

SPECIFIC HEAT, THERMAL DIFFUSIVITY AND THERMAL CONDUCTIVITY IN THE PHASE TRANSITION OF THE NaN_3 SINGLE CRYSTAL

EUDOVÍT KUBIČÁK, Bratislava

INTRODUCTION

When its physical characteristics in dependence on temperature are measured, the NaN_3 crystal shows certain anomalies. Its structure is rhomboedric with the space group $R\bar{3}c$ of the calcite type [1]. This basic structure is practically preserved until the melting point (305 °C) but at 275 °C a phase transition sets in [2 — 17].

There exist two models to explain the behaviour of the NaN_3 crystal during the phase transition: The model of static or dynamic disorder of NO_3 groups on the one hand, and the model of free rotation of NO_3 groups on the other. The views of authors [2 — 17] regarding the suitability of some of the mentioned models differ. I shall discuss the experiments and conclusions of the different authors [2 — 17] with respect to the elucidation of the behaviour of the NaN_3 crystal during the phase transition.

When the electric conductivity of NaN_3 is measured, no perceptible change occurs during the phase transition [2, 3]. There is a sudden rise of the dielectric constant at this temperature [2]. In the X-ray diffraction analysis [4] of NaN_3 the diffraction maxima from the oxygen atoms are gradually disappearing and at the critical temperature they disappear altogether — as shown in Lane's photographs. Siegel [6] maintains that the X-ray diffuse scattering of NaN_3 single crystals proves the static disorder above the critical point. According to Shinnaka [5], who also investigated the X-ray diffuse scattering on NaN_3 , at 275 °C there sets in a transition from the ordered into the disordered state, similarly as in binary alloys. Hexter [9] tried to ascertain the vibration frequency of NO_3 ions from absorption spectra in the range 500 — 3000 cm^{-1} . He excluded the free rotation of NO_3 groups. Bijvoet, Ketelarr [7] and Ketelarr, Strijk [8], who examined the structure of NaN_3 by intense X-rays, confirm the hypothesis of the rotation of groups, but they admit a disordered state above the critical point as well. Experiments with

polarized infra-rays point to the model of free rotation of NO_3 groups round a trigonal axis. They exclude point rotation round the N atoms. The paramagnetic resonance of Na^{23} in NaN_3 [10, 11] points to a dynamically disordered model above the critical point. Kornfeld and Čudinov [13] measured the constant of elasticity in dependence on temperature. Their measurements were theoretically elaborated by Dzialošinskij and Liščic [14]. They confirmed from the point of view of thermodynamics that the transition was a second order transition, wherein some constants of elasticity are changed by leaps. Several authors measured the thermal expansion coefficients and carried out the DT analysis [15, 16]. They proved that the phase transition was of the second order. Sokolov and Šmidt [17] measured the specific heat of polycrystalline NaN_3 by means of the calorimetric method. At 275 °C they found the typical λ -point of specific heat, which fact proves a phase transition of the second order.

To complement experimental findings about the behaviour of the NaN_3 crystal during the phase transition, the present paper gives measurements of specific heat, thermal diffusivity and thermal conductivity, and discusses the measurement curves.

EXPERIMENTAL METHOD

The measurement was done on a single crystal of NaN_3 . The single crystal was grown by the method in paper [2]. The necessary pieces of the sample were cut in the direction (100). The cut surfaces were sanded. The measurement was done by the method described in Krempeký's papers [18—20]. The principles of the arrangement of the experiment are shown in Fig. 1. The pulse source of heat was obtained by discharging batteries of capacitors. The plane resistance was effected by a constantan net of $\varnothing = 0.5$ mm, and was about 50 Ω/cm^2 . A Cu-constantan thermocouple was used. The course of heat re-

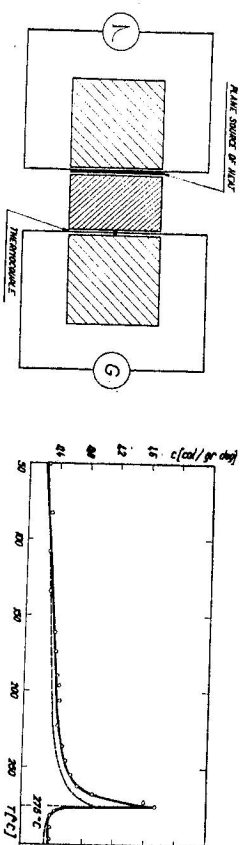


Fig. 1. The measuring of specific heat, thermal diffusivity and thermal conductivity by the pulse method.

