PRESSURE AND TEMPERATURE DEPENDENCE OF THE NUCLEAR QUADRUPOLE RESONANCE OF ^{75}As IN THE FERROELECTRIC PHASE OF KH_2AsO_4

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The influence of high hydrostatic pressure up to 2.5 kbar on the NQR spectrum of ^{75}As nuclei in KH_2AsO_4 was studied from 77K to T_c. The pressure dependences of the H_2AsO_4 group tunnelling energy and dipole-dipole interaction derived from the pressure shift of the Curie temperature permitted the description of the temperature and pressure dependences of the NQR frequencies throughout the entire range of temperature and applied pressure.

1. Introduction

Potassium dihydrogen arsenate KH_2AsO_4 (KDA) belongs to the highly relevant hydrogen bonded ferroelectric group, the properties of which are the subject of intensive study, both theoretically and experimentally [1]. KDA crystals consist of tetrahedral AsO_4 groups, connected by O–H...O bonds. The proton dynamics in the bonds plays an essential role in the description of the phenomena occurring in these crystals. The microscopic model of the ferroelectric transition has been proposed by Slater [2], Blinc [3], De Gennes [4], Brout, Muller and Thomas [5], as well as by Kobayashi [6]. According to their theory, the transition is triggered by a transition of the order-disorder type in the system of protons. The tunnelling of protons between two positions of equilibrium in the O–H... O bridge is strongly coupled to a well defined transversal optical mode. The phase transition results from the instability of the low-frequency mode of the coupled system.

In the paraelectric phase, the crystals exhibit a structure of the tetragonal symmetry D_{2d} with two weight units per elementary cell. In the ferroelectric phase, the structure is

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orthorhombic, C_{2v}, and spontaneous polarization is apparent along the c-axis. The electric field gradient (EFG) acting on the ^{75}As nucleus is strongly dependent on the mutual configuration of the four protons contributing to O–H... O bonding of the AsO_4 group. Figure 1 shows the structural elements of the KDA crystal in the ferroelectric phase (only two protons, in the hydrogen bonds at the upper edge of the AsO_4 tetrahedron, are shown). The presence of a proton in the immediate vicinity of oxygen lowers the electron density at the oxygen nuclei. The other two protons (at the lower edge of the tetrahedron) are

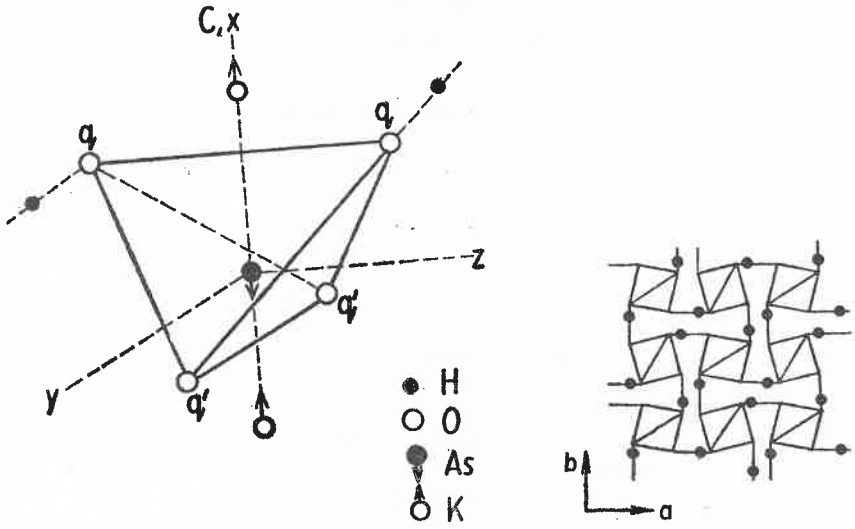

Fig. 1. Structural elements of the KDA crystal and their disposition in the unit cell

more remote. Thus, the effective charges q and q'characterizing the electron densities about the oxygen nuclei on the upper and lower edge of the tetrahedron are different. As a consequence, the ^{75}As nucleus is acted on by a field gradient, defined by the mutual disposition of the four protons of the bridges. The EFG is moreover enhanced by the displacement of the As atom with respect to the centre of the tetrahedron causing additional distortion of the latter [7]. The insignificantly small displacement (about 0.05 Å) of the relatively remote potassium ions does not contribute essentially to the magnitude of the EFG acting on the ^{75}As nucleus. The NQR frequency is determined by the effective EFG on the ^{75}As nucleus and hence provides a measure of the distortion of the AsO_4 tetrahedron, contributing, essentially to the spontaneous polarization.

