

Thermal Conductivity and Heat Capacity of Dianin's Clathrates under Pressure

Ove Andersson,^{*,†} Vladimir Murashov,[‡] and Mary Anne White[‡]

Department of Experimental Physics, Umeå University, S-901 87 Umeå, Sweden, and
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

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The thermal conductivities, λ , and heat capacities of polycrystalline Dianin's compound and its CCl_4 and ethanol clathrates have been investigated in the temperature range 40–300 K for pressures up to 1 GPa. All high-pressure results for λ show typical crystal-like behavior, whereas previous atmospheric pressure results for single crystals as well as recent results on polycrystalline samples show glasslike behavior. The change from glasslike to crystal-like dependence might be caused by a frequency shift of localized vibrations on pressurization, moving the localized vibrations outside the frequency range of the dominant heat carriers and reducing thermal resistance due to resonance scattering.

Introduction

Thermal conductivity, λ , is among the most fundamental properties of a material and can, in fact, limit applications. For example, in the search for new thermoelectrics, high-lattice thermal conductivity is a limiting factor at present. In general, thermal conductivity models are well-established for metals and simple crystalline insulators, such as alkali halides. In the latter, phonon–phonon Umklapp scattering is the main source for thermal resistivity, at least at temperatures on the order of and above the Debye temperature. This scattering results in the commonly observed T^{-1} dependence for λ of simple crystals.

Quite different behavior is found for some materials, especially glasses, which exhibit much lower λ and the opposite sign for the temperature coefficients, i.e., $d\lambda/dT > 0$. The detailed theoretical interpretation of this behavior is less firmly established than for simple crystals. In general, all glasses show a positive or “glasslike” temperature dependence of λ , but not all crystals show a T^{-1} or “crystal-like” dependence. While minor deviations from $\lambda \propto T^{-1}$ in crystalline materials might be attributed to scattering from structural disorder such as dislocations and grain boundaries, there are some substances which show glasslike $\lambda(T)$ despite being crystalline. Examples are clathrate hydrates,¹ other clathrates,^{2–5} and a crystalline polymer.⁶ These extreme deviations from the normal crystalline behavior are both unusual and of practical value, especially in enhancing the figure of merit for thermoelectrics. If the reasons for this thermal conductivity behavior are known, they could provide further understanding of λ of glasses and complex crystals.

Clathrates are inclusion compounds in which cages in the host lattice structure can accommodate various types of guest molecules.⁷ In clathrate hydrates, the host is H_2O , and it forms several kinds of Archimedean polyhedral cages through hydrogen bonds. Clathrate hydrates with guest species tetrahydrofuran, 1,3-dioxolane, cyclobutanone, ethylene oxide, methane, propane, and Xe all show glasslike behavior for λ .⁸ (In one investigation, $\lambda(T)$ was crystal-like for a slowly cooled specimen, but this finding is not supported by other investigations.⁸) Unfortunately,

clathrate hydrates are not stable without the guest molecules. Consequently, it is not possible to directly investigate if their behavior is due to the lattice structure, e.g., their unusually large unit cell, or due to interactions between guest and host molecules. The latter, in which the interaction causes resonance scattering of phonons, is the most frequently employed model^{4,5,9–12} and has also been used to explain the anisotropic thermal conductivity of highly oriented polyethylene.¹³ Indeed, on the basis of the thermal resistivity associated with low-frequency “rattlers”, reduced thermal conductivity for potential thermoelectric materials was postulated by Slack and Tsoukala¹⁴ and realized by Nolas et al.¹⁵ Although the evidence for the resonance mechanism for thermal resistance is somewhat indirect, incoherent inelastic neutron scattering of methane hydrate¹⁶ and recently of xenon hydrate¹² has shown that the guest species interact strongly with the host lattice. In principle, application of pressure could affect resonance scattering of heat-carrying acoustic phonons, possibly changing the thermal conductivity behavior. To explore these questions, we have undertaken a high-pressure investigation of the organic compound known as Dianin's compound [4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman], which forms both clathrates and an isostructural form that is stable without guests.

