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Temperature dependences of the ^{39}K and ^{85}Rb quadrupole coupling constants in paraelectric KH_2PO_4, KH_2AsO_4, RbH_2PO_4, and RbH_2AsO_4

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Temperature dependences of ^{39}K and ^{85}Rb nuclear-quadrupole resonance frequencies have been measured in tetragonal paraelectric phases of KH_2PO_4, KH_2AsO_4, RbH_2PO_4, and RbH_2AsO_4. The measured quadrupole coupling constants are compared to the quadrupole coupling constants calculated in a point-charge model in which a cation bears a positive charge e whereas the negative charge $-e$ of a PO_4^- or AsO_4^- ion is, in a time average, equally shared by the four oxygen atoms. The influence of the anisotropic thermal expansion of the crystal lattices on the temperature dependence of the quadrupole coupling constants is calculated in the same model. Both the calculated and measured quadrupole coupling constants as well as the calculated and measured temperature coefficients of the quadrupole coupling constants agree within the experimental error. Thus the "antiferroelectric" Slater configurations of the H_2PO_4 and of the H_2AsO_4 groups which seem to have a strong influence on the ^{75}As NQR frequencies in the tetragonal paraelectric phase are of a local nature and they have nearly no influence on the potassium and rubidium NQR frequencies.

I. INTRODUCTION

KH_2PO_4 (KDP)-type systems have a number of interesting properties. They undergo ferroelectric or antiferroelectic phase transitions. Under a partial substitution of cations some of these systems—as for example $Rb_{1-x}(NH_4)_xH_2PO_4$—exhibit glassy properties. It is therefore worthwhile to study these systems in great detail in order to elucidate the microscopic mechanisms which are responsible for the macroscopic properties of these systems.

In KDP, KH_2AsO_4 (KDA), RbH_2PO_4 (RDP), and RbH_2AsO_4 (RDA) the ferroelectric phase transitions are associated with the ordering of hydrogens in the O-H—O hydrogen bonds. Each PO_4 or AsO_4 group is bonded to four other PO_4 or AsO_4 groups by four O-H—O hydrogen bonds which lie approximately parallel to the crystal a-b plane. Above the phase transition temperature T_c in the tetragonal paraelectric phase within each hydrogen bond the hydrogen moves between two equivalent equilibrium positions: O-H—O and O—H-O. At each instant of time two hydrogens out of four surrounding a PO_4 or AsO_4 group are covalently bonded to the group whereas the other two hydrogens are hydrogen bonded to the group. The arrangement of the four hydrogens around a $PO_4(AsO_4)$ group can be described by two "ferroelectric" and four "antiferroelectric" Slater configurations (Fig. 1). Below T_c the hydrogen motion freezes in and within each domain only one of the two "ferroelectric" configurations is present. It is still not definitely known which Slater configurations are indeed present above T_c. The question is whether there are only the two "ferroelectric" configurations present with equal probabilities or the "antiferroelectric" configurations also appear in addition to the "ferroelectric" ones but with lower probabilities than the ferroelectric configurations.

Nuclear-quadrupole resonance (NQR) and quadrupole perturbed nuclear magnetic resonance have proved to be sensitive techniques which can also detect minor changes in the crystal structure. These changes namely change the electric-field-gradient tensor at the sites of the quadrupole nuclei and shift the resonance frequencies of these nuclei which can be measured with a high precision. In the above systems some NQR and quadrupole perturbed

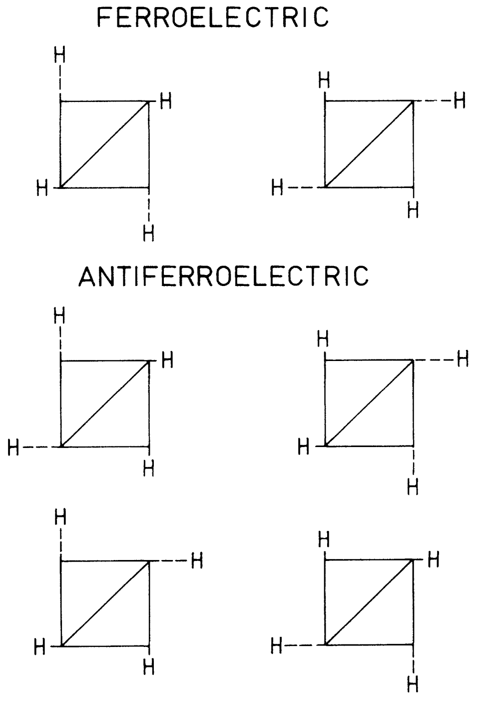

FIG. 1. Two ferroelectric and four antiferroelectric Slater configurations of a H_2PO_4 or H_2AsO_4 group.

NMR measurements have already been performed.