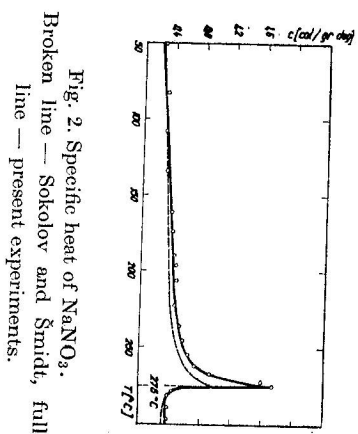


Fig. 2. Specific heat of NaN_3 . Broken line — Sokolov and Šmidt, full line — present experiments.

corded by a stylogalvanometer in the apparatus. The size of the crystal between the source and the indicator was $18 \times 18 \times 3$ mm. With the given parameters of the crystal at room temperature the maximum of heating was 0.7°C and the time of the maximum heating was about 9 sec.

RESULT AND DISCUSSION

The course of specific heat (Fig. 2) is in agreement with the measurements done by Sokolov and Šmidt [17] on polycrystalline NaNNO_3 . The peak in Fig. 2 is higher than that given by Sokolov and Šmidt. Three samples were measured, each repeatedly at temperatures ranging between 25 – 300°C . The course of the experiments was in every case the same.

The course of thermal diffusivity is in Fig. 3. As shown in the figure, there is a leap at 275°C in thermal diffusivity, comparable to the leap of the elasticity constant measurements at the critical point as found by Kornfeld and Čudinov [13].

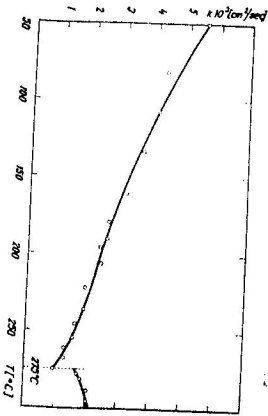


Fig. 3. Thermal diffusivity of NaNNO_3 .

According to Debye's model we can deduce from the kinetic theory of gases [21] for the thermal conductivity a simplified relation

$$\lambda = \frac{1}{3} c \cdot v_s \cdot l$$

where c is the specific heat [cal/cm^3], v_s is the sound velocity of the crystal, l is the free path of the phonons and λ is the thermal conductivity. According to [24] we have

$$\lambda = c \cdot \rho \cdot k$$

where c is the specific heat [$\text{cal}/\text{gr}^\circ$], ρ is the density of the crystal and k is the thermal diffusivity.

By comparing we obtain

$$k = \frac{1}{3} v_s \cdot l$$

The phonons taking part in the energy flux are not monochromatic. At a given temperature the spectrum of the phonons existing in the crystal is given by the density of states and the Bose-Einstein distribution law. Usually the free path and the velocity of the phonons depend on the frequency, and so we have for the thermal conductivity

$$\lambda = \frac{1}{3} \sum_j c_j \cdot v_j \cdot l_j$$

where c_j , v_j , l_j are the specific heat, the velocity of the phonon, and the free path of the phonon, belonging to the j -mode. The thermal diffusivity of the j -mode will be

$$k_j = \frac{1}{3} v_j \cdot l_j$$

Thermal diffusivity generally is a tensor magnitude and the above discussion refers to the tensor component of the thermal conductivity in the direction of the measurement, as it becomes evident from the description of the measurement.

The leap in thermal diffusivity (Fig. 3) can be explained as follows: 1. According to [13] one of the constants of elasticity changes by leaps. The change of the constants of elasticity is connected with the change of velocity of the phonons [22]. In the thermal diffusivity (Fig. 3) we have a leap towards a higher value. This would correspond to the leap of the constant of elasticity at the critical point towards lower values. According to Kornfeld and Čudinov [13] the constant of elasticity ϵ_{33} increases at a rise of temperature below the critical point and it increases above the critical point. At the critical point it has a leap towards lower values. The other constants of elasticity have a break at this point. In the above way we could explain the leap of thermal diffusivity, not its further increase, however, as evident from Fig. 3.

The leap of the constant of elasticity causes a change of frequencies of the phonons towards higher values [22]. In some types of lattice imperfections the scattering of the phonons depends upon their frequencies. By the change in the frequency distribution of the phonons there will occur a change in their free paths [23]. Within this range of temperatures the three-phonon processes predominate as causes of scattering. According to Klemens [23] there is within the range of temperatures $T > \Theta$ a relaxation time of the unklapprocesses $\tau \sim \omega/T$, where ω is the angular frequency of the phonons. The free path will then be $l_j = v_j \cdot \tau_j$. In the last relation v_j and τ_j increase, as evident from the foregoing, hence the thermal diffusivity acquires a greater value.

2. The leap of thermal diffusivity may be further explained by the change in the free path, in consequence of an increase scattering of disordered NO_3 groups. Comparing the course of specific heat (Fig. 2) with the course of thermal diffusivity (Fig. 3), we can eliminate this effect. The course of specific heat shows a large number of disordered NO_3 groups. If the leap of thermal diffusivity were caused by disordered NO_3 groups. If the leap of thermal sequence of the phonon scattering in point imperfections (disordered NO_3 groups) — a leap towards lower values.