In a previous paper [8], we had recourse to changes in the effective EFG tensor in the phase transition (observed as changes in NQR frequency) as a sensitive and accurate monitor of the transition. Using the disappearance of NQR frequency at the Curie temperature T_c as a monitor of the phase transition, we elucidated the Curie point versus pressure dependence, determined the change in crystal volume in the transition, and laid stress on the essential role of the hydrogen bonds in the dynamical properties of the crystal. The aim of the present work is to elucidate the pressure and temperature dependence of

the NQR frequency of the ^{75}As nuclei in KDA in the range from 77K to T_c and under pressures up to 2.5 kbar, and to determine quantitatively the meaning of the preceding dependence for the microscopic parameters characterizing its dynamical properties, such as the tunnelling energy and dipole-dipole interaction of the H_2AsO_4 groups.

2. *Experimental details*

NQR measurements were performed with a USSR made ISSz-I-12 type pulse spectrometer. The NQR frequency of the ^{75}As nuclei was measured by the beat method using an external generator. The polycrystalline KDA specimen, provided by the J. Stefan Institute at Ljubljana, was placed in a thin-walled teflon container within the resonance coil. The high pressure chamber was of beryllium bronze and was closed off with two plugs; one, through which the electric leads connecting coil and spectrometer passed, was made of a quartz monocrystal polished to optical accuracy and proved very well adapted to NQR work under high hydrostatic pressure, whereas the other served for the copper-constantan thermocouple and capillary supply of compressed helium gas from a UNIPRESS three-stage helium compressor. The details of our pressure device are given in reference [9].

The pressure chamber was placed in a cryostat through which nitrogen vapour was made to flow at a variable rate for temperature control. All measurements were carried out under increasing temperature. The thermocouple was carefully calibrated to within 0.1 deg using a semiconductor CRIOPAN cryogenic probe. Pressure was measured with an accuracy of ± 20 bar by means of a manganine coil, previously calibrated with reference to the pressure-induced phase transition of bismuth.

3. *Results and discussion*

The temperature-dependence of the NQR frequency of the ^{75}As nuclei in KDA is shown, for various values of pressure, in figure 2. With increasing temperature the NQR frequency decreases steeply, and the NQR signal vanishes at the phase transition temperature T_c. An increase in pressure lowers the NQR frequency, the effect being stronger in the neighbourhood of the phase transition. The experimentally observed changes in NQR frequency vs. temperature and pressure are anomalously large compared with other crystals. The temperature-dependence of the NQR frequency for ^{75}As nuclei in the ferroelectric phase of KDA-like crystals was first observed by Zhukov et al. [10] who suggested that the very strong change in EFG in these crystals was related to proton tunnelling in the O–H...O bonds. The temperature-dependence of the quadrupole splitting constant of the ^{75}As nuclei in the ferroelectric and paraelectric phases of KDA has been analyzed by Blinc and Björkstam [11] as well as Blinc et al. [12].

As is seen from Fig. 2, the transition temperature T_c decreases with increasing pressure, the pressure coefficient amounting to $dT_c/dp = -2.1$ deg/kbar [8]. Throughout the applied pressure range, the decrease in T_c is linear. Fig. 3 shows the NQR frequency versus pressure for several selected temperatures. The respective slope coefficients $\partial\nu_{NQR}/\partial p$ increase as we approach T_c, and the graphs of $\nu_{NQR}(p)$ become nonlinear.