The ^{75}As NQR frequencies in paraelectric KDA and RDA (Ref. 1) are low ($\sim$4 MHz) as compared to the ones observed in the ferroelectric phases $\sim$40 MHz) (Ref. 2) and they exhibit a strong, nonlinear, decrease with increasing temperature. The temperature coefficient, $d\nu_Q/\nu_Q dT$ is not constant. It is of the order of -10^{-3} K^{-1}. Blinc and Bjorkstam[1] ascribed the nonlinear temperature dependences of the ^{75}As NQR frequencies in paraelectric KDA-type systems to the nonzero probability of finding a H_2AsO_4 group in an "antiferroelectric" Slater configuration. From the temperature dependences of the ^{75}As NQR frequencies they calculate the energies of the "antiferroelectric" Slater configurations. They obtained these Slater energies in fair agreement with the ones calculated from the transition temperatures T_c.

The ^{87}Rb quadrupole coupling constants in RDA (Ref. 3) and RDP (Ref. 4) show in contrast to the arsenic ones nearly linear temperature dependences with positive temperature coefficients of approximately 6×10^{-4} K^{-1} and 2.5×10^{-4} K^{-1}, respectively. These temperature dependences may, in principle, arise from the increasing probabilities of finding a H_2PO_4 or an H_2AsO_4 in an "antiferroelectric" Slater configuration with increasing temperature—as in case of arsenic—and also from the anisotropic thermal expansion of the crystal lattice. However the linear temperature dependences of the ^{87}Rb NQR frequencies suggest that it is the thermal expansion which dominates the temperature dependences of the rubidium NQR frequencies. In order to probe the contribution of the anisotropic thermal expansion of the crystal lattice to the temperature coefficients of the ^{39}K and ^{85}Rb NQR frequencies in the paraelectric phases of KDP, KDA, RDP, and RDA we decided to perform precise measurements of these frequencies and in addition to perform the calculation of the NQR frequencies and their temperature coefficients in a point-charge model. The comparison of the experimental and theoretical results may be used to see whether the "antiferroelectric" Slater configurations produce only slight local changes of the phosphate or arsenate groups or they produce also some changes in the environment of these groups so that they can be treated as collective excited states.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

^{39}K has a spin-$\frac{3}{2}$ and thus it has in zero magnetic field two doubly degenerate quadrupole energy levels. The nuclear-quadrupole resonance frequency ν_Q is equal to

$$\nu_Q=\tfrac{1}{2}eQV_{ZZ}\sqrt{1+\eta^2/3}\ . \tag{1}$$

Here eQ is the nuclear-quadrupole moment and V_{ZZ} is the largest principal value of the electric-field-gradient (EFG) tensor $\mathbf{V}$ composed of the second derivatives, $V_{ij}=\partial^2V/\partial x_i\partial x_j$, of the electrostatic potential V with respect to the coordinates. The asymmetry parameter η of the EFG tensor is the difference $(V_{XX}-V_{YY})$ of the two smaller principal values of the EFG tensor $(|V_{XX}|\le|V_{YY}|\le|V_{ZZ}|)$ divided by V_{ZZ}. It ranges between 0 and 1.

^{85}Rb has a spin-$\frac{5}{2}$. It has in zero magnetic field three doubly degenerate quadrupole energy levels. The three NQR frequencies are for $\eta=0$—which is the case in RDP and RDA—equal

$$\begin{aligned}\nu_{5/2-1/2}&=9eQV_{ZZ}/20h\ ,\\ \nu_{5/2-3/2}&=6eQV_{ZZ}/20h\ ,\\ \nu_{3/2-1/2}&=3eQV_{ZZ}/20h\ .\end{aligned} \tag{2}$$

The transition with the highest NQR frequency $\nu_{5/2-1/2}$ is, however, forbidden for $\eta=0$.

Since the ^{39}K and ^{85}Rb NQR frequencies are rather low we performed the measurements by nuclear-quadrupole double-resonance based on magnetic-field cycling. Here the NQR frequencies are indirectly detected by observing the NMR signal of hydrogen nuclei (protons).

In a magnetic-field cycle the proton spin system is first polarized in a high static magnetic field B_0. Then the static magnetic field is adiabatically reduced to a low value B which may even be zero. After a time τ spent in the low magnetic field B the static magnetic field is adiabatically increased to the initial value B_0 and the proton NMR signal S_H is measured. It decreases with increasing τ approximately as $S_H\propto\exp(-\tau/T_1(B))$. Here $T_1(B)$ is the spin-lattice relaxation time of protons in the external magnetic field B.

