Raman Spectra of Tetragonal KH_2PO_4†

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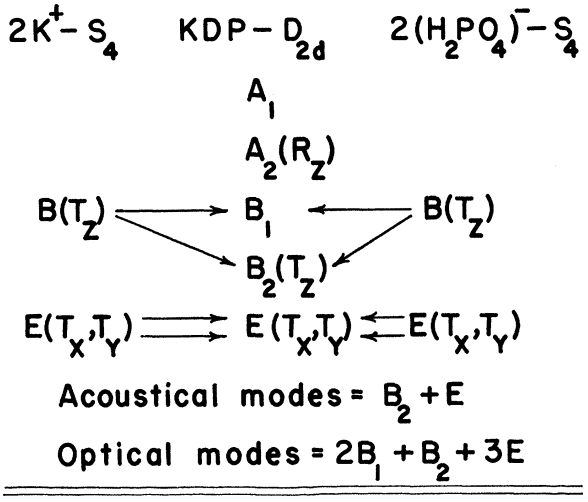
Raman spectra of crystalline KH_2PO_4 at 294 °K are reported for shifts up to 700 cm^{-1}. Five of the six optical-phonon modes of the K^+-$(H_2PO_4)^-$ lattice are unequivocally identified; their positions and linewidths are accurately determined. Analysis of the spectral structures above 300 cm^{-1} shows that the tetrahedral $(PO_4)^{3-}$ ion remains essentially as an "individual" molecule in the crystal, and its vibrational modes are split by the local crystalline field of S_4 symmetry.

Recent interest in the ferroelectric transition[1] and polarization flucuations[2] of crystalline KH_2PO_4 (KDP) suggests a need for investigating the optical-phonon spectra (lattice modes) of the crystal. Popova and Stekhanov[3] reported room-temperature laser-excited Raman spectra with the scattered polarization unanalyzed. They identified three of the six lattice modes of the K^+-$(H_2PO_4)^-$ lattice as predicted by simple group theory. We present in this paper Raman spectra of KDP at 294 °K for shifts up to 700 cm^{-1}; the polarization of both incident and scattered radiation is analyzed to avoid possible ambiguity in spectral differentiation. Better resolution and much improved signal-to-noise ratio in our spectra allow us to (i) identify unequivocally five of the six optical-phonon modes, and (ii) report accurate linewidths as well as positions of these modes. In addition, we have also identified lines above 300 cm^{-1} and their structure in all polarizations. Group-theoretical arguments lead us to conclude that the vibrational modes of the $(PO_4)^{3-}$ ion in the KDP crystal are split under crystalline fields of the local symmetry S_4. These modes therefore remain essentially molecular vibrations.

The KDP crystal at room temperature may be regarded[4] as consisting of K^+ and $(H_2PO_4)^-$ ions belonging to the space group D_{2d}^{12}. The primitive cell for this model contains two K^+ ions and two $(H_2PO_4)^-$ ions, both occupying sites[4,5] of S_4 symmetry. The point group of the crystal which depicts the long-wave optical phonons and the center of the Brillouin zone is D_{2d}. A simplified method[6,7] using the correlation table of point groups may be applied to determine the zone-center optical-phonon spectra. Each ion in the primitive cell may undergo translational motion with components along the z direction and in the xy plane. For the S_4 sites which both the K^+ and the $(H_2PO_4)^-$ ions occupy, these motions belong to the B and E species, respectively. These species of the site group S_4 are correlated with the irreducible representations of the crystal point group D_{2d} by the connecting arrows, according to the correlation table.[7] A convenient format for carrying out this correlation is shown in Table I. In the center column all of the species of the crystal point group D_{2d} are listed. Only the translational species of the K^+ and $(H_2PO_4)^-$ ions which occupy the site group S_4 are listed in the left and right columns of the table. The number of times a particular species occurs in the final decomposition is given by the number of arrows which terminate on that species symbol. In this manner, the lattice vibrations of KDP are decomposed into $2B_1+2B_2+4E$ phonon modes of the lattice. The acoustical-phonon modes are the translational species $B_2(T_z)+E(T_x, T_y)$ indicated in the table. Subtracting these from the total phonon modes, the remainder $2B_1+B_2+3E$ are the species corresponding to the optical-phonon modes. This classification agrees with the detailed analysis of Shur.[8]

Experimentally, a 50-mW He-Ne laser was used for excitation. The scattered light was analyzed with a Czerny-Turner double monochromator;

TABLE I. Correlation table of group D_{2d} and normal modes of the K^+-$(H_2PO_4)^-$ lattice.