The ordering of protons along the O–H... O bonds, which is the factor determining the EFG on the ^{75}As nuclei, plays a primordial role in the model of Blinc and Zeks [13] and in the dynamical theory of Kobayashi [6]. The motion of the four protons about the AsO_4 group is strongly correlated and coupled to displacements of the As nuclei. Taking into account this correlation the H_2AsO_4 group as a whole, characterized by 16 configuration Slater states [2], has to be dealt with as an elementary dipole, rather than the

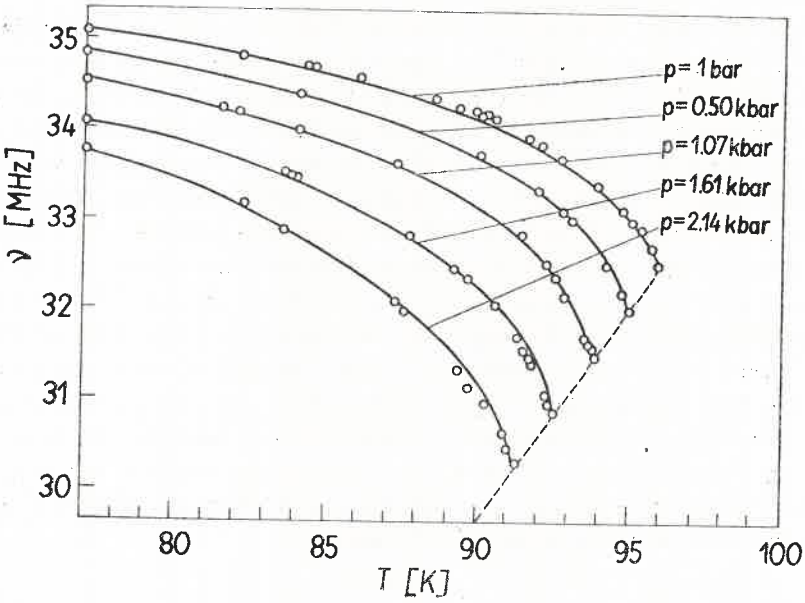

Fig. 2. Temperature-dependence of the NQR frequency of ^{75}As nuclei in KDA at various values of pressure. Continuous lines show the theoretical relations of Eq. (8)

isolated O–H... O dipoles described by pseudospin 1/2. Nonetheless, restricting considerations to the two lowest configurational eigenstates of the H_2AsO_4 group only (Fig. 4), one can apply the following Hamiltonian to the crystal [6]

$$\mathcal{H} = \mathcal{H}_p + \mathcal{H}_l + \mathcal{H}_{pl}, \tag{1}$$

where H_p describes tunnelling of the H_2AsO_4 group between the two minima of the potential, H_l the crystal lattice vibrations, and H_{pl} tunneling-lattice vibration coupling.

The H_2AsO_4 tunnelling term H_p can be expressed in the form of the Ising Hamiltonian for pseudospin 1/2 [13]

$$\mathcal{H}_p = -2\Omega \sum_l S_l^x - \tfrac{1}{2} \sum_{ll'} J_{ll'} S_l^z S_{l'}^z, \tag{2}$$

with S_l^x, S_l^z pseudospin components, Ω tunnelling energy, and $J_{ll'}$ the parameter of H_2AsO_4—H_2AsO_4 dipole coupling, favouring the emergence of a ferroelectric state.

The H_2AsO_4 tunnelling energy is given as [8]

$$\Omega = \frac{\hbar^2}{\sqrt{\pi}\, m^* \zeta^2} q^3 \exp(-q^2); \quad q^2 \equiv \frac{2m^* E_0 \zeta^2}{\hbar^2}, \tag{3}$$