In the case of KDP the low magnetic field B was set to zero and during the stay in zero magnetic field a rf magnetic field was applied to the sample with the amplitude of approximately 2 mT. The rf magnetic field was subject to sudden 180° changes each 3 ms.[5,6] In resonance, i.e., when the frequency of the rf magnetic field was equal to the ^{39}K NQR frequency we observed a decrease of the proton NMR signal at the end of the magnetic-field cycle. This is the effect of a faster relaxation of protons caused by the ^{39}K nuclei which have energy levels quantized in the "rotating frame" where the energy separation of the potassium energy levels is comparable to the width of the proton NMR line. The 180° phase shifts are used to invert the populations of the potassium energy levels in the "rotating frame." They keep the spin temperature of the ^{39}K nuclei high.

The temperature dependence of the ^{39}K NQR frequency ν_Q in KDP as measured by the above technique is presented in Fig. 2(a). It nearly linearly increases with increasing temperature with the temperature coefficient $d\nu_Q/\nu_Q dT=5.0\times10^{-4}$ K^{-1}. At 22 °C the ^{39}K NQR frequency is equal to $\nu_Q=(845\pm5)$ kHz. Due to the crystal symmetry the asymmetry parameter η of the EFG tensor at the potassium site is zero. Thus the quadrupole coupling constant eQV_{ZZ}/h is equal to $eQV_{ZZ}/h=\pm2\nu_Q=\pm(1690\pm10)$ kHz. For a ^{39}K$^+$ ion the Sternheimer antishielding factor γ_∞, which relates the lattice value $\mathbf{V}_l$ of the EFG tensor to the EFG tensor $\mathbf{V}$ "seen" by the atomic nucleus as $\mathbf{V}=(1-\gamma_\infty)\mathbf{V}_l$, is equal to -12.2. The electric quadrupole moment of a ^{39}K nucleus is equal to 9×10^{-26} cm^2.[7] Thus the largest principal value $(V_{ZZ})_l$ of the lattice-produced EFG tensor $\mathbf{V}_l$ at the potassium sites is at room temperature equal to

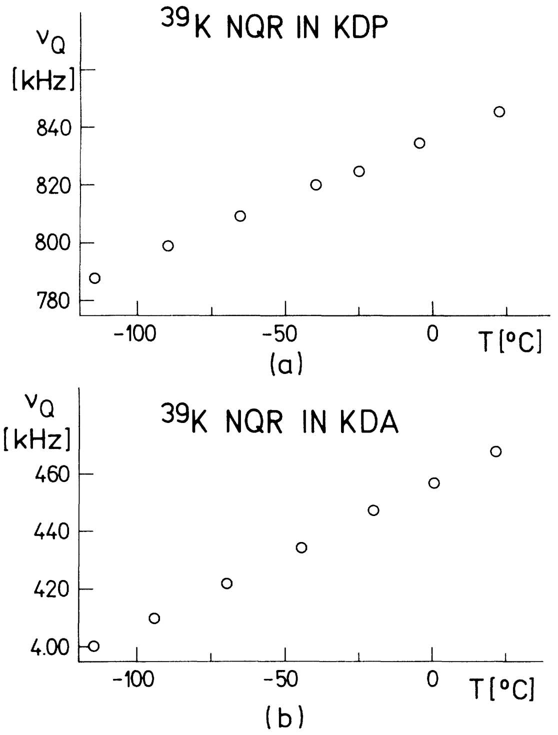

FIG. 2. ^{39}K NQR frequencies in KDP (a) and in KDA (b).

$$(V_{ZZ})_1 = \pm 2\nu_Q h/[eQ(1-\gamma_\infty)] = \pm 5.9\times 10^{19}\ \mathrm{V/m^2}\ . \tag{3}$$

In KDA the spin-lattice relaxation time of protons is in zero magnetic field rather short. This is presumably the effect of proton-arsenic cross relaxation. Therefore the same technique as in the case of KDP cannot be used. We determined the ^{39}K NQR frequencies from the low magnetic field B (or ν_H) dependence of the proton signal S_H at the end of the magnetic-field cycle.[8] Here ν_H, $\nu_H = \gamma_H B/2\pi$, is the proton Larmor frequency in the low magnetic field B. The nonzero magnetic field B namely broadens the NQR transition. When the static magnetic field B is chosen in such a way that the proton Larmor frequency ν_H lies within the magnetically broadened NQR line, then the two spin systems after the adiabatic demagnetization resonantly couple what results in an additional decrease of the proton signal S_H at the end of the magnetic-field cycle. A deep is thus observed in the ν_H dependence of the proton NMR signal S_H around $\nu_H = \nu_Q$. From the position and shape of the dip in the Larmor frequency dependence of S_H around $\nu_H = \nu_Q$, one can determine ν_Q.

