SOME THERMODYNAMIC PROPERTIES OF THE CO_2 AND N_2O CRYOCRYSTALS

Nguyen Quang Hoc and Do Dinh Thanh
Hanoi National Pedagogic University
Nguyen Tang
Hanoi University of Technology

Abstract *On the basis of the moment method, the thermodynamic properties of a stro anharmonic crystal with the face centred cubic (FCC) structure are considered. Usin investigated results some thermodynamic quantities of many atomic molecular cryocry of type N_2 as the CO_2 and N_2O crystals are obtained. The results are compared with experimental data.*

I. Introduction

The thermodynamic properties of the CO_2 and N_2O cryocrystals were investig by many experimental [3-6, 9-14] and theoretical works [7, 8]. Most of the obtained re are experimental ones.

In the papers [1] Nguyen Tang and Vu Van Hung applied successfully the ge results obtained for FCC crystal to the case of inert gas crystals. In the paper [2 applied the general results to the N_2 and CO crystals. In this paper we shall cont to investigate the molecular cryocrystals of type N_2. Here we have only considered s thermodynamic quantities, for instance, the nearest neighbour distance a, the the expansion coefficient β, the specific heats at constant volume and constant pressure C_V and the isothermal and adiabatic compressibilities χ_T, χ_S of the CO_2 and N_2O cry at zero pressure. Some calculated results coincide relatively well the experimental da

II. Determination of srystal parameters

Using the Lennard - Jones interaction potential (6 - 12), the two coordinat spheres approximation, the definition of the FCC crystal parameters in [1], the experi tal data for the carbondioxide crystal , $\varepsilon/k_B = 218.82K, \sigma = 3.829 \times 10^{-10}m$ [3], an the nitrous oxide crystal, $\varepsilon/k_B = 235.48K, \sigma = 3.802 \times 10^{-10}m$ [3], we obtain the v of the crystal parameters at temperature 0K.

Crystals	k[J/ m^2]	ω[10^{13} s^{-1}]	γ[10^{21} J/ m^4]	γ_1[10^{21} J/ m^4]	γ_2[10^{21} J/ m^4]	a$_0$[1(
CO_2	3.8823	2.2066	2.1624	0.1038	0.4368	4.1
N_2O	4.2386	2.2891	2.3945	0.1150	0.4836	4.1

Table 1. Parameters of the CO_2 and N_2O crystals at T = 0K

(The extrapolation values are determined from the experimental data for CO_2 crystal, $a_0 \cong 3.9274 \times 10^{-10}m$ and for N_2O crystal, $a_0 \cong 3.9885 \times 10^{-10}m$ [3]).

II. Some thermodynamic properties of the CO_2 and N_2O cryocrystals

The determination of the thermodynamic quantities as the nearest neighbour distance a, the volume expansion coefficient β, the specific heats at constant volume and constant pressure C_V, C_P , the isothermal and adiabatic compressibilities χ_T, χ_S and the Gruneisen constant γ_G of the CO_2 and N_2O crystals is carried out similarly as in the case of the N_2 and CO crystals.

Our obtained results are compared with the experimental data in Fig. 1- 8. In these figures we have reported some theoretical and experimental results in [3] because in this work the thermodynamic properties of the cryocrystals of type N_2 are completely investigated. In comparison with experiments, for some values of quantities a, β our results coincide relatively well, but for quantities $C_V, C_P, \chi_T, \chi_S, \gamma_G$ (if using the formula $\gamma_G = \beta V/\chi_T C_V$) they only coincide in the order of magnitude. If using the more accurate interaction potential, of course, the obtained results will be better.

If using the formular $\gamma_G = (1/3)\ln(\omega/\omega_0)/\ln(a/a_0)$ [1] the values of the Gruneisen constant equal to

$$\gamma_G = 3.23 \pm 0.17 \quad \text{for} \quad CO_2,$$
$$\gamma_G = 3.12 \pm 0.06 \quad \text{for} \quad N_2O$$

The limiting temperature T_{lim} corresponding to where the quantum effects can be neglected is equal to (see [1])

$$T_{\text{lim}} \approx 1.3494 \times 10^{-10}\omega.$$

When determining the values of T_{lim} for the CO_2 and N_2O crystals we notice that $T_{lim} = 162.8K$ corresponds $T = 180K$ for the CO_2 crystal (at pressure $P = 0$). Therefore, in the case of the CO_2 crystal one cannot neglect the quantum effects for $T \leq 180K$. Because at pressure $P = 0$ CO_2 is in the crystalline state in the temperature range from to 215K, under this condition the CO_2 crystal seems to be a nearly quantum one.

