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Neutron-Scattering Study of the Ferroelectric Phase Transition in CsD_2PO_4 †

D. Semmingsen,* W. D. Ellenson, B. C. Frazer, and G. Shirane

Brookhaven National Laboratory, Upton, New York 11973

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A neutron-scattering study of the ferroelectric transition in CsD_2PO_4 has yielded quasi-elastic diffuse distributions of intensity typical of a one-dimensional system with chain-like ordering parallel to the ferroelectric b axis of this monoclinic crystal. Therefore, despite such suggestive similarities as the large isotope shift in T_c , the transition is quite different from that of tetragonal KD_2PO_4 where the diffuse scattering clearly exhibits characteristics of three-dimensional dipolar interactions.

Although KD_2PO_4 has been the object for several neutron-scattering¹⁻³ studies, studies of structural phase transitions of hydrogen-bonded materials with neutrons are still relatively few. In addition to KD_2PO_4 , $\text{ND}_4\text{D}_2\text{PO}_4$ ⁴ and $\text{H}_2\text{C}_4\text{O}_4$ (squaric acid)⁵ have also been studied, to mention only those materials in which considerable isotope effects are associated with the transition.

The crystal structure⁶ of CsH_2PO_4 is quite different from that of KH_2PO_4 , the well-known tetragonal prototype of the ferroelectric phosphates and arsenates. Nevertheless, as in the latter family, this material does undergo a phase transition to a ferroelectric state ($T_c = 153$ K),⁶⁻⁸ and also there is a large isotope effect on T_c upon substitution of deuterium for hydrogen (T_c reported to be 267 K for CsD_2PO_4).⁸ Clearly, there is a central role for strong hydrogen bonds in the transition mechanism. Despite these suggestive similarities the results of the present study demonstrate that the nature of the transition in the Cs compound has unique characteristics which set it apart from the KH_2PO_4 family.

CsH_2PO_4 crystallizes in the monoclinic space

group $P2_1/m$ with two formula units per unit cell. Measurements in the present study show that CsD_2PO_4 is isostructural with CsH_2PO_4 since there are only small differences in the lattice parameters. At 265 K the following lattice parameters for CsD_2PO_4 were obtained: $a = 7.906$, $b = 6.364$, $c = 4.889$ Å, and $\beta = 107.7^\circ$. Moreover, since no violation of the systematic extinction ($0k0$) with $k = 2n + 1$ was found in the low-temperature phase of either material, the ferroelectric space group in both cases is $P2_1$, with the polar axis being the unique b axis, as suggested by Uesu and Kobayashi.⁶

The neutron scattering experiments reported here were carried out on a single crystal of CsD_2PO_4 . Sample crystals were prepared from CsH_2PO_4 by several recrystallizations from 99.8% D_2O . The crystal used in the experiments had well-developed $\{011\}$ and $\{100\}$ faces and a mass of about 1.5 g. For most measurements the crystal was aligned so that the scattering took place in the a - b plane. The crystal was of good quality, giving rocking curves with full width at half-maximum of 0.18° . Neutron-scattering ex-

periments were carried out with triple-axis and double-axis spectrometers at the Brookhaven high-flux beam reactor using graphite monochromator and analyzer crystals and a collimation of 20'-10'-10' or 20'-10'-10'-20' for the double- or triple-axis instrument, respectively. The temperature range covered in the experiments was 200 to 300 K.

Survey measurements disclosed the presence of diffuse distributions of quasielastic scattering intensities in several regions of reciprocal space. These intensities were found to be temperature dependent, with peaking at 264 K, a temperature somewhat lower than the T_c reported by Levstik *et al.*⁸ for CsD_2PO_4 . This variation may be due to some small difference in the degree of sample deuteration. A Curie-Weiss-type behavior of intensity versus temperature was found with no hysteresis in the transition temperature. A survey was also made of the lowest-lying phonon modes propagating in the a and b directions. Acoustic-phonon branches were easily observable but no additional optic phonons whose frequencies approached zero as T_c was approached were found. Thus the diffuse scattering is interpreted as being due to either a heavily damped phonon mode or an ordering mode with atomic shifts between distinct sites.

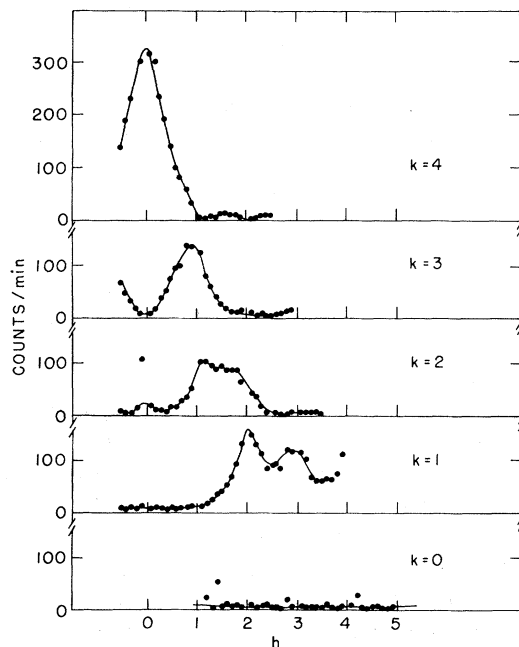


FIG. 1. Distribution of diffuse scattering in the $(hk0)$ zone at $T = 267$ K measured in scans along h , perpendicular to the ferroelectric axis.

