his helpful technical assistance.

References

1. V.B. Kokshenev, Yu.G. Kravchenko and I.N.

- Krupskii, Sov. J. Low Temp. Phys. **11**, 172 (1985).
2. V.G. Manzhelii, V.B. Kokshenev, L.A. Koloskova *et al.*, Sov. J. Low Temp. Phys. **1**, 624 (1975).
3. B.I. Verkin and A.F. Prihot'ko, *Cryocrystals* (In Russian Kiev: Naykova Dumka) (1983).
4. Yu.G. Kravchenko and I.N. Krupskii Sov. J. Low Temp. Phys. **12**, 46 (1986).
- 5 L.A. Koloskova, I.N. Krupskii, V.G. Manzhelii *et.al.*, Sov. Phys. Solid State **15**, 403 (1973).
6. L.A. Koloskova, I.N. Krupskii, V.G. Manzhelii *et.al.*, Sov. Phys. Solid State **16**, 1993 (1974).
7. G. Leibfried and E. Schlömann, *Warmeleitung in Elektrisch Isolierenden Kristallen* (Gottingen: Nachr. Akad. Wiss. Math. Physik) (1954).
8. I.N. Krupskii and V.G. Manzhelii, Sov. Phys. JETP **28**, 1097 (1969).
9. V.A. Slusarev and Yu.A. Freiman, J. Low Temp. Phys. **9**, 675 (1972).
10. P. Leroux-Hugon and J.J. Veyssie, Phys. Stat. Sol. **8**, 561 (1965).