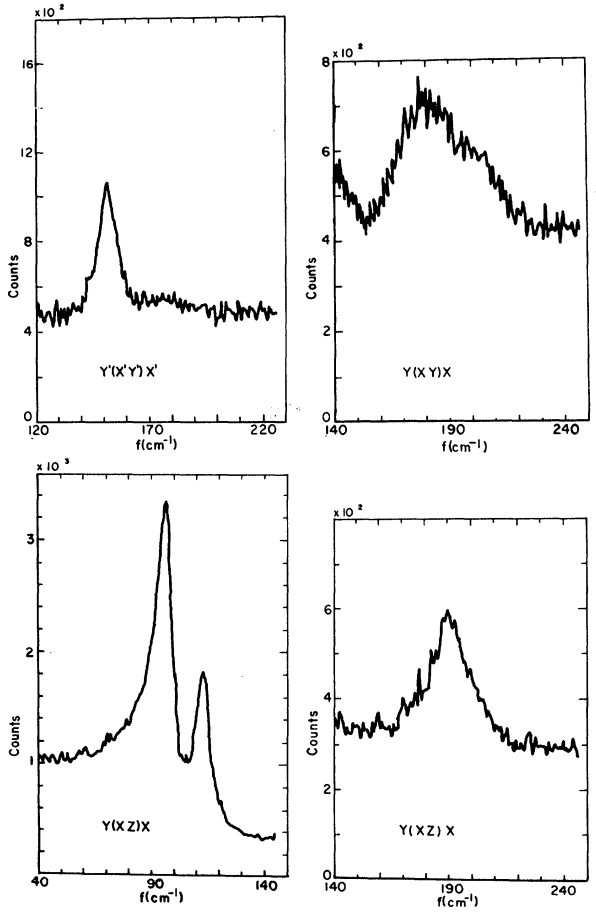


FIG. 1. Raman spectra of the K^+-$(H_2PO_4)^-$ lattice; linewidth of the instrumentation function is 4 cm^{-1}; B_1 mode at 151 cm^{-1}, B_2 mode at 180 cm^{-1}, and E modes at 96, 114, and 190 cm^{-1}.

photon-counting detection techniques were used and the results were stored in a multichannel analyzer. A digital-timer circuit was constructed for the multichannel analyzer to increase the counting time. The intensity of our light source and the dispersion of our monochromator are comparable to those used by Popova and Stekhanov,[3] but the advantage of our detection system is that for a given spectral range we can dwell for a long time and thus increase the signal-to-noise ratio.[9] Two KDP samples of orthorhombic shape were used. The three mutually perpendicular edges of one crystal were parallel to the crystallographic axes x, y, and z. The second crystal was fabricated such that the x' and y' edges were 45° with respect to the x and y axes, and the z edge remained as in the first crystal. This second orientation was chosen to help unscramble the resulting spectra. The scattering volume for the experiment was about 1 cm × 2000 μ^2.

The spectra in the region of the optical phonons of the K^+-$(H_2PO_4)^-$ lattice are shown in Fig. 1. The slit width used was 200 μ which gives a measured linewidth of 4 cm^{-1} for the instrument function. The notation for the incident and scattered polarizations is conventional[10]: $y(xz)x$, for example, indicates a measurement of the intensity of the Raman tensor element α_{xz} scattering along the x axis with light incident in the y direction. The intensity scale in the figure refers to experimental photon counts. According to the symmetry of the Raman tensors[7] for the point group D_{2d} given in Table II, five of the six lattice modes of the various symmetry species are identified. The position and the full linewidth at half-maximum, Δf, of the Raman-active lines in Fig. 1 are readily determined. They are 151 ($\Delta f = 10$) for the B_1 mode, 180 ($\Delta f = 27$) for the B_2 mode, and 96 ($\Delta f = 9$), 114 ($\Delta f = 7$), 190 ($\Delta f = 21$) for the E modes, all in cm^{-1}. The quality of our spectra in Fig. 1 is obviously superior to that reported by Popova and Stekhanov,[3] whose quoted width for the instrument function is 6 cm^{-1} in this spectral region. Owing perhaps to the lack of scattered signal, Popova and Stekhanov did not analyze the polarization of the scattered radiation, and as a result they were unable to resolve the broad B_2 mode at 180 cm^{-1} from the E mode at 190 cm^{-1}. Their early data[11] showed a line at 58 cm^{-1} and it was included as an E mode in Shur's calculation.[8] Since they could not locate this line in their recent work,[3] and neither can we find this line, its existence is questionable. The three E modes we report here are probably the only optical lattice modes of E species as predicted by group theory. The only optical lattice mode yet unfound is a B_1 mode which is either very weak or has a frequency of less than 4 cm^{-1}. We have searched for this mode down to a shift of 4 cm^{-1} without success.