Figure 1 shows the results of measurements on CsD_2PO_4 in the $(hk0)$ zone with scans of the diffuse quasielastic intensity along h (perpendicular to the polar axis). The sharp peaks resulting from Bragg reflections have been removed. The diffuse intensities in Fig. 1 have a rather broad extent and it is seen that the intensity does not peak systematically at the reciprocal lattice points. It was also found that in the temperature range $T_c \pm 40$ K the shape of the diffuse intensity did not depend markedly on temperature, but intensities grow as the transition temperature is approached. In Fig. 2, the results of scans along k (parallel to the polar axis) are shown near $(2.15\ 1\ 0)$ and the diffuse scattering is seen to be extremely narrow in this direction. Measurements at room temperature in the $(0kl)$ and $(h0l)$ zones, as well as experiments with tilting out of the $(hk0)$ zone, revealed that the scattering is confined to layers perpendicular to the unique axis. These results are consistent with an interpretation that the scattering is of one-dimensional (1-D) origin. Variations in intensity along the h directions are then due to variations in the 1-D structure factor.

Figure 3 shows a detailed mapping of the quasielastic scattering around (040) compared with the 3-D scattering observed in KD_2PO_4 , due to polarization fluctuations.^{1,2} The scattering is seen to be much more anisotropic in CsD_2PO_4 than in KD_2PO_4 . Furthermore, in CsD_2PO_4 the 1-D

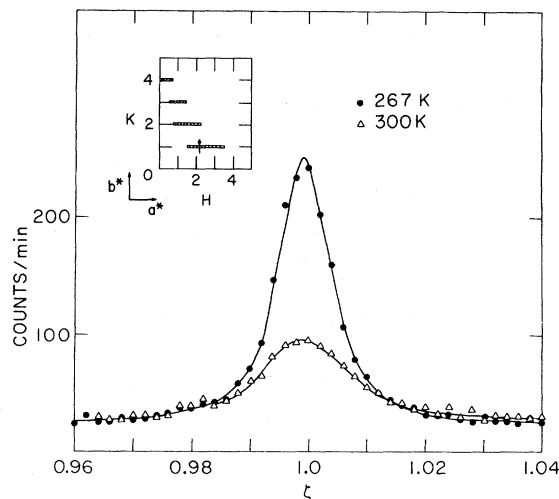


FIG. 2. Scans at $E = 0$ of the temperature dependence of the diffuse scattering at $(2.15\ \xi\ 0)$. The inset shows the $(hk0)$ scattering plane. The hatched area gives the regions of significant diffuse scattering, the arrow gives the position and direction of the scan.

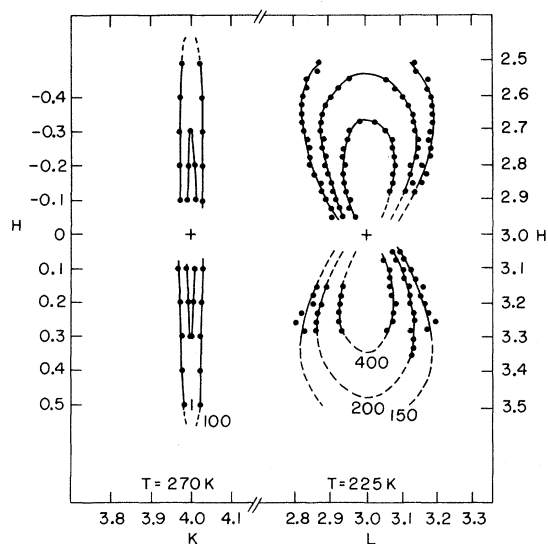


FIG. 3. To the left, intensity contours in the $(hk0)$ zone near (040) with $E=0$ in CsD_2PO_4 ; to the right, results from scans in KD_2PO_4 in the $(h0l)$ zone near (303) (from Ref. 2). The figures are drawn to the same scale in inverse angstroms. The intensity units are arbitrary.

structure factor just happened to peak around (040) , while the intensity distribution in other regions of the $(hk0)$ zone extends over several reciprocal lattice units along h . Thus, the scattering in CsD_2PO_4 has an entirely different nature from that in KD_2PO_4 .

No structural study of the ferroelectric phase of either CsH_2PO_4 or CsD_2PO_4 has yet been reported. For the paraelectric phase of CsH_2PO_4 the results of a recent structural study⁶ revealed that there are two crystallographically different hydrogen bonds which are also of substantially different lengths (2.43, 2.56 Å). The shorter of these bonds is situated across the center of inversion and joins the phosphate groups into zig-zag chains running along the unique b axis. The other bond occupies a general crystallographic position and ties the chains into hydrogen-bonded layers parallel to the (100) plane. From the structural results at room temperature we infer that only one of the two hydrogen bonds is involved in the ferroelectric phase transition. The two P-O distances involved in the longer hydrogen bond have values consistent with the hydrogen atom being located closer to one of the oxygen atoms. Therefore, this bond would appear to be already "ordered" even in the room-temperature phase. From this we conclude that the ordering of hydrogen (deuterium) atoms at the ferroelectric

transition in CsH_2PO_4 (CsD_2PO_4) takes place only in the bonds associated with the chains running along the b axis.