The thermal conductivities of single crystals of Dianin's compound, and its ethanol and CCl_4 clathrates have been studied at atmospheric pressure.^{4,5} The results show glasslike behavior for all samples. That is, even the empty host lattice exhibits a positive $d\lambda/dT$. These somewhat unexpected results could be described using the relaxation time model for λ , in which Umklapp, boundary, and resonance scattering were taken into account. The latter, which was the dominant scattering source, was ascribed to interaction of localized optic modes with the acoustic modes of the host lattice. The localized modes were associated with low-frequency vibrations (e.g., the methyl groups) in the empty host lattice and with both these and the guest molecules in the clathrates. The more mobile ethanol guests lowered the thermal conductivity more, whereas the rather rigid CCl_4 guests did not appreciably change the thermal conductivity in comparison with that of the empty host lattice.

The present work concerns an investigation of powdered samples of Dianin's compound and its ethanol and CCl_4 clathrates at elevated pressures as well as at atmospheric

* Corresponding author.

[†] Umeå University.

[‡] Dalhousie University.

pressure. Normally, the application of high pressure increases the magnitude of λ but does not significantly change the isobaric temperature dependence of λ . In fact, for clathrate hydrates, results at high pressure as well as those at atmospheric pressure show glasslike behavior for λ .^{1,8} For Dianin's compound, however, we find that the temperature dependence changes from glasslike at atmospheric pressure to crystal-like at high pressures.

Experimental Section

The transient hot-wire method¹⁷ was used to measure the thermal conductivity λ at elevated pressures, and the steady-state radial heat flow method was used to confirm the high-pressure results. The methods can be used for solid samples if high pressure is applied to obtain good thermal contact between the hot-wire probe and the powdered specimen as well as between the grains in the specimen. In addition to data for λ , the hot-wire method yields values for the heat capacity per unit volume.

In the hot-wire method, the hot-wire probe was a Ni wire (0.1 mm diameter) placed horizontally in a ring of constant radius within a Teflon cell. The hot-wire probe, surrounded by the medium under investigation, was heated by a 1.4 s pulse of about constant power, and the wire resistance was measured versus time, which enabled the temperature rise of the wire to be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding λ and ρc_p . For temperatures above 100 K, the inaccuracies in λ and ρc_p were estimated as $\pm 2\%$ and $\pm 5\%$, respectively. Due to the decreased sensitivity of the hot-wire (smaller derivative of resistance with respect to temperature), the inaccuracy in λ increased with decreasing temperature and was $\pm 4\%$ at 40 K. The inaccuracy in ρc_p has not been estimated below 100 K but is significantly larger than $\pm 5\%$. The standard deviation in the measurements was an order of magnitude smaller than the inaccuracy.

For the steady-state radial heat flow method, we used a cylindrical geometry with a 40 mm long heater (1 mm in diameter) placed in the center of a Teflon cell, which was filled with sample (40 mm in diameter). The temperature difference between two different radii was measured using a Chromel versus Alumel thermocouple, which had been calibrated against a commercially available silicon diode thermometer. The results were corrected for the axial heat loss (about 15%), which was calculated using finite element analysis.

The Teflon cells were mounted in a piston-cylinder type of pressure vessel of 45 mm internal diameter, and the load was applied using a 5 MN hydraulic press. Temperature was varied by cooling or warming the whole pressure vessel and measured using an internal Chromel versus Alumel thermocouple. The inaccuracy in temperature was estimated as ± 0.5 K. Pressure was determined from load/area with an empirical correction for friction which had been established using the pressure dependence of the resistance of a manganin wire. The inaccuracy in pressure was estimated as ± 40 MPa at 1 GPa and room temperature and, due to increased friction, ± 60 MPa at the lowest temperatures. The vessel was cooled with a refrigerator using a closed helium gas cycle. The apparatus has been described in detail elsewhere.¹⁸

A modulated heat flow method¹⁹ was used to measure λ of polycrystalline sample at atmospheric pressure.