The temperature dependence of the ^{39}K NQR frequency in KDA, as measured by the above technique, is shown in Fig. 2(b). The NQR frequency again nearly linearly increases with increasing temperature with the temperature coefficient $d\nu_Q/\nu_Q dT = 11.6\times 10^{-4}$ K^{-1}. The quadrupole coupling constant, which is equal to $\pm 2\nu_Q$, increases with the same temperature coefficient. At room temperature the ^{39}K NQR frequency is equal to (468 ± 5) kHz. The quadrupole coupling constant is thus equal to $\pm(936\pm 10)$ kHz and the lattice value $(V_{ZZ})_1$ of the largest principal value of the EFG tensor is at the potassium site equal to $\pm 3.3\times 10^{19}$ V/m^2.

In RDP the ^{85}Rb NQR frequencies were measured by two techniques. At low temperatures, close to T_c, the proton spin-lattice relaxation time is in zero magnetic field equal to a few tenths of a second and the double-resonance technique using adiabatic demagnetization into zero magnetic field and rf irradiation can still be used. At higher temperatures protons relax in zero magnetic field much faster. In the latter case we determined the lowest ^{85}Rb NQR frequency $\nu_{3/2-1/2}$ from the lower edge of the dip which occurs in the B dependence of S_H at the end of the magnetic-field cycle around $\nu_H = \nu_{3/2-1/2}$.[9] In the case of $\eta = 0$ this lower edge, which is relatively sharp, appears at $\nu_H = \nu_{3/2-1/2}/(1+2\gamma_{Rb}/\gamma_H)$, where γ_{Rb} and γ_H are the giromagnetic ratios of ^{85}Rb and ^{1}H, respectively. The quadrupole coupling constant is then calculated from expressions (3) as $eQV_{ZZ}/h = \pm 20\nu_{3/2-1/2}/3$. At low temperatures we obtained the same values of the lowest ^{85}Rb NQR frequency by both techniques. In RDA the ^{85}Rb NQR frequency $\nu_{3/2-1/2}$ was also determined from the lower edge of the rubidium dip in the Larmor frequency dependence of S_H.

The temperature dependences of the lowest ^{85}Rb NQR frequencies in RDP and RDA are shown in Fig. 3. Both NQR frequencies increase nearly linearly with increasing temperature. The temperature coefficients of the NQR frequencies, which are equal to the temperature coefficients of the quadrupole coupling constants, are equal to 2.3×10^{-4} K^{-1} in RDP and to 7.0×10^{-4} K^{-1}

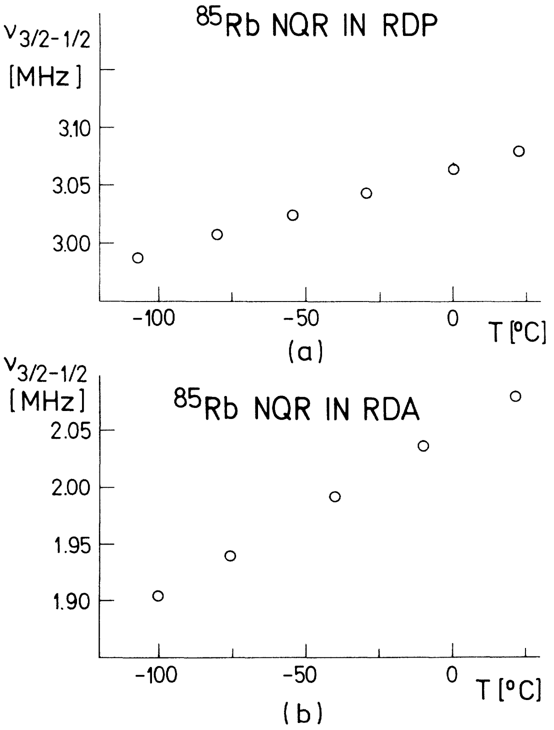

FIG. 3. ^{85}Rb NQR frequencies $\nu_{3/2-1/2}$ in RDP (a) and in RDA (b).

in RDA. At room temperature the ^{85}Rb quadrupole coupling constant is in RDP equal to ±20.6 MHz, whereas it is in RDA equal to ±13.9 MHz. The ^{85}Rb quadrupole constants and their temperature dependences agree with the ^{87}Rb quadrupole constants and their temperature dependences as measured in the same substances by quadrupole perturbed NMR (Refs. 3 and 4) if the ratio of the nuclear electric quadrupole moments $Q(^{85}\mathrm{Rb})/Q(^{87}\mathrm{Rb})=2.063$ is taken into account.[10] The Sternheimer antishielding factor is for a $^{85}\mathrm{Rb}^+$ ion equal to $\gamma_\infty=-49.3$ whereas the electric quadrupole moment of its nucleus, i.e., equal to $Q(^{85}\mathrm{Rb})=0.286\times10^{-24}$ cm^2.[7] Thus the lattice values $(V_{ZZ})_1$ of the largest principal values of the EFG tensor at the rubidium sites are in RDP and RDA at room temperature equal to $\pm5.9\times10^{19}$ V/m^2 and $\pm4.0\times10^{19}$ V/m^2, respectively.