For N_2O crystal at $T > 182K (T_{lim} < 185K)$ the quantum effects are neglected. Unlike CO_2, this crystal has the temperature interval $(0 - 180K)$ corresponding to the existence of the crystalline state, in which it has quantum effects. We notice T_{lim} decreases when the temperature increases, that is similar as in the case of the Debye temperature.

Thus in this paper we have used the results obtained by the moment method for investigating the thermodynamic properties of the CO_2 and N_2O crystals. In comparison with experiments some our results are relatively good. The obtained results for the CO_2 and N_2O crystals are worse than ones for the N_2 and CO crystals. The results will be better if applying the more accurate potential and calculating fully the internal molecular motion.

In conclusion, the moment method gives the neighbouring way to study app mately several structural and thermodynamic properties of the molecular cryocrysta type N_2 with the FCC structure.

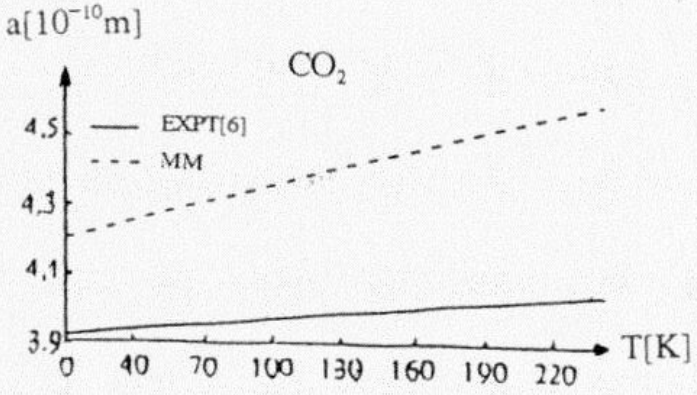


Fig.1. The temperature dependence of the nearest neighbour distance, which is determined by the moment method (MM) and the experimental data (EXPT)[6] for the CO_2 crystal.

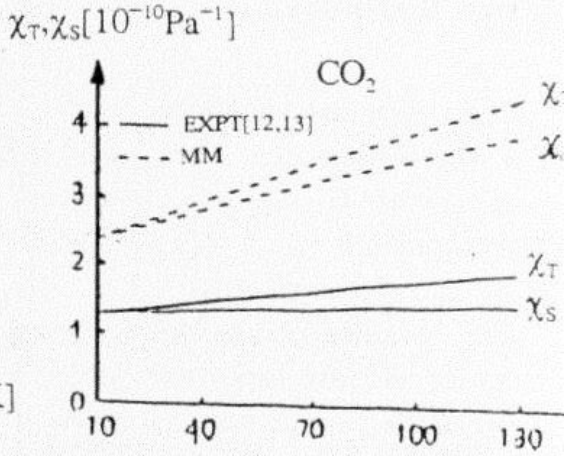


Fig.2. The temperature depend of the isothermal and adiabatic comp ibilities, which is determined by the and the EXPT [12, 13] for the CO_2 tal.

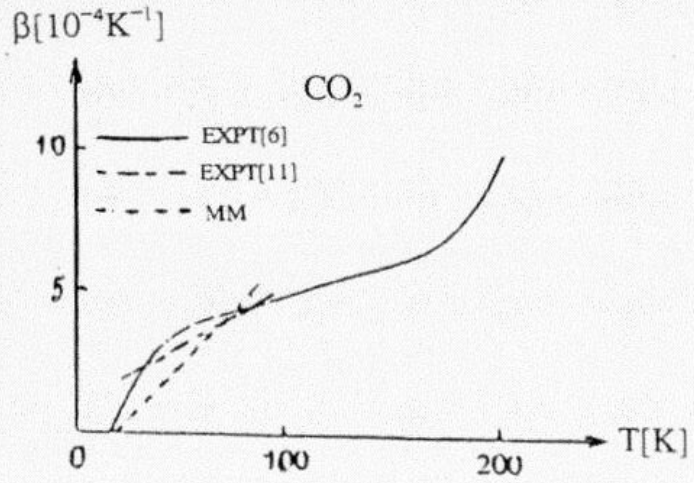


Fig.3. The temperature dependence of the volume thermal expansion coefficient, which is determined by the MM and the EXPT [6, 11] for the CO_2 crystal.