The polycrystalline materials were prepared according to a published procedure.²⁰ The CCl_4 adduct was characterized using X-ray analysis, and the results agree within experimental inaccuracy with those previously published: rhombohedral, space group $R\bar{3}$, with $a = 27.134(8)$ Å, $c = 10.933(2)$ Å, and

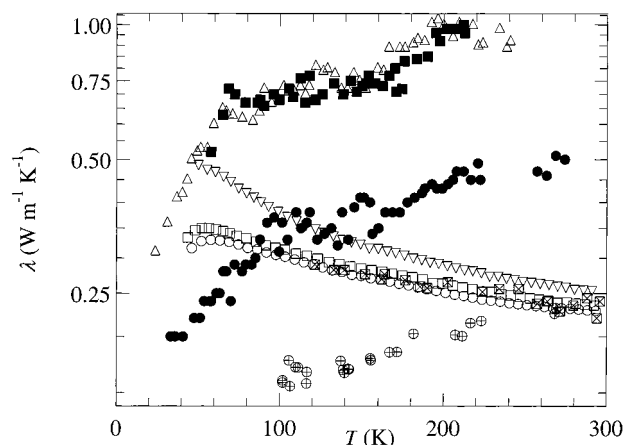


Figure 1. Thermal conductivity as a function of temperature for Dianin's compound: (∇ , Δ) without guests, (\circ , \bullet) ethanol clathrate, and (\square , \blacksquare) CCl_4 clathrate, where the first symbols represent data at 0.2 GPa for polycrystalline specimen (CCl_4 clathrate at 0.15 GPa) and the second symbols represent single-crystal data at atmospheric pressure.^{4,5} (\oplus , \boxplus) represent data for polycrystalline samples of ethanol and CCl_4 clathrate at atmospheric pressure and 0.15 GPa, respectively.

$Z = 10$.²¹ Furthermore, the X-ray diffraction patterns before and after the high-pressure experiments were the same to within experimental inaccuracy, which shows that pressurization does not cause an irreversible change of structure that could be detected with X-ray analysis. In some of the high-pressure measurements, the material was taken from the same batch as that used for the atmospheric pressure measurements, which eliminates the possibility that the difference between the high- and low-pressure results is due to different materials.

Results and Discussion

Figure 1 shows results for $\lambda(T)$ of polycrystalline specimen using the hot-wire and the radial heat flow methods under pressure, together with results obtained for single crystals^{4,5} and polycrystalline specimen at atmospheric pressure. All samples show simple crystal-like behavior for λ at high pressures, although they exhibit a deviation from the "ideal" T^{-1} dependence. A fit of a function $\lambda \propto T^{-x}$ yielded $x = 0.4$ for the empty Dianin's compound, whereas the two clathrates both yielded $x = 0.3$. These results indicate that Umklapp processes provide an important contribution to the thermal resistivity, but other scattering processes are significant for the thermal resistivity. The results are typical for complex crystals but significantly different from the glasslike results observed previously for these materials as single crystals at atmospheric pressure (Figure 1).

The different behaviors for λ could be associated with the sample morphology (powder, compared with single crystals from the earlier work^{4,5}) or the application of pressure. To investigate the former, we measured λ of powdered samples of the ethanol clathrate of Dianin's compound using a modulated heat flow method without applied pressure.¹⁹ The powdered samples should yield smaller values for λ and slightly different temperature dependence if we assume perfect thermal contact between the grains. (Normally, λ of single simple crystals show better agreement with T^{-1} dependence than that of a polycrystalline sample since the temperature dependence of the latter can be somewhat weaker due to boundary scattering.) The results for $\lambda(T)$ of the powdered samples without applied pressure are shown in Figure 1; they show the expected decrease in λ for the powdered sample, but essentially the same glasslike $\lambda(T)$ behavior as the single crystals, indicating that the sample

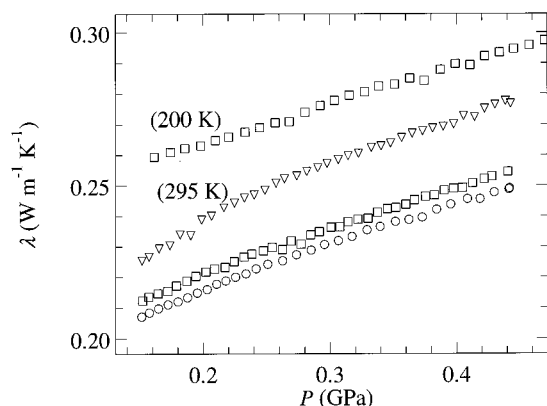


Figure 2. Thermal conductivity as a function of pressure for Dianin's compound: (∇) empty compound, (\circ) ethanol clathrate, and (\square) CCl₄ clathrate.

morphology does not play an important role in the change in thermal conductivity behavior observed in the high-pressure experiment.