The spectra in Fig. 2 were taken with a measured 7-cm^{-1} linewidth for the instrument function and cover frequency shifts up to 700 cm^{-1}. The $y(xy)x$ spectrum in Fig. 2(c) is in agreement with the spectrum given by Kaminow[2] in which he made no attempt to identify the optical modes of the K^+-$(H_2PO_4)^-$ lattice. In general, our spectra in Fig. 2 show several detailed features. There is a shoulder in the $y(xy)x$ spectrum and a high background in the $y(xz)x$ spectrum in the low-frequency region. The causes for these features and for other askew lines could perhaps be explained in terms of anharmonic interactions. In particular, the broad left shoulder of the 470-cm^{-1} line may be due to the existence of weaker lines in that region,[3] but we were unable to resolve the details. The lines below 300 cm^{-1} are the optical lattice modes detailed in Fig. 1. The strong peaks above 300 cm^{-1} may be associated with the internal vibrations[12] of the $(H_2PO_4)^-$ ion.

It is well known[13] that the vibrational modes of a

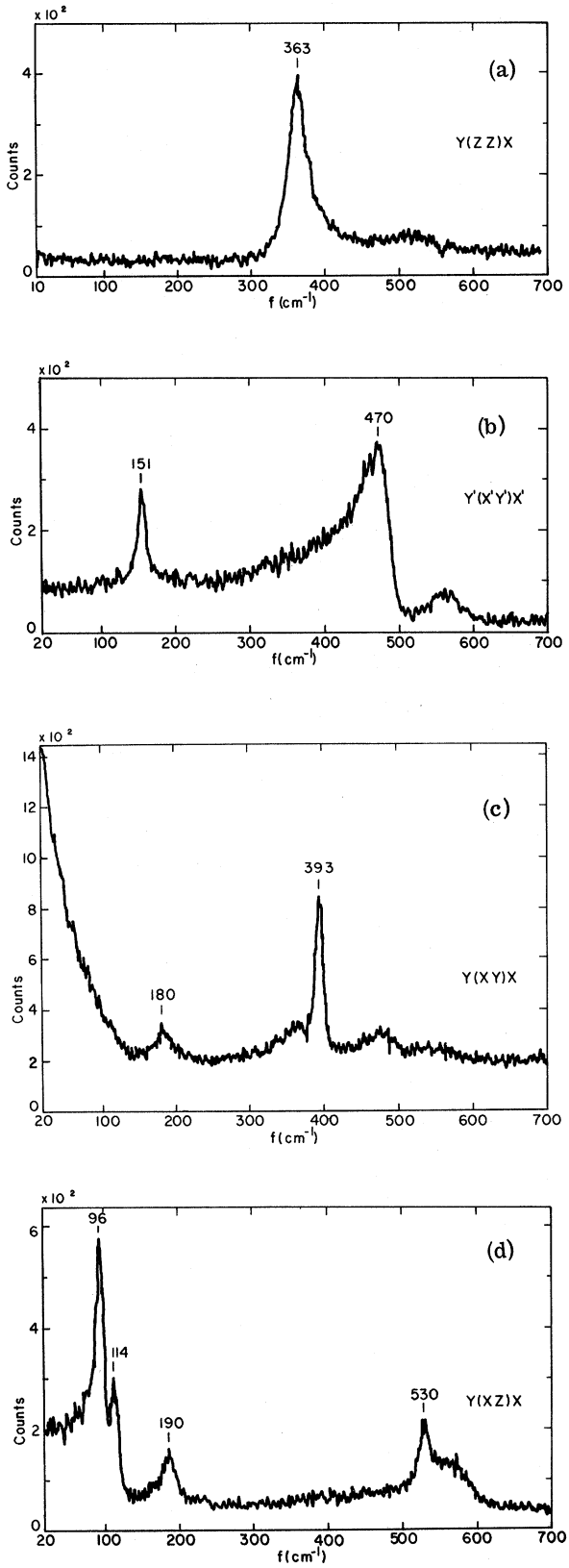


FIG. 2. Raman spectra of KDP; (a) A_1 species, (b) B_1 species, (c) B_2 species, and (d) E species.