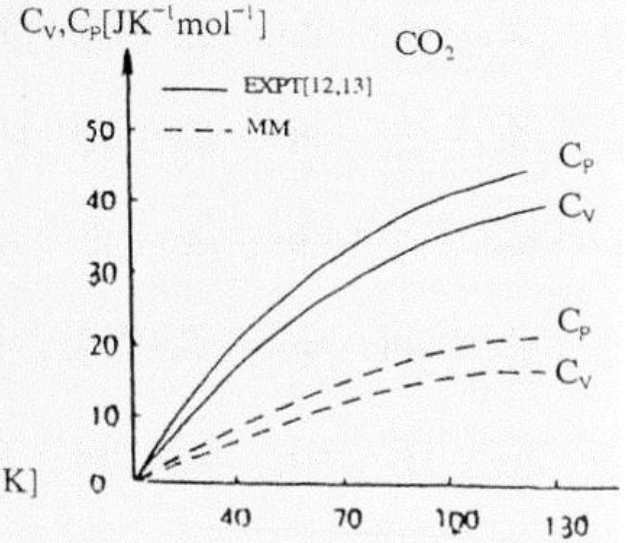
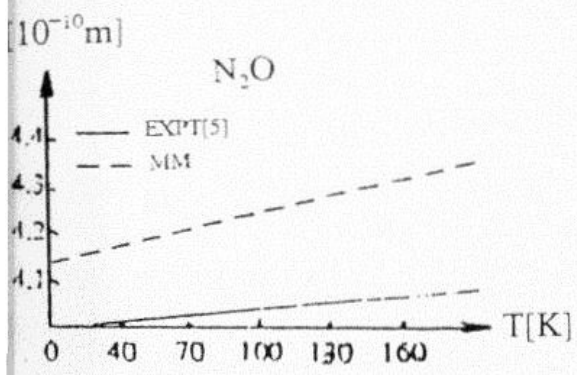


Fig.4. The temperature depend of the specific heats at constant vol and constant pressure, which is determ by the MM and the EXPT [12, 13] for CO_2 crystal.



ig.5. The temperature dependence of
ie nearest neighbor distance, which is
etermined by the moment method (MM)
id the experimental data (EXPT)[5]
r the N_2O crystal.

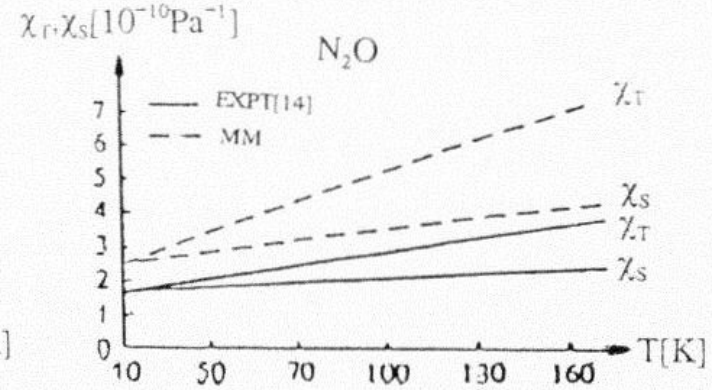
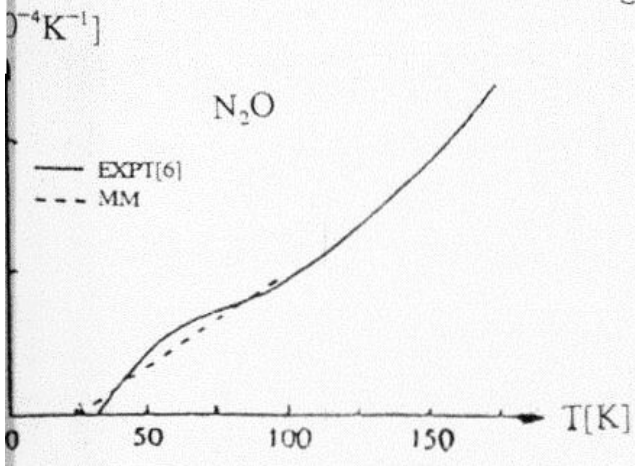


Fig.6. The temperature dependence of the isothermal and adiabatic compressibilities, which is determined by the MM and the EXPT [14] for the N_2O crystal.



ig.7. The temperature dependence of
ie volume thermal expansion coeffi-
ent, which is determined by the MM
id the EXPT [6] for the N_2O crystal.