III. CALCULATION OF THE EFG TENSOR

In the calculation of the EFG tensor we use the following model: (1) Each K^+ or Rb^+ ion bears a positive electric charge e which may be different from the elementary charge e_0. (2) The excess negative charge $-e$ of a $\mathrm{PO_4}^-(\mathrm{AsO_4}^-)$ ion is in time average equally shared by the four oxygens. In the vicinity of each oxygen the electric charge $-e/4$ is slightly shifted from the oxygen position along the O-H-O hydrogen bond (Fig. 4).

The EFG tensor at a site of a nucleus produced by an electric charge e_i at a distance $\mathbf{r}_i=(x_i,y_i,z_i)$ from the nucleus is axially symmetric around the direction of the vector $\mathbf{r}_i$. Its largest principal value V_{ZZi} is equal to

$$V_{ZZi}=e_i/(2\pi\varepsilon_0 r_i^3)\ . \tag{4}$$

The component of that EFG tensor along a given, say z direction, V_{zzi}, is expressed as

$$V_{zzi}=V_{ZZi}(3z_i^2-r_i^2)/2r_i^2\ . \tag{5}$$

In the tetragonal KDP-type systems the EFG tensor is at a cation site due to the crystal symmetry axially symmetric around the c axis. Thus it is necessary only to calculate the sum of the tensor components V_{cci} [expression (5) with $z=c$] over the crystal lattice which is equal to $(V_{ZZ})_1$. In order to shorten the time of the calculation of the lattice sums we performed the calculation in two steps.

In the first step we put a negative charge $-e$ at the position of a P or As atom and calculate the principal value $(V_{cc})_1$ at a rubidium or potassium site produced by these charges and the positive charges $+e$ of cations. The contribution $(V_{cc})_1$ to the principal value V_{cc} of the EFG tensor may be expressed as

$$(V_{cc})_1=kF_1(\varepsilon)\ . \tag{6}$$

Here $k=e/(2\pi\varepsilon_0 a^3)$, a is the lattice constant, and $\varepsilon=c/a$ is the ratio of the two lattice constants in the tetragonal paraelectric phase. The dependence of $F_1(\varepsilon)$ on ε is shown in Fig. 5(a). It is at $\varepsilon=0.94$ (KDP, KDA) equal to -14.1 whereas it is at $\varepsilon=0.96$ (RDP, RDA) equal to -12.8.

In the second step we perform the calculation of the component $(V_{cc})_2$ of the EFG tensor arising from the small neutral groups centered at the P or As positions in the crystal lattice which have positive charges $+e$ at the P or As positions and negative charges $-e/4$ close to the oxygen positions displaced by a distance s from the oxygen positions along the hydrogen bonds, formed by the oxygens (Fig. 4). These groups are relatively small and their contribution to the EFG tensor at a cation site become negligible already when they are at a distance of a few unit cells from the cation site. The contribution $(V_{cc})_2$ to the EFG tensor may be expressed as

$$(V_{cc})_2=kF_2(\varepsilon,s)\ , \tag{7}$$

where s is the distance between the oxygen site and the

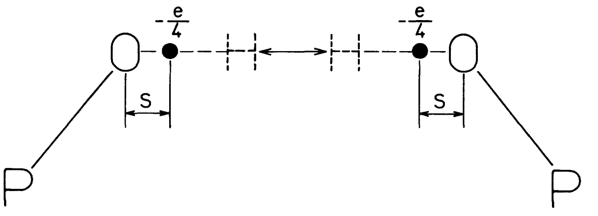

FIG. 4. Position of the excess electric charge $-e/4$ within a hydrogen bond.