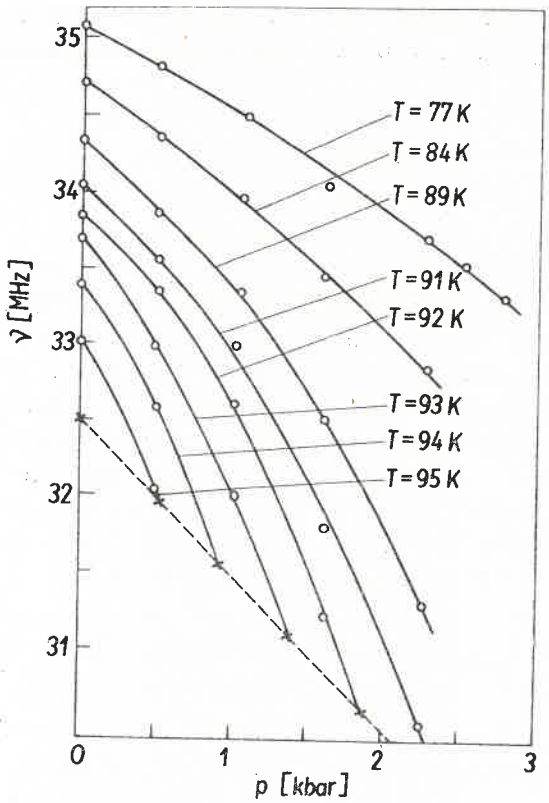

Fig. 3. Hydrostatic pressure-dependence of the NQR frequency of ^{75}As nuclei in KDA, for several selected temperatures

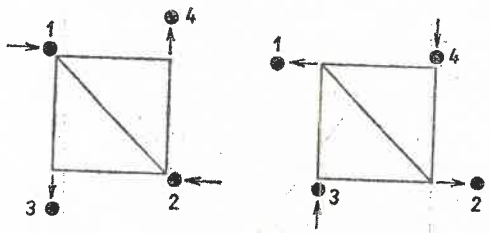

Fig. 4. Configuration of H_2AsO_4 groups corresponding to the two lowest configurational states, characterized by pseudospin 1/2

with 2ζ the distance between the potential minima in the O–H...O bond; E_0 ground state energy in the absence of tunnelling and m^* effective mass, equal to $4m_p + cm_{AS} \simeq 4\,m_p$, where m_p is the mass of the proton and c characterizes proton–As coupling.

The tunnelling of H_2AsO_4 as a whole is coupled to the optical lattice vibration mode, describing vibrations of K atoms with respect to the H_2AsO_4 group. The "softening" of the thus coupled mode when approaching the phase transition temperature is responsible

for the emergence of the ferroelectric transition. T_c is defined as the temperature at which the frequency of the coupled tunnelling mode and of optical lattice vibrations tends to zero, and is expressed as:

$$4\Omega - J \tanh \frac{\Omega}{kT_c} = 0. \tag{4}$$

In the present model, the tunnelling frequency Ω is the essential parameter. The frequency Ω is closely related to the parameters of the potential along the O–H...O bond which, in turn, are strongly dependent on the bond length R. Mechanically, the bonds O–H...O are the weakest of all. The strong dependence of R on pressure effects considerably the shape of the potential along the bond, in particular by lowering the barrier separating the two equivalent positions of the proton and diminishing the parameter ζ. This, in turn, leads to an increase in Ω and a decrease in J since $J \sim \zeta^2$ [13]. The pressure-induced decrease in T_c is thus due to an increase in the frequency of the H_2AsO_4 group tunnelling through an increasingly narrow and low potential barrier entailing an enhanced tendency to disordering with respect to the ordering action of the dipole field. We determined Ω earlier [8] from the pressure-dependence of T_c applying the relation:

$$\frac{dT_c}{dp} = -\alpha S_1 T_c \left[2 + (2q^2+1) \left(\frac{kT_c}{2\Omega} \sinh \frac{2\Omega}{kT_c} - 1 \right) \right], \tag{5}$$

where $\alpha S_1 = -\zeta^{-1} d\zeta/dp = 5.43 \cdot 10^{-3}$ kbar^{-1} [8].