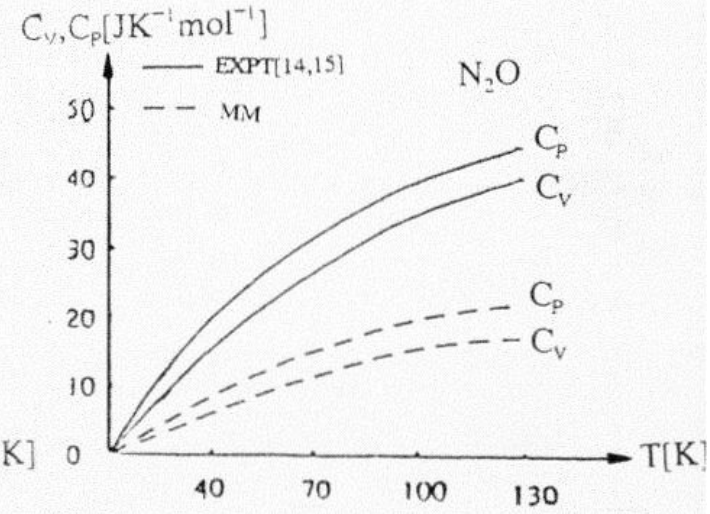


Fig.8. The temperature dependence of the specific heats at constant volume and constant pressure, which is determined by the MM and the EXPT [14, 15] for the N_2O crystal.

This work was supported by the National Basic Research Program in Natural ences under Contract KT 04 -3.1.10.

REFERENCES

[1] Nguyen Tang and Vu Van Hung. *Phys. Stat. Sol.*, (b)**149**(1988), p511; **161**(1
p 165.
[2] Nguyen Quang Hoc and Nguyen Tang. *Commun. Phys.*, **4** N1 (1994), p 65.
[3] B.I.Verkina and A.Ph. Prikhotko (Pod. red.), *Cryocrystals*, Kiev, 1983 (in sian).
[4] Yu.A.Freiman, *Fizika Nizkikh. Temperatur* **16**(1990), p 956 (in Russian).
[5] I.N.Krupskii, A.I.Erenburg, *Fizika Nizkikh. Temperatur* **6**(1980), p 1174 (in sian).
[6] I.N.Krupskii, A.I.Prikhvatilov and A.S.Barylnik, Fizika Nizkikh. *Temperature* **8**
p 533 (in Russian).
[7] A.Kode, and T.Kihara. *Chem., Phys.*, **5**(1974), p 34.
[8] T.B.Mac Rury, W.A.Steele, and B.J.Berne. *J.Chem., Phys.*, **64**(1976), p 1288
[9] R.Stevenson. *J. Chem., Phys.*, **27**(1957), p 673.
[10] J.De.Smedt, W.H.Keesom. *Proc. Kon. Ned. Akad. Wetench.* **B.27**(1924), p
[11] W.H.Keesom, J.W.Kohler. *Physic* **1**(1934), p 655.
[12] V.G.Manzhelii, A.M.Tokachev, M.I.Bagatskii and E.I.Voitovich. *Phys. Stat.* (b)**44**(1971), p 39.
[13] W.F.Giauque, and C.J.Egan. *J. Chem., Phys.*, **5**(1937), p 45.
[14] T.Atake, H.Cnihara. *Bull. Chem., Soc., Jap.*, **47**(1974), p 2126.
[15] R.W.Blue, and W.F.Giauque. *J. Amer., Chem., Soc.*, **75**(1935), p 991.

TẠP CHÍ KHOA HỌC ĐHQGHN, KHTN, t.XVI, n^{0}4 - 2000

MỘT SỐ TÍNH CHẤT NHIỆT ĐỘNG CỦA CÁC TINH THỂ LẠNH CO_2 VÀ N

Nguyễn Quang Học, Đỗ Đình Thanh
Trường Đại học Sư phạm Hà Nội
Nguyễn Tăng
Trường Đại học Bách khoa Hà Nội

Trên cơ sở các kết quả nghiên cứu tính chất nhiệt động của tinh thể phi điều mạnh với cấu trúc lập phương tâm mặt bằng phương pháp mô men tính toán một s lượng nhiệt động của các tinh thể lạnh phân tử nhiều nguyên tử loại N_2 như các thể CO_2 và N_2O và so sánh kết quả thu được với thực nghiệm.