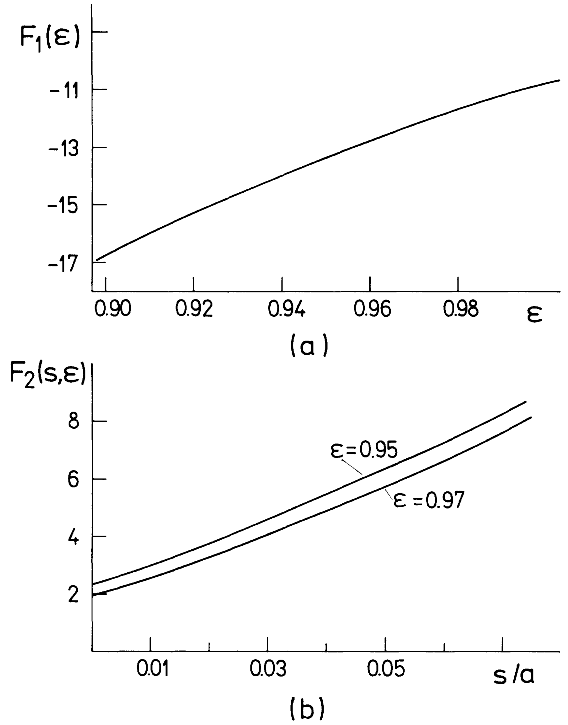

FIG. 5. (a) The $\varepsilon=c/a$ dependence of the function $F_1(\varepsilon)$ which measures the largest principal value $(V_{ZZ})_1$ of the EFG tensor in units of $e/(2\pi\varepsilon_0 a^3)$ calculated in a simple model in which the negative electric charge $-e$ of a phosphate or arsenate ion is located in the center of the ion, i.e., at the P or As position. (b) The s dependence of the function $F_2(s,\varepsilon)$ which represent the correction to the function $F_1(\varepsilon)$ for the case of an equal distribution of the electric charge $-e$ over the four oxygen positions within a phosphate (or arsenate) ion.

center of the negative charge $-e/4$ which is close to the oxygen site. The dependence of $F_2(\varepsilon,s)$ on s is for two values of ε and for the oxygen coordinates of RDP shown in Fig. 5(b). It can be seen that $F_2(\varepsilon,s)$ exhibits strong dependences on both ε and s.

The lattice value $(V_{ZZ})_1$ of the EFG tensor is expressed as

$$(V_{ZZ})_1=(V_{cc})_1+(V_{cc})_2=k[F_1(\varepsilon)+F_2(\varepsilon,s)]$$
$$=kF(\varepsilon,s)\ . \qquad (8)$$

The temperature coefficient $\alpha_V, \alpha_V=d(V_{ZZ})_1/(V_{ZZ})_1dT$, of the quadrupole coupling constant which arises from the temperature dependence of $k, k=e/(2\pi\varepsilon_0 a^3)$, and from the temperature dependence of $\varepsilon, \varepsilon=c/a$, can be expressed as

$$\alpha_V=-3\alpha_a+(\varepsilon(\partial F/\partial\varepsilon)/F)(\alpha_c-\alpha_a)\ . \qquad (9)$$

Here α_a and α_c are the thermal-expression coefficients of the crystal lattice along the a and c axes, respectively.

Both $(V_{ZZ})_1$ and α_V depend on ε and s. Whereas the value of ε is known from the crystallographic studies the value of s is not known and s may be used as an adjustable parameter in fitting the calculated value of the EFG tensor and its temperature coefficients to the measured ones. Another adjustable parameter in this model is the electric charge e which is transferred from the cation to the anion. It does not influence the temperature coefficient of the EFG tensor, but it influences the quadrupole coupling constant which is proportional to e.

IV. DISCUSSION

In KDP the lattice constants are at room temperature equal to $a=0.745$ nm, $c=0.697$ nm, and $c/a=0.936$. The relative coordinates of oxygen within the unit cell are (0.149, 0.083, 0.126).[11] The thermal-expansion coefficients of the crystal lattice are $\alpha_a=2.5\times10^{-5}\ \mathrm{K}^{-1}$ and $\alpha_c=4.4\times10^{-5}\ \mathrm{K}^{-1}$.[12] The largest principal value $(V_{ZZ})_1$ of the EFG tensor at the potassium site as determined by NQR is equal to $\pm5.8\times10^{19}\ \mathrm{V/m^2}$, which is in units of k_0, $k_0=e_0/(2\pi\varepsilon_0 a^3)$ equal to $\pm8.4k_0$. Here e_0 is the elementary electric charge. The temperature coefficient α_V of the quadrupole coupling constant is measured as being equal to $5.0\times10^{-4}\ \mathrm{K}^{-1}$.

The calculated principal value $(V_{ZZ})_1$ of the EFG tensor at a potassium site in KDP is as a function of the oxygen-negative charge distance s shown in Fig. 6(a). The electric charge e of an ion is chosen as being equal to the elementary charge e_0. The temperature coefficient α_V of the quadrupole coupling constant as calculated by the expression (9) is as a function of the distance s shown in Fig. 6(b). In both cases the theoretical and experimental values agree at $s=0.032$ nm where $(V_{ZZ})_1=-8.4k_0$. Thus the electric charge of an ion is within the accuracy of the point-charge model equal to the elementary charge e_0 and the distance s from the oxygen position to the center of the excess electric charge $-e/4$ is equal to 0.032 nm.

In KDA the unit-cell dimensions are $a=0.763$ nm and $c=0.716$ nm. The ratio $\varepsilon=c/a$ is equal to 0.939. The relative coordinates of an oxygen atom within the unit cell are (0.161, 0.087, 0.134).[13] The thermal-expansion coefficients are $\alpha_a=2.4\times10^{-5}\ \mathrm{K}^{-1}$ and $\alpha_c=4.7\times10^{-5}\ \mathrm{K}^{-1}$.[12] The NQR measurements give $(V_{ZZ})_1=\pm3.3\times10^{19}\ \mathrm{V/m^2}=\pm5.0k_0$ and $\alpha_V=11.6\times10^{-4}\ \mathrm{K}^{-1}$.

