

THERMAL EXPANSION AND EQUATION OF STATE OF KCN OF DIFFERENT ISOTOPIC COMPOSITION

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Thermal expansion and equation of state of isotopically different samples of KCN were measured in the temperature range 175–300 K and pressure up to 2 GPa by the neutron powder diffraction technique. No evidence of influence of isotopic composition on the thermal expansion or the compression isotherms were found.

1. INTRODUCTION

The influence of isotopic composition on the thermodynamic properties of substances is usually considered to be a manifestation of the quantum nature of matter. At high temperatures in the classical limit any mass effect on thermodynamic quantities disappears and hence any quantum isotopic effect vanishes. However, isotope effects of a nonquantum nature may exist under certain circumstances in condensed systems. For instance, variations of the isotopic composition in molecular systems can change the moments of inertia of the molecules, which can then influence the thermodynamic properties of the system. This is quite obvious in an ideal classical system of polyatomic molecules, where the rotational part of the free energy, entropy and thermal capacity directly depends on the molecular moments of inertia [1]. As we will see further, in the case of condensed systems one might also expect to find corresponding contributions to the compressibility and thermal expansion as well.

Below we report the data on thermal expansion and equation of states (175–300 K and 0–2.0 GPa) of KCN, substituted with various isotopes of carbon and nitrogen so that the CN^- ions have the same mass number but with different moments of inertia. The corresponding experimental data were obtained by making use the neutron powder diffraction technique.

The phase diagram and various physical properties of normal KCN have been reported in a number of papers (see for example [2–7]). The general conclusion is that in the temperature and pressure range under study, KCN has the NaCl type crystalline structure in which the orientations of the CN^- ions are disordered over a number of directions. Furthermore, the orientations of individual ions are not fixed but change very rapidly. To simplify the description,

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one may say that CN^- ions in the KCN-I phase experience almost free rotation at near ambient temperatures. In this case, using the classical approach the rotational contribution to the free energy can be written in the form [1]

$$F_{\text{rot}} = -NT \ln T - NT \ln(2J_{\text{eff}}/\hbar^2). \quad (1)$$

The value of the rotational quantum, $\hbar^2/2J$, for CN as a diatomic gas molecule, where J is the moment of inertia, is about 3 K. This looks exactly like the expression for an ideal gas of diatomic molecules except that a true moment of inertia J has been replaced with an effective value J_{eff} to take into account, at least crudely, the interaction of a molecule with its environment. The corresponding contribution to the pressure can be derived from (1):

$$p_{\text{rot}} = - \left(\frac{\partial F}{\partial V} \right)_T = \left(\frac{NT}{J_{\text{eff}}} \right) \left(\frac{\partial J_{\text{eff}}}{\partial V} \right)_T. \quad (2)$$

It is natural to assume that the effective moment of inertia J_{eff} increases with density, and hence from (2) it follows that molecular rotation gives a negative contribution to the total pressure. As can be seen from (2), the «rotational» pressure depends on the isotopic composition (by means of J_{eff}), and hence the compression isotherm and the thermal expansion curves of KCN may be split due to the difference in effective moments of inertia of isotopically substituted CN^- ions.

2. EXPERIMENTAL

Isotopically enriched samples of KCN were obtained from the Cambridge Isotope Laboratories and had a composition KC^{15}N (C — natural abundance; 99% ^{15}N) and K^{13}CN (99% ^{13}C ; N — natural abundance). These materials were used without further purification. Both samples were subjected to an ion beam analysis at the Los Alamos National Laboratory Ion Beam Materials Science Facility; both materials were found to have 180 ppm of Na contamination.

Variable temperature neutron powder diffraction studies were performed on the HIPD instrument at the Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory. Samples of the two KCN materials were placed in 6.35×38.1 -mm vanadium cans with a small amount of He gas and subsequently sealed. The thermal expansion was studied in the temperature range of 175–300 K in 25 K steps, making use of a Displex (Air Products) system, which provides temperature control to within 0.1 K. The neutron diffraction patterns were obtained in 2–4 h each with the spallation neutron source operating at a proton current of $\sim 70 \mu\text{A}$; data taken in the backscattering detectors ($2\theta = 151^\circ$) were used for subsequent data analysis. To obtain accurate values of the ambient lattice parameters for the KCN samples, neutron powder diffraction patterns were also obtained at 300 K from each KCN mixed with a small amount of CaF_2 , which provided an internal lattice parameter standard ($a_0 = 5.46384 \text{ \AA}$ at 300 K). The lattice parameter of this sample of calcium fluoride was previously determined in our laboratory by X-ray powder diffractometry with CuK_α radiation.