The change in behavior for λ might, therefore, be induced by the high-pressure conditions. To confirm the hot-wire result, we used the well-established radial heat flow method under pressure. The results at 0.15 GPa are shown in Figure 1, and the data agree well with the hot-wire results. After the sample had been compacted at high pressure, the pressure was released to study the low-pressure behavior. The results showed somewhat weaker temperature dependence than at high pressure, but the glasslike dependence observed in the atmospheric pressure investigation could not be verified. (The hot-wire method cannot be used at low pressures due to the thermal resistance between wire and sample.) One possibility is that the sample changes irreversibly after application of high pressure, even though the X-ray analysis does not support this hypothesis.

At pressures above 0.03 GPa (0.06, 0.15, 0.2, and 0.4 GPa), λ of all the samples showed a crystal-like behavior. The results had similar temperature dependencies but were shifted in magnitude by an amount which agrees well with that obtained from results of isothermal pressurization (Figure 2). The isothermal results for λ at room temperature and at 200 K for the CCl₄ clathrate show the commonly observed, almost linear, increase of λ with increasing pressures in the range 0.05–0.4 GPa.

The density dependence of λ can be calculated from data for $\lambda(P)$ and the bulk modulus and is generally described by the Bridgman parameter $g = (\partial \ln \lambda / \partial \ln \rho)_T$. The bulk moduli B of Dianin's compound and its clathrates have not been measured directly, but for the ethanol clathrate, it can be calculated from the measured values for the elastic constants, which yields $B = 7.8$ GPa.²² The resulting value for g is 5 at 295 K, which is in the range 5–10 that crystals normally exhibit.²³

Data for $\rho c_p(T)$ at 0.2 GPa are shown in Figure 3. The ethanol and CCl₄ clathrate exhibit slightly larger values than that of the empty compound, but the differences are within the experimental inaccuracy. The results are in good agreement with atmospheric pressure results. At 295 and 50 K at 0.2 GPa, we obtain 1.54 and 0.28 MJ m⁻³ K⁻¹ for CCl₄ clathrate, in comparison with 1.57 and 0.28 MJ m⁻³ K⁻¹ at atmospheric pressure.²⁴

The data for ρc_p of the CCl₄ adduct for pressures up to 1 GPa at room temperature are shown in Figure 4. (The other samples were not investigated at this high pressure.) Normally, data for ρc_p change smoothly with pressure. However, in this case, one can observe a weak dip at 0.7 GPa, which might be

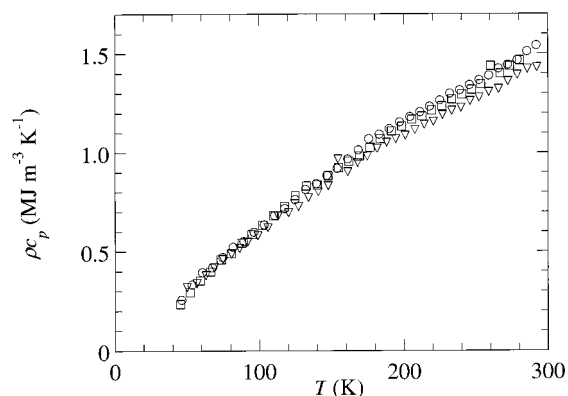


Figure 3. Heat capacity per unit volume as a function of temperature at 0.2 GPa for: (∇) empty compound, (\circ) ethanol clathrate, and (\square) CCl₄ clathrate.

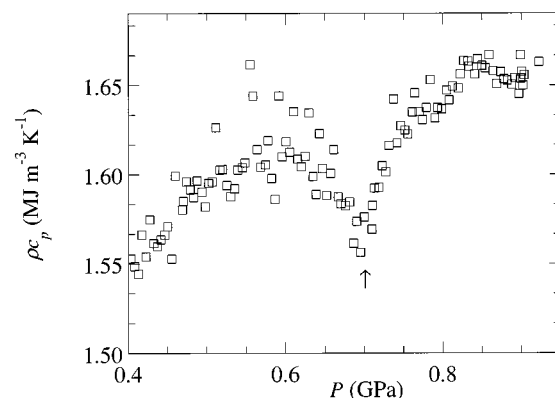


Figure 4. Heat capacity per unit volume as a function of pressure for CCl₄ clathrate at 295 K. The arrow indicates the pressure for a possible phase transition.

associated with a phase transition. Since the isobaric data at 0.4 GPa show no signs of a transition, the hypothetical phase line may not intersect the atmospheric pressure isobar. In any case, this possible phase transition cannot explain the different behaviors in λ at atmospheric and high pressures.