On insertion of the value $\Omega = 33$ cm^{-1} thus derived into Eq. (4) we obtained $J = 287.8$ cm^{-1} (under atmospheric pressure). We obtained the pressure-dependence of Ω and J from Eq. (4) by having recourse to the experimental $T_c/(p)$ dependence and assum-

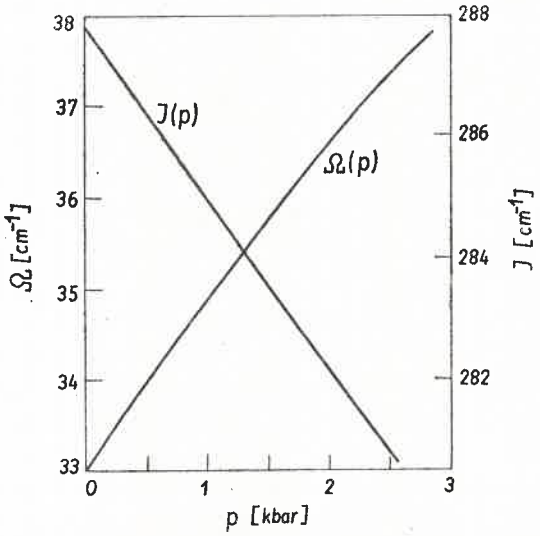

Fig. 5. Tunnelling energy Ω and dipole-dipole interaction energy J in KDA versus pressure

ing, after Peercy and Samara [14] $d \ln J/dp = -1$ per cent per kbar. Graphs of $\Omega(p)$ and $J(p)$ thus derived are shown in Fig. 5.

The mean value of the pseudospin z-component, $\langle S_z \rangle$, is an implicit function of the temperature T, tunnelling energy Ω, and dipole interaction J [1]:

$$\langle S_z \rangle = \tfrac{1}{2} \frac{J\langle S_z \rangle}{\sqrt{(2\Omega)^2 + (J\langle S_z \rangle)^2}} \tanh \frac{\sqrt{(2\Omega)^2 + (J\langle S_z \rangle)^2}}{2kT}. \tag{6}$$

On the basis of $\Omega(p)$ and $J(p)$, given in Fig. 5, the dependence of $\langle S_z \rangle$ on temperature can be found for various pressures, and it is possible to search for the correlations between the pressure- and temperature-dependence of the NQR frequency and the pseudospin z-component. By having recourse to the implicit relation:

$$\sqrt{(2\Omega)^2 + (J\langle S_z \rangle)^2} = \tfrac{1}{2} J \tanh \frac{\sqrt{(2\Omega)^2 + (J\langle S_z \rangle)^2}}{2kT} \tag{7}$$

we performed calculations of $\langle S_z \rangle$ versus T for values of Ω and J corresponding to the various pressures applied in the experiment. The theoretical relationships $\langle S_z \rangle(\Omega, J, T)$ obtained were compared to the experimental relation $\nu(p, T)$ derived from NQR studies in the temperature range from 77K to T_c and for pressures up to 2.14 kbar (Fig. 2). The pressure and temperature dependence of the NQR frequency of ^{75}As nuclei in KDA can be expressed as follows:

$$\nu(p, T) = A(p) + B(p) \langle S_z \rangle (\Omega, J, T), \tag{8}$$

where $\langle S_z \rangle (\Omega, J, T)$ is given by Eq. (7) whereas A and B are experimental parameters, determined from the NQR vs. pressure measurements. Fig. 6 shows A and B vs. pressure. In the range of pressures applied, A is a decreasing and B an increasing linear function of the latter. The steep decrease in A with increasing pressure ($dA/dp = -1$ MHz/kbar) points to an enhancement of the local symmetry of the EFG tensor under conditions of high pressure, so that a decrease in NQR frequency is observed. The increase in local symmetry due to the decrease in distortion of the AsO_4 tetrahedron is accompanied by an increase in the sensitivity of the crystal to external agents, (p, T), apparent as an increase in B (with $dB/dp = 2.2$ MHz/kbar). Equation (8) contains the pressure functions $A(p)$ and $B(p)$ describing the ferroelectric state of the crystal. They cannot be extrapolated to the paraelectric state, for which the EFG tensor has been studied in detail by Blinc et al. [12] applying the NMR method. This results from the complex nature of the phase transition, in which the parameters observed vary jumpwise. Hitherto, no quantitative verification of Slater's model in the ferroelectric phase of the KDA crystal is available. Eq. (8) is an attempt to fit the often made assumption that the EFG is proportional to the ordering parameter to the experimental results. As a matter of fact the EFG may be also proportional to the ordering parameter in the higher powers (quadratic, cubic, etc.) [12]. But within the experimental errors we are not able to determine the higher order terms. The constant