The compression isotherms of the two KCN samples at 300 K up to 2 GPa were obtained with the toroidal high pressure cell [8, 9]. To provide hydrostatic conditions, the samples were mixed with Fluorinert-70 (3M Co.) and placed into the cell along with a piece of lead, which was used as a pressure sensor [10]. Neutron diffraction patterns were obtained on HIPD in

8–12 h each with the spallation neutron source operating at a proton current of $\sim 70 \mu\text{A}$; data taken at $2\theta = \pm 90^\circ$ was used for subsequent data analysis.

3. DATA ANALYSIS

A problem with neutron time-of-flight measurements is that the measured lattice parameters are affected by the location of the sample scattering center in the diffractometer. The placement of the sample, particularly in the high pressure cell, is not sufficiently reproducible to eliminate this source of a systematic bias in measured lattice parameters. To mitigate this systematic effect, we have employed the data analysis procedures that follow. Both variable pressure and variable temperature diffraction data were processed using the General Structure Analysis System (GSAS) suite of computer programs [11] via Rietveld refinement to obtain the lattice parameters of each KCN, the Pb pressure standard, and the CaF_2 calibration material as appropriate. Refinement of the 300 K diffraction data of the two KCN/ CaF_2 mixtures gave $a_0 = 6.5278(2) \text{ \AA}$ for K^{13}CN and $a_0 = 6.5280(2) \text{ \AA}$ for K^{15}N . The use of an internal standard (CaF_2) eliminates the sample position bias, thus these KCN lattice parameters are at least self-consistent. These values were then used to calibrate both the variable temperature and variable pressure measurements, which are listed in Tables 1 and 2. The corrections for Table 1 were determined from the intercept at 300 K of a linear fit to the measured lattice parameters with temperature. The corrections correspond to offsets of $\Delta a/a = -0.5 \cdot 10^{-4}$ and $0.8 \cdot 10^{-4}$ for K^{13}CN and K^{15}N , respectively. Sample position errors of less than 0.1 mm within the diffractometer would give these offsets, and they are smaller than the random errors in the individual lattice parameter values obtained from the Rietveld refinements. The corrections for the variable pressure data were done in a similar way. A simple second order polynomial was fit to the lattice parameters for each KCN with pressure. The intercept at ambient conditions was then used to correct both the KCN and Pb lattice parameters. The pressure was then recalculated from the equation of state for lead to give the values in Table 2. These corrections are much larger than for the variable temperature data and correspond to $\Delta a/a = 3.2 \cdot 10^{-3}$ and $0.8 \cdot 10^{-3}$ for K^{13}CN and K^{15}N , respectively. These arise from 2–3 mm sample position errors in the location of the pressure cell relative to the standard sample position in HIPD.

Table 1
Thermal expansion data for isotopically substituted KCN* at ambient pressure

$T, \text{ K}$	$a_0 (\text{K}^{13}\text{CN}), \text{ \AA}$	$a_0 (\text{K}^{15}\text{N}), \text{ \AA}$
300	6.5278	6.5290
275	6.5196	6.5184
250	6.5119	6.5118
225	6.5040	6.5037
200	6.4960	6.4947
175	6.4876	6.4876

* Standard deviations for these measurements are $(1-2) \cdot 10^{-4} \text{ \AA}$. Propagation of error from calibration data gives an estimated error of $4 \cdot 10^{-4} \text{ \AA}$.

Table 2

Compressibility data for isotopically substituted KCN at 300 K*

P , GPa	a_0 (K ¹³ CN), Å	P , GPa	a_0 (K ¹⁵ N), Å
0.290(35)	6.4809(10)	0.194(19)	6.5126(9)
0.822(16)	6.4066(10)	0.583(22)	6.4556(9)
0.894(46)	6.4146(10)	1.153(26)	6.3882(10)
1.049(19)	6.3782(10)	1.844(33)	6.3142(12)
1.406(21)	6.3448(10)		
1.873(28)	6.2996(11)		
1.925(27)	6.2922(26)		

* Values in parentheses are estimated standard deviations obtained via propagation of error from the Rietveld refinements.