The previous atmospheric pressure results for λ of single crystals of Dianin's compound and its clathrates at ordinary pressures were interpreted using the relaxation time model,^{25,26} in which resonance scattering was the major source for phonon scattering. Since the results here for the ethanol clathrate of Dianin's compound are glasslike at atmospheric pressure, the resonance scattering model can also account for these results. The high-pressure results, however, cannot be interpreted in terms of strong resonance scattering, as it yields a positive $d\lambda/dT$. One possible explanation for this difference is that application of high-pressure moves the localized vibrations to outside the frequency range of the dominant heat carriers. As a consequence, the localized vibrations are less effective in phonon scattering, and the main sources for phonon scattering at high pressure would be the same as those in other complex crystals. To investigate this hypothesis, we studied the Raman spectra of the CCl₄ clathrate under pressure to explore if any low-frequency modes are strongly affected by pressure. The results, using a diode laser with an excitation wavelength of 782 nm, are shown in Figure 5. As can be seen, there are several modes at low wavenumbers, which are potential candidates as resonance scatters. However, in the range investigated here (>70 cm⁻¹), there are no significant changes with pressure. Consequently, if pressure moves the optic-acoustic interaction off resonance, either the responsible heat-scattering optic mode must

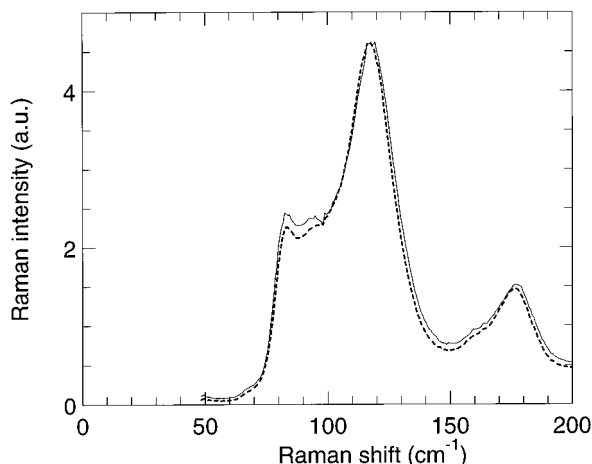


Figure 5. Raman intensity as a function of Raman shift for Dianin's clathrate with CCl_4 guests: broken line at atmospheric pressure and solid line at about 1 GPa. The maximum intensity at 1 GPa was scaled to coincide with that at atmospheric pressure.

be below 70 cm^{-1} , which is the most likely range for such scatters, or else the frequencies of the dominant heat-carrying acoustic phonons change strongly with pressure.

Complex crystals commonly show a more or less pronounced deviation from the "ideal" T^{-1} dependence of λ but not to such an extent that the behavior is usually glasslike. The origin for the deviation from T^{-1} dependence is not well-established in detail, but it can be roughly accounted for by scattering by phonons (Umklapp) and structural disorder, where the latter is associated with a relaxation time of a type similar to boundary scattering (i.e., almost or entirely independent of phonon frequency). The equation for the relaxation time model of λ , is given by^{25,26}

$$\lambda = \frac{k_B^4 T^3}{2\nu\pi^2\hbar^3} \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (1)$$

where θ_D is the Debye temperature, ν is the phonon velocity, $\tau(x)$ is the resultant relaxation time, and $x = \hbar\omega/k_B T$, where ω is the phonon angular frequency and the other symbols have their usual meanings. The relaxation time for three-phonon Umklapp processes at $T \geq \theta_D$ is of the form^{25,26}

$$\tau_u^{-1}(x) = Ax^2 T^3 \quad (2)$$

where A is the scattering strength for Umklapp scattering.