According to Klemens [23] within this range of temperature the three-phonon processes are predominant. The scattering on lattice imperfections within this range of temperatures is negligible. One of the main reasons for the leap of thermal diffusivity is the leap of the elasticity constant.

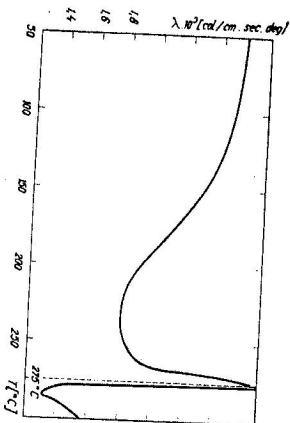


Fig. 4. Thermal conductivity of NaNO_3 .

The curve of thermal conductivity λ is in Fig. 4. Because of a great dispersion of values of c and k the values of λ were taken from the curves of specific heat c and specific diffusivity k .

CONCLUSIONS

The conclusions arrived at seem to point to the fact that the leap in thermal diffusivity is influenced by the leap of the elasticity constant ss . It may be possible, however, that at the critical point and near it other effects are decisive as well.

The structure of NaNO_3 above the critical point has not been elucidated satisfactorily either. By comparing the conclusions arrived at by other authors [1 — 17] and the results of the present experiments, it seems most probable that the NO_3 groups above the critical point have not the basic position but statistically they can take the positions which may be rotated by 180° about the trigonal axis by means of lattice vibrations. At temperatures below 275°C the structure of NaNO_3 preserves both a long and a short range order. The long range order above the critical point does not exist [5].

I wish to express my thanks to Mr. J. Eckstein for single crystals of NaNO_3 , which he kindly gave me for my measurements, and Mr. J. Krempaský for his advice as regards the technique of measurement.

REFERENCES

- [1] Wyckoff R. W. C., Phys. Rev. *16* (1920), 149.
- [2] Mariani E., Eckstein J., Rubínová E., Czech. J. Phys. *B 17* (1967), 552.
- [3] Davis W. J., Rogers S. E., Ubbelohde A. R., Proc. Roy. Soc. London *A 220* (1953), 14.
- [4] Kracek F. C., Posnjak E., Hedrick S. B., J. Amer. Chem. Soc. *53* (1931), 3331.
- [5] Shinaka Y., J. of Phys. Soc. of Japan *19* (1964), 1281.
- [6] Siegel L. A., J. Chem. Phys. *17* (1949), 1146.
- [7] Bijvoet J. M., Ketelaar J. A., J. Amer. Chem. Soc. *54* (1932), 625.
- [8] Ketelaar J. A., Strijk B., Rev. Trav. Chim. *64* (1954), 174.
- [9] Nexter R. M., Spektrochim. Acta *10* (1958), 291.
- [10] Eades R. G., Hughes D. G., Andrew E. R., Proc. Phys. Soc. *71* (1958), 1019.
- [11] Andrew E. R., Eades R. G., Hennemel J. W., Hughes D. G., Proc. Phys. Soc. *79* (1962), 954.
- [12] Sato Y., Gesi K., Takagi Y., J. of Phys. Soc. of Japan *19* (1964), 449.
- [13] Корнфельд М. И., Чудинов А. А., ЖЭТФ *1* (1967), 33.
- [14] Дзидошинский И. Е., Лифшиц Е. М., ЖЭТФ *1* (1967), 299.
- [15] Kracek F., J. Amer. Chem. Soc. *53* (1931), 2909.
- [16] Равич Г. Б., Егоров Б. Н., Ж. неорг. хим. *11* (1960), 2603.
- [17] Солодов В. А., Шмигд Н. Е., Изв. Сekt. Физ.-хим. Анал. *26* (1955), 123.
- [18] Krempaský J., Czech. J. Phys. *B 14* (1964), 533.
- [19] Krempaský J., Czech. J. Phys. *B 15* (1965), 865.
- [20] Krempaský J., Čas. pro fys. *A 16* (1966), 136.
- [21] Debye P., *Vorträge über die Kinetische Theorie der Materie und der Elektrizität*, Teubner Verlag Berlin 1914, 17—60.
- [22] Born M., Huang K., *Dynamical Theorie of Lattice*, Oxford University Press London 1954.
- [23] Klemens P. G., Proc. Phys. Soc. London *A 68* (1955), 1113.
- [24] Тихонов А. Н., Самарский А. А. *Уравнения математической физики*, МИИТТИ Москва—Ленинград 1951.

Received April 28th, 1967

Fyzikální ústav SAV,
Bratislava