If the ordering along a chain of hydrogen-bonded phosphate groups is not correlated with other chains, then the quasielastic scattering will be spread out in the $(hk0)$ reciprocal planes with a distribution of intensity characteristic of the 1-D structure factor for the chain. This 1-D behavior of the material is of particular interest and in fact so far no clear evidence of critical scattering due to 3-D ordering has been found. Any such scattering, therefore, is probably extremely narrow in q temperature. In this respect the scattering differs from that found in $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ where the 1-D scattering from chains of $\text{Pt}(\text{CN})_4$ was found to be modulated by 3-D critical scattering peaking at the reciprocal lattice points.⁹ From Fig. 1, it is evident that this is not the case in CsD_2PO_4 . Furthermore, preliminary calculations with simple 1-D models qualitatively reproduce the observed scattering and indicate that most of the atomic displacements of heavy atoms take place along chains.

As the phase transition is approached from above, the correlation within a chain develops. The scattering will reflect these correlations by growing in intensity and the width of the diffuse ridges will narrow. From the measurements in Fig. 2, we can roughly estimate an upper limit to the width of the "Bragg planes." At 267 K this is 0.004 \AA^{-1} which corresponds to a lower limit on the correlation length of about 250 Å. The measurements at 300 K appear to show some broadening and a conservative estimate of the correlation length is about 100 Å.

Further experiments on CsD_2PO_4 and CsH_2PO_4 with neutron-scattering techniques are now in progress. These include measurements with higher resolution to obtain a more reliable measure of correlation along the chains and to search more carefully for 3-D critical scattering, as well as to determine the static structure in the ferroelectric phase.

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*Visiting scientist from the University of Oslo, Oslo, Norway.

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Identification of Shallow Electron Centers in Silver Halides

Shiro Sakuragi and Hiroshi Kanzaki

Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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On the basis of the excitation-induced absorption spectra in silver halides doped with impurities, two kinds of shallow electron centers are identified. One is an electron bound at a silver interstitial ion and corresponds to the intrinsic electron center in silver halides. Addition of chalcogen impurities enhances the spectra of this origin. The other is an electron bound at substitutional divalent cations, the transition energy of which shifts systematically depending on the kind of impurity.

Transient absorption of pure silver halides during band-to-band excitation at liquid helium temperature was first observed by Brandt and Brown.¹ On the basis of the subsequent studies,²⁻⁴ the optical transition has been interpreted as due to an electron polaron bound in an attractive Coulomb field. The origin of the positive charge center, however, has not yet been identified.

In this Letter we report an observation of zero-phonon bands in silver halides doped with impurities. Firstly, the absorption band observed in a pure crystal is enhanced by addition of chalcogen impurities. This provides evidence that the positive charge center in pure silver halides is a silver interstitial ion. Secondly, substitutional divalent cations produce a new set of absorption bands, the energy of which shifts depending on the kind of impurity. This establishes that the divalent cations can be responsible for shallow electron centers of similar nature.

In the present study, pure crystals are obtained by zone-refining in a halogen atmosphere. Doped crystals are grown in vacuum by the Bridgman method after adding the impurity to zone-refined crystals. The doped samples are rapidly cooled from high temperature (300–350°C in helium atmosphere). This procedure, as well as the low concentration of impurities, is effective in suppressing the spectrum broadening. The impurity concentrations are estimated from the amounts

added, and the values for the samples in Figs. 1 and 2 are less than 3×10^{-6} mol for chalcogens and about $(3-9) \times 10^{-6}$ for divalent cations.

For infrared measurements, samples 200–250 μm thick are immersed in pumped liquid helium. Total light from a platinum screen source⁵ is

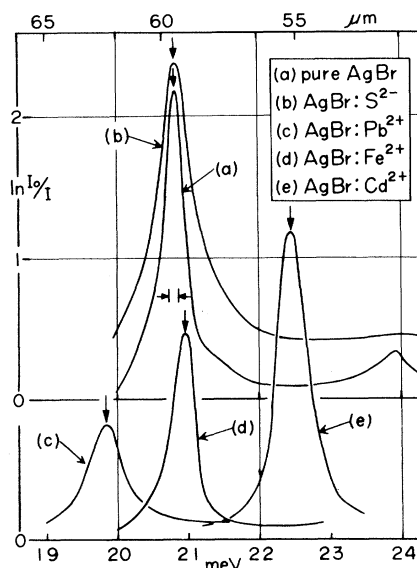


FIG. 1. Typical absorption spectra around zero-phonon band for AgBr doped with impurities during band-to-band excitation at 2 K. The spectral bandwidth used is indicated.