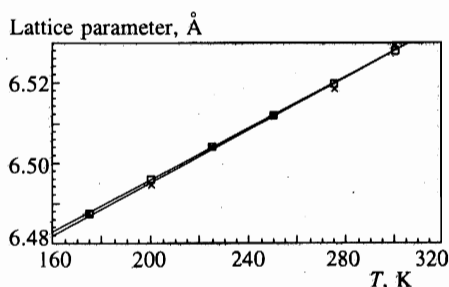


Рис. 1

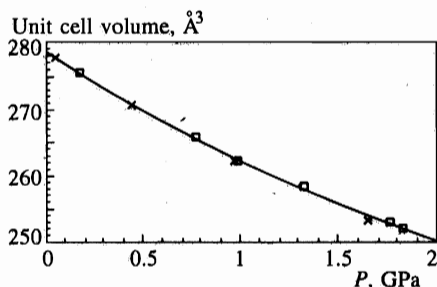


Рис. 2

Fig. 1. Lattice parameter thermal expansion of KCN. The data for K¹³CN are plotted as squares and for K¹⁵N as crosses. The lines are a guide to the eye

Fig. 2. Isothermal compression curve for KCN at 300 K. The data for K¹³CN are plotted as squares and for K¹⁵N as crosses. The line is a guide to the eye

4. DISCUSSION

The data obtained (Tables 1 and 2) are illustrated by Figs. 1 and 2. The linear thermal expansions from the data shown in Fig. 1 are $0.320 \cdot 10^{-3}$ Å/K for K¹³CN and $0.327 \cdot 10^{-3}$ Å/K for K¹⁵N. A fit of the combined compression data for the two KCN materials in Fig. 2 to a Murnaghan equation [12] gives the parameters $V_0 = 279.0(5)$ Å³, $B_0 = 13.3(9)$ GPa and $B'_0 = (\partial B / \partial P)_{P=0} = 5.6(10)$ (to be compared with values $B_0 = 13.2$ GPa and $B'_0 = 4.2$ previously obtained for «natural abundance» KCN [5]). As seen from Fig. 1, the thermal expansion experiments reveal that there is no distinct difference in lattice parameters of isotopically substituted samples of KCN over a large range of temperatures. The high-pressure compression isotherms (Fig. 2) also reveal no difference although scattering of the data is much

higher than in the temperature experiments.

Given that the reduced masses of the $^{13}\text{C}^{14}\text{N}$ and $^{12}\text{C}^{15}\text{N}$ ions differ by $\sim 1\%$, their true moments of inertia will differ by the same amount¹⁾. Our accuracy in the lattice parameter determinations are $< 0.01\%$ and $< 0.1\%$ for the temperature and pressure runs, respectively. So we must see an isotopic effect unless the function $J_{\text{eff}}(V)$ has a special form. First, it could be equal to a constant, $J_{\text{eff}} = \text{const}$, in the density range studied; in this case there is no «rotational» contribution to the equation of state. However, it seems to be highly improbable because of the condensed nature of the substances under study. Second, it could depend on density in a linear way like $J_{\text{eff}} = J_0(1 + a/V)$. In this case the «rotational» contribution to the equation of state could be large, though it would depend only slightly, if at all, on isotopic composition. Another possibility is that the «free rotation» approach can not be applied to the alkali cyanide family²⁾. Anyway further study is needed to resolve this problem and precise thermal capacity measurements would play a decisive role in the attempt to observe the classical isotopic effect.

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¹⁾ The moment of inertia of a diatomic molecule $J = m_r l^2$, where $m_r = m_1 m_2 / (m_1 + m_2)$ is a reduced mass and l is an interatomic distance. So, neglecting a possible slight difference in the length of CN group due to the isotopic composition variations, we get for the moments of inertia of $^{13}\text{C}^{14}\text{N}$ and $^{12}\text{C}^{15}\text{N}$ values of 8.92 \AA^2 and 8.82 \AA^2 , respectively at $l = 1.15 \text{ \AA}$.

²⁾ Obviously that the centers of mass of ions $^{13}\text{C}^{14}\text{N}$ and $^{12}\text{C}^{15}\text{N}$ do not coincide with their symmetry centers. That means that at «free» rotation the effective diameters of these ions would differ by $\sim 0.04 \text{ \AA}$, and it would influence the lattice parameters.