$A(p)$ for $T > T_c$ cannot be dealt with as the magnitude of the gradient in the paraelectric phase, since it is meaningful at the jump only. The constant B is a proportionality factor and, as yet, lacks a molecular meaning. The expressions for $\langle S_z \rangle$ is justified strictly within the framework of the Blinc-Zeks two-spin model, which leads to a transition of the II-nd kind. One way to improve the model is to add the four-spin interaction terms, which then

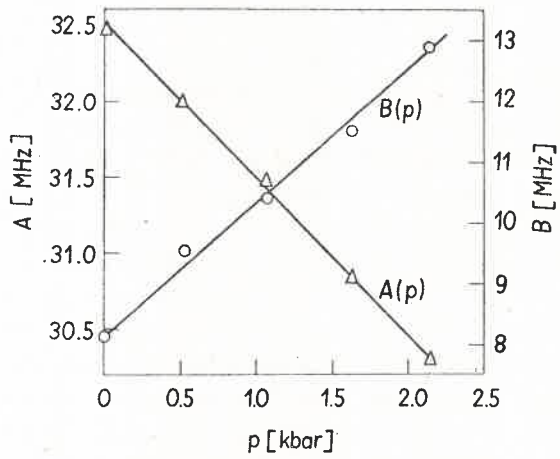

Fig. 6. Parameters A and B versus pressure

allow for the first order transitions. The four-spin model is a better approximation of the real situation existing in the crystal, but the NQR experiment is not sensitive enough to distinguish between those two models. The four-spin model should provide a microscopic explanation of our experimental parameters A and B, but it should not influence the description of the experiment drastically, because the phenomenological function $\nu(p, T)$ applied by us really describes the experimental results in the ferroelectric phase, as one can see from the graphs. The first order character of the transition is described by the A and B parameters, which change jumpwise at T_c. Such a large difference between the constant $A_f(p)$ at the boundary between the ferroelectric phase and the constant $A_p(p)$ corresponding to the EFG in the paraelectric phase provides information on the complex nature of the phase transition in KDA.

The continuous curves of Fig. 2 are plots of Eq. (8). The good agreement with experiment is evidence of the correlation between $\nu(p, T)$ and $\langle S_z \rangle(\Omega, p, T)$, and is proof of the consistency of the model applied. The values of $\Omega(p)$ and $J(p)$, determined from the pressure shift in T_c, permit the description of the temperature and pressure-dependent behaviour of the NQR frequency throughout the entire range of temperatures and pressures.

With regard to Eq. (8), the isothermal pressure-dependence of the NQR frequency is given by the following thermodynamical expression:

$$\left(\frac{\partial \nu}{\partial p}\right)_T = \frac{dA}{dp} + \langle S_z \rangle \frac{dB}{dp} + B\left(\frac{\partial \langle S_z \rangle}{\partial \Omega}\frac{\partial \Omega}{\partial p} + \frac{\partial \langle S_z \rangle}{\partial J}\frac{\partial J}{\partial p}\right)_T. \tag{9}$$

On calculation of the derivatives $\partial\langle S_z\rangle/\partial\Omega$ and $\partial\langle S_z\rangle/\partial J$ from Eq. (8), one obtains the following relation:

$$\left(\frac{\partial\nu}{\partial p}\right)_T = \frac{dA}{dp} + \langle S_z\rangle \frac{dB}{dp} - B\left[\frac{4\Omega}{J^2\langle S_z\rangle}\frac{\partial\Omega}{\partial p} - \left(\frac{\sqrt{(2\Omega)^2+(J\langle S_z\rangle)^2}}{4J^2\langle S_z\rangle}\frac{\sinh\dfrac{\sqrt{(2\Omega)^2+(J\langle S_z\rangle)^2}}{kT}}{\cosh^2\dfrac{\sqrt{(2\Omega)^2+(J\langle S_z\rangle)^2}}{2kT} - \dfrac{J}{4kT}} - \frac{\langle S_z\rangle}{J}\right)\frac{\partial J}{\partial p}\right] \tag{10}$$

describing the isothermal pressure-dependence of the NQR frequency of ^{75}As nuclei in KDA. The isobaric temperature-dependence is given by

$$\left(\frac{\partial\nu}{\partial T}\right)_p = B\left(\frac{\partial\langle S_z\rangle}{\partial T}\right)_p. \tag{11}$$