The measured quadrupole coupling constant is in KDA equal to the calculated one at a distance $s=0.052$ nm. At this value of s the calculated value of α_V is equal to $15.1\times10^{-4}\ \mathrm{K}^{-1}$. The measured and calculated thermal coefficients α_V agree at $s=0.044$ nm where the calculated value of $(V_{ZZ})_1$ is equal to $-6.0k_0$. A possible explanation of this discrepancy is that the electric charge e of an ion is lower than the elementary charge e_0, which means that the valence electron is not completely transferred from the potassium to the arsenate ion. If this is the case then the electric charge of an ion is in KDA equal to $0.83e_0$ and the distance s is equal to 0.044 nm.

In RDP the unit-cell dimensions are $a=0.761$ nm, $c=0.729$ nm, and $c/a=0.959$. The relative coordinates of oxygen in the unit cell are (0.142, 0.086, 0.120).[14] The thermal-expansion coefficients are $\alpha_a=2.2\times10^{-5}\ \mathrm{K}^{-1}$ and $\alpha_c=4.6\times10^{-5}\ \mathrm{K}^{-1}$.[12] The NQR measurements give $(V_{ZZ})_1=\pm5.9\times10^{19}\ \mathrm{V/m^2}=\pm8.9k_0$ and $\alpha_V=2.3\times10^{-4}\ \mathrm{K}^{-1}$.

The experimental and theoretical values of $(V_{ZZ})_1$ agree at $s=0.019$ nm where the calculated value of α_V is equal to $4.1\times10^{-4}\ \mathrm{K}^{-1}$. The experimental and theoreti-

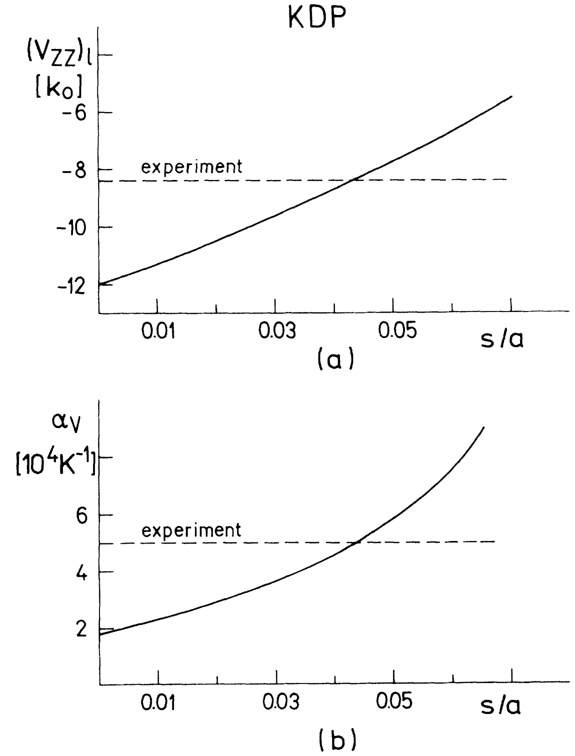

FIG. 6. The calculated value of the largest principal value $(V_{ZZ})_1$ at the potassium site in KDP (a) and the calculated value of the temperature coefficient α_V in KDP (b) as functions of the distance s. The experimental values are represented by the broken lines.

cal values of α_V agree at $s=0.002$ nm where the calculated value of $(V_{ZZ})_1$ is equal to $-10.6k$. There can be different reasons for this discrepancy. Perhaps the literature values of the Sternheimer antishielding factor γ_∞ and of the rubidium nuclear-quadrupole moment $Q(^{85}\mathrm{Rb})$ are wrong or—what we supposed in the case of KDA—the valence electron is not completely transferred from the rubidium to the phosphate ion. In the latter case, which we believe is the most probable, the temperature coefficient α_V does not depend on the excess electric charge e of an ion whereas the value of $(V_{ZZ})_1$ is proportional to it. Thus a consistent picture can be obtained if $s=0.002$ nm and $e=0.84e_0$.

In RDA the unit-cell dimensions are $a=0.779$ nm, $c=0.747$ nm, and $c/a=0.958$.[12] The relative coordinates of oxygen within the unit cell have to our knowledge not yet been determined. After a comparison of the known data in KDP, KDA, and RDP we tentatively used in the calculations the following relative coordinates of oxygen: (0.154, 0.090, 0.128). The thermal-expansion coefficients are $\alpha_a=1.7\times10^{-5}$ K^{-1} and $\alpha_c=4.9\times10^{-5}$ K^{-1}.[12] The NQR data give $(V_{ZZ})_1=\pm3.7\times10^{19}$ V/m^2$=\pm5.5k_0$ and $\alpha_V=7.0\times10^{-4}$ K^{-1}.