free tetrahedral $(PO_4)^{3-}$ ion consist of an A_1 mode at 980 cm^{-1}, an E mode at 363 cm^{-1}, and two F_2 modes at 515 and 1082 cm^{-1}. All of these species of the point group T_d are Raman active. Whether the phosphate ion behaves essentially as an "individual" molecule in the crystalline KDP deserves some investigation. If the phosphate ion binds strongly with the lattice as does the SiO_2 molecule in a quartz crystal,[14] one would expect the original molecular vibrations to disappear and new lattice modes with species under the crystal point group symmetry D_{2d} to be formed. Our polarized Raman data in Fig. 2 do not suggest this to be the case. The lines shown in Fig. 2 near 363 and 515 cm^{-1} are characteristic of the molecular vibrations of the $(PO_4)^{3-}$ ion modified slightly by the surrounding crystalline field. Owing to this small perturbation, the E mode of T_d symmetry of the $(PO_4)^{3-}$ ion at 363 cm^{-1} is split into lines at 363 and 393 cm^{-1} in the crystal. Similarly, the F_2 mode of the tetrahedral $(PO_4)^{3-}$ ion at 515 cm^{-1} is split into lines at 470 and 530 cm^{-1}. In Table II we decompose the E and F_2 modes of T_d symmetry into species of the point groups of lower symmetry D_{2d} and S_4. Such decomposition and the transformation of Raman tensors given in the table are well known from group theory.[7] By comparing the Raman spectra with the tensors listed, we can determine which is the correct decomposition and thus detect what has happened to the $(PO_4)^{3-}$ ion in the crystal. For example, the 393-cm^{-1} line (E mode) appears in the $y(xy)x$ spectrum but not in the $y'(x'y')x'$ spectrum of Fig. 2 corresponding to Raman tensor element α_{xy} but not element $\alpha_{x'y'}$. From Table II we can see that the 393-cm^{-1} line corresponds to the B species of the S_4 group, and not B_1 species of the D_{2d} group. Similarly, the 470-cm^{-1} line (F_2 mode) appears in the $y'(x'y')x'$ spectrum and not the $y(xy)x$ spectrum of Fig. 2, indicating that this line corresponds to the B species of group S_4 and not the B_2 species of the D_{2d} group. Therefore, the local crystalline field in KDP causes the E and F_2 vibrations of the $(PO_4)^{3-}$ ion to split into $A+B$ and

TABLE II. Spectral decomposition for the $(PO_4)^{3-}$ ion under crystalline field and the Raman tensors of the point groups D_{2d} and S_4.

D_{2d}		T_d	S_4	
$(\alpha_{xx}+\alpha_{yy},\alpha_{zz})$	A_1		A	$(\alpha_{xx}+\alpha_{yy},\alpha_{zz})$
	A_2	E		
$(\alpha_{xx}-\alpha_{yy}=\alpha_{x'y'})$	B_1		B	$(\alpha_{xx}-\alpha_{yy}=\alpha_{x'y'},\alpha_{xy})$
(α_{xy})	B_2	F_2		
$(\alpha_{yz},\alpha_{zx})$	E		E	$(\alpha_{yz},\alpha_{zx})$

$B+E$ vibrational modes of the S_4 symmetry, respectively. The motion of the constituent atoms must, of course, comply with the space group symmetry of the crystal and the two B species of S_4 symmetry, according to Table I, are correlated into the B_1+B_2 zone-center phonons. All these modes behave essentially as "individual" molecular vibrations and may be considered as examples of Einstein phonons.

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Average Magnetic Hyperfine Fields at ^{106}Pd Nuclei in Ni-Pd Alloys

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The average magnetic hyperfine fields at ^{106}Pd nuclei in a series of Ni-Pd alloys have been measured at 77 °K by means of the integral perturbed-angular-correlation method using the (622.0–511.8)-keV γ-ray cascade in ^{106}Pd. The observed magnetic fields have been corrected for the external applied field and the sample magnetization, and extrapolated to 0°K. The average hyperfine fields H_{hf} at the Pd nuclei were found to be negative in the ferromagnetic alloys over the full concentration range, varying from (-194 ± 9) kG in Ni metal to (-41 ± 10) kG in an alloy of 90% Pd. Our estimates for the contribution to the hyperfine field of Pd arising from the local moment on the Pd atom are too small to account for the net measured fields. Thus, we ascribe the origin of the remaining large negative fields to interactions with neighboring atoms through the conduction electrons.

I. INTRODUCTION

The magnetic properties of palladium metal and its alloys have been the subject of considerable study, particularly in the last few years. Among the most interesting properties is the occurrence of ferromagnetism in Pd alloyed with very small concentrations of Fe, Co, and Ni.[1,2] At these small concentrations of the 3*d* metal, susceptibility and neutron studies have indicated that giant moments are associated with each impurity atom.[1-3] These moments, up to 12 μ_B per impurity atom, are much greater than can be produced by 3*d* states on the impurity alone. Thus, it is reasonable to assume that the Pd atoms nearby one of these impurities carry a moment and are intimately associated with the long-range ferromagnetic coupling observed for alloys with these small concentrations of 3*d* metal. The part played by conduction electrons in the long-range ferromagnetic coupling between impurities is,