Hence, simple calculations lead to the formula:

$$\left(\frac{\partial\nu}{\partial T}\right)_p = \frac{-B[(2\Omega)^2+(J\langle S_z\rangle)^2]}{2kJT^2\langle S_z\rangle\left[\cosh^2\dfrac{\sqrt{(2\Omega)^2+(J\langle S_z\rangle)^2}}{2kT} - \dfrac{J}{4kT}\right]}. \tag{12}$$

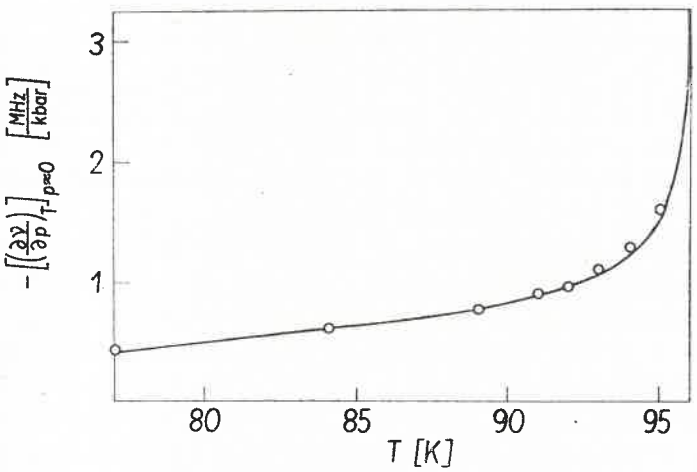

Fig. 7. Isothermal slope coefficients $(\partial\nu/\delta p)_T$ at $p \approx 0$ versus temperature. The curve shows the theoretical dependence predicted by Eq. (10)

In order to compare the formulae derived with experiment, we calculated the slope coefficient $(\partial\nu/\partial p)_T$ of the NQR frequency for various temperatures, in the pressure region $d \approx 0$ (i.e. the initial slope coefficient, characterizing the shape of the ν vs. pressure graphs).

On insertion of the values $\partial J/\partial p = -2.8\ \mathrm{cm}^{-1}/\mathrm{kbar}$, $\partial\Omega/\partial p = 1.7\ \mathrm{cm}^{-1}/\mathrm{kbar}$, $dA/dp = -1$ MHz/kbar, $dB/dp = 2.2$ MHz/kbar, $\Omega = 33\ \mathrm{cm}^{-1}$, $J = 287.8\ \mathrm{cm}^{-1}$ and $B = 8.16$ MHz into formula (10) and on applying Eq. (7) we obtained the theoretical dependence of the slope coefficient $[(\partial\nu/\partial p)_T]_{p\approx 0}$ for the entire range of temperatures applied experimentally (the curve in Fig. 7). On comparison with the experimentally determined slope coefficients of Fig. 3 very good agreement was obtained, indicating the correctness of the model. Formula (10), in addition to providing the slope coefficients, describes the nonlinear behaviour of $\nu(p)_T$ i.e. the experimentally observed increase in slope coefficient with increasing pressure shown in Fig. 3.

The behaviour od $\partial\nu/\partial p$ in KDA is very similar to that observed by Peercy [15] for the pressure-dependence of the frequency of the soft ferroelectric mode $\partial\omega/\partial p$ in the isomorphous crystal KH_2PO_4 (KDP). Raman spectral studies by Peercy show the ferroelectric mode frequency to decrease with increasing pressure at $T < T_c$. In the neighbourhood of T_c the $\omega(p)$ dependence is very strong and nonlinear.

Finally, we wish once again to stress the particular utility of NQR under high hydrostatic pressure for studies of the lattice dynamics of ferroelectric substances.

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