The theoretical and experimental values of $(V_{ZZ})_1$ agree at $s=0.035$ nm whereas the theoretical and experimental values of α_V agree at $s=0.016$ nm. If we again assume that the reason for this discrepancy is the electric charge e of an ion which is lower than the elementary charge e_0 (the valence electron has a nonzero density at the rubidium site) then the experimental and theoretical values agree at $s=0.016$ nm and $e=0.75e_0$.

The measured EFG tensor at the cation sites in paraelectric KDP, KDA, RDP, and RDA as well as its temperature coefficient α_V agree rather well with the calculated values if it is assumed that the excess electric charge $-e$ of an anion is in time average equally shared by the four oxygens and if the center of the electric charge $-e/4$, belonging to an oxygen, is displaced by a small distance s from the oxygen site in the direction of the O-H-O hydrogen bond.

A small difference in s, which is observed in fitting the experimental value of $(V_{ZZ})_1$ to the calculated value and in fitting the experimental value of α_V to the calculated value, is ascribed to the electric charge e of an ion, which is slightly lower than the elementary electric charge e_0. The ratio e/e_0 is within the accuracy of the measurements and calculation equal to ~1 in KDP, 0.83 in KDA, 0.84 in RDP, and 0.75 in RDA. Thus by exchanging potassium by rubidium the electric charge e seems to drop by approximately $0.1e_0$. An exchange of a phosphate group by an arsenate group seems to cause a drop of the electric charge e which is again approximately equal to $0.1e_0$.

The distance s from an oxygen atom to the center of the electric charge $e/4$ is equal to 0.032 nm in KDP, 0.044 nm in KDA, 0.002 nm in RDP, and to 0.016 nm in RDA. It seems that an exchange of potassium by rubidium decreases the distance s by approximately 0.03 nm whereas an exchange of a phosphate ion by an arsenate ion increases the distance s by approximately 0.01 nm. We may suppose that the distance s depends on the length of the O-H-O hydrogen bond. But in KDP and RDP in which the O-H-O hydrogen bonds are nearly of the same lengths a large difference in the distance s is observed. Thus we believe that the distance s depends mainly on the electron structure of the phosphate (or arsenate) group.

The linear temperature dependences of the ^{39}K and ^{85}Rb NQR frequencies in paraelectric KDP, KDA, RDP, and RDA with the temperature coefficients which are rather close to the calculated ones suggest that the "antiferroelectric" Slater configurations of the H_2PO_4 and H_2AsO_4 groups, which can be observed by the ^{75}As NQR, have nearly no influence on the NQR frequencies of cation nuclei. These Slater configurations thus represent only the local excited states of the H_2PO_4 and H_2AsO_4 groups whereas they have nearly no influence on the nearest environment. The temperature dependences of the ^{39}K, ^{85}Rb, and ^{87}Rb NQR frequencies in KDP, KDA, RDP, and RDA are thus mainly the consequences of the anisotropic thermal expansion of the crystal lattice.

V. CONCLUSIONS

Nuclear-quadrupole resonance frequencies of ^{39}K and ^{85}Rb have been measured in paraelectric KDP, KDA, RDP, and RDA as functions of temperature. The nuclear quadrupole coupling constants and the principal values of the electric-field-gradient tensor have been calculated from the NQR frequencies.

The largest principal values $(V_{ZZ})_1$ of the EFG tensor and their temperature coefficients α_V have been calculated in a point charge model in which a cation bears an excess electric charge $+e$, which is in general lower than the elementary electric charge e_0, whereas the negative electric charge $-e$ of a phosphate (or arsenate) group is in time average equally shared by the four oxygens. The center of the electric charge $e/4$, belonging to an oxygen, is shifted by a small distance s from the oxygen along the O-H-O hydrogen bond.

At reasonable values of the electric charge $e(0.75e_0\le e\le e_0)$ and of the distance $s(0.002\text{ nm}\le s\le0.044\text{ nm})$ we obtain a fair agreement of the experimental and theoretical values of the nuclear-quadrupole coupling constant. Also the temperature coefficients of the quadrupole coupling constant calculated under an assumption that they depend only on the anisotropic thermal expansion of the crystal lattice agree rather well with the measured ones.

The electric charge e of an ion which is in KDP approximately equal to the elementary charge e_0 seems to drop by approximately $0.1e_0$ when potassium is exchanged by rubidium. An approximately equal drop of the electric charge e seems to occur when a phosphate group is exchanged by an arsenate group.

The distance s from the oxygen site to the center of the electric charge $-e/4$ within the O-H-O hydrogen bond seems to exhibit a minor dependence on the hydrogen bond length whereas it seems to depend mainly on the electron structure of the PO_4^- and AsO_4^- ions.

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