To account for various scattering processes associated with structural defects, e.g., point defects, boundaries, etc., in analyzing the present data, the following resultant relaxation time was used in eq 1:

$$\tau^{-1}(x) = Ax^2 T^3 + Bx^4 T^4 + \nu/C \quad (3)$$

where B and C are constants which normally are associated with point defect and boundary scattering, respectively. However, at these relatively high temperatures, the difference in the temperature dependence of λ arising from scattering processes with slightly different dependences on phonon frequencies is small. For example, scattering from dislocations ($\tau^{-1} \propto \omega$) yields about the same dependence as one governed by a constant relaxation time, i.e., the same as for boundary scattering. Consequently, the last two terms in eq 3, also can account for scattering processes which have slightly different dependence on phonon frequency than point defect and boundary scattering.

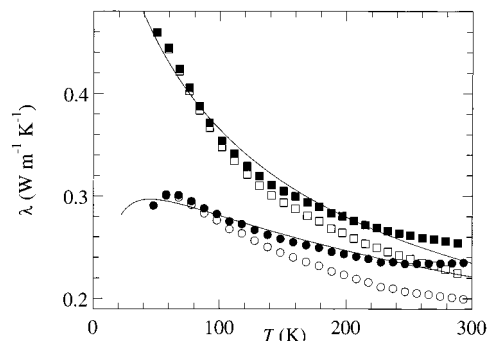


Figure 6. Thermal conductivity as a function of temperature for Dianin's compound: (□, ■) without guests and (○, ●) ethanol clathrate, where the first symbols represent isobaric data at 0.2 GPa and the second symbols represent the same data transformed to isochoric conditions pertaining to the volume at the lowest temperature. The lines are theoretical fits of eq 1 to the isochoric data.

The theory described by eq 1 comes from a constant volume approach and does not take into account changes in experimental values of λ arising from thermal expansion. It follows that in order to make the best comparison with theory, the measured isobaric data should be transformed to isochoric conditions. The change in λ due to expansion alone is given by

$$\left(\frac{\partial \ln \lambda}{\partial T} \right)_p - \left(\frac{\partial \ln \lambda}{\partial T} \right)_\rho = -g\alpha \quad (4)$$

where g is again the Bridgman parameter and α is the volume thermal expansivity. Assuming that the value for g of the ethanol clathrate, discussed above, also gives a good estimate for the CCl_4 clathrate and the empty compound, the isobaric experimental data for λ were transformed to isochoric conditions. The transformation introduced less than 15% change in λ , and the data for the empty compound and the ethanol clathrate are shown in Figure 6.

The results of the fits of eq 1 to the isochoric data for λ with τ given by eq 3 are also shown in Figure 6. The values for θ_D (170 K) and ν ($2.2 \times 10^3 \text{ m/s}$) were taken from ref 27 and assumed to be the same for all samples. The results for A and B were on the order of 10^5 for all samples, which in the case of A agrees with results for other substances, e.g., ice.²⁸ The values for B are larger than those generally found in pure crystals,^{25,28} but about the same value has been reported for C_{60} .²⁹ The value for C was on order of 10^{-5} for Dianin's compound without guests and on order of 10^{-6} for the ethanol and CCl_4 clathrates. The relative importance of the various scattering processes must be interpreted with caution due to uncertainty in the theory for λ of complex crystals and uncertainty in the form of the resultant relaxation time. In addition, the parameter fits are less sensitive at these relatively high temperatures. However, the fits show that the results can be approximately described using the normal relaxation time model. For Dianin's compound without guests, the model indicates that Umklapp and point defect scattering are the most important thermal resistance processes, but a scattering process which exhibits little dependence on phonon frequency also contributes to a significant extent, especially at low temperatures. In the ethanol clathrate of Dianin's compound, the effect of the latter is so pronounced that the maximum of λ falls within the temperature range of the measurements.

In conclusion, Dianin's compound without guests, and its ethanol and CCl_4 clathrates show results for $\lambda(T)$ at high pressures which are crystal-like, in contrast with the glasslike dependence which is observed at atmospheric pressure. The relaxation time model indicates that Umklapp and point-defect

scattering are the most significant sources of thermal resistance at high pressures, in contrast with results at atmospheric pressure which show glasslike behavior which is plausibly associated with strong resonance scattering of heat-carrying phonons. Further direct investigations of phonon interactions in Dianin's compound at elevated pressures could be very interesting. These could provide information about the mechanism of the change in thermal conductivity behavior with pressure and therefore help delineate the origins of thermal resistance in glasses and complex crystals.

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