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DISAPPEARANCE OF A LOW FREQUENCY KH_2PO_4 MODE UPON TRANSITION TO THE FERROELECTRIC PHASE

by

Ch. SCHENK*, E. WIENER**, B. WECKERMANN* and W. KLEY*

* Euratom
** Avnear

1968

Joint Nuclear Research Center
Ispra Establishment - Italy

Reactor Physics Department
Experimental Neutron Physics

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Summary

With the aid of a cold neutron spectrometer, the time-of-flight spectra of single crystals of KH_2PO_4 and KD_2PO_4 were measured for different orientations of the momentum exchange vector with respect to the crystallographic axes. For the KH_2PO_4 case with the momentum exchange vector pointing mainly in the direction of the hydrogen bond, the temperature dependence of the spectrum was investigated. It was found that the broad incoherent band around 50 cm^{-1} appearing strongly in KH_2PO_4 at room temperature disappears below the Curie temperature and that the mean-square displacement of the protons in the direction of their bonds is greatly reduced.

KEYWORDS

NEUTRON SPECTROMETERS
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DEUTERIUM COMPOUNDS
MOMENTUM
TEMPERATURE
BINDING ENERGY
FREQUENCY
FERROELECTRIC MATERIALS

DISAPPEARANCE OF A LOW FREQUENCY KH_2PO_4 MODE UPON TRANSITION TO THE FERROELECTRIC PHASE

Introduction (*)

An indication that the short hydrogen bonds (d_{OO} = 2.5 Å) play the triggering role in the KH_2PO_4 ferroelectric transition is provided by the observation[1] that the Curie temperature is subject to an enormous deuteration isotope effect $T_c(KH_2PO_4) = 123$ K whereas $T_c(KD_2PO_4) = 222^0$K. Detailed neutron diffraction analysis, carried out by Bacon and Pease[2], has revealed that a change in the hydrogen configuration occurs at the transition; in the ferroelectric phase there is an ordered asymmetric protonic configuration, whereas above T_c there is an elongated symmetric protonic distribution along the hydrogen bonds. The elongated picture in the nonpolar phase can indicate either a statistically disordered configuration of localized protons, supporting Slater's[3] order-disorder theory, or a configuration in which the proton is actually near both oxygens as the result of one of several possible anharmonic motions. Several theories based on the second alternative have been developed[1,4-7], most of them involving proton quantum tunneling in a double minimum potential well. Approximations to the complicated many-body problem were tried by some authors[4-6], while the possibility of including the effective forces in a single-particle model was explored by Imry et al[7]. The "dynamic" theories[4-7] differ in their predictions of the proton dynamics, especially near the critical temperature, and thus they can be checked experimentally. Another theory, advanced by Cochran[8], is based on general lattice dynamics considerations, and predicts that in this case, as in the displacive ferroelectrics, the softening of a transverse optical mode on approaching T_c is responsible for the phase transition.

*) Manuscript received on August 14, 1968.

The fact that the proton has a relatively high cross section for neutron scattering, which is mostly incoherent, makes neutron scattering a powerful tool in the investigation of proton dynamics. In early investigations on KH_2PO_4 [9,10] the samples used were in the powdered form, which does not permit easy separation of the coherent and incoherent contributions to the scattering. In addition, when a cold neutron facility is used, no reliable conclusions can be drawn as regards the behavior of the spectra in the high wavenumber region, because of the low population in this region at low temperatures. It may be mentioned here that optical spectroscopy is incapable of revealing the proton dynamics behavior of KH_2PO_4, especially as regards the proton tunneling transitions[10], because of the existence of strict selection rules.

Neutron inelastic scattering is governed by the Debye Waller factor, $2W = \langle \vec{K}.\vec{U}_q \rangle^2$, where $\vec{K} = \vec{k}_i - \vec{k}_f$ is the momentum transfer, and U_q is the displacement vector for the proton vibrations. The fact that the one phonon inelastic neutron scattering cross section is proportional to 2W, enables one to distinguish proton directional modes along the various crystallographic axes of single crystals even in the completely incoherent case. A first indication that the use of single crystals might lead to new information, avoiding the averaging effect of the powdered samples used so far, was the anisotropy found in the total neutron cross section of single crystals of KH_2PO_4 [11]. Nevertheless, since all the scattering contributions are mixed up in such total cross section measurements, they can only be regarded as a preliminary check.

In the present paper we describe differential neutron scattering measurements on single crystals of KH_2PO_4. The results give further insight into the lattice dynamics of this crystal, especially the incoherent contribution of the protons, governed by the geometrical restrictions of the Debye

Waller factor. The short hydrogen bonds in KH_2PO_4, linking the PO_4 groups, lie alternately almost along the X and Y axes of the crystal (with a small deviation of 0.5°). They are thus perpendicular to the ferroelectric axis, which coincides with the Z axis of the crystal. Alignment of the crystal permits comparison of the inelastic neutron scattering spectra obtained when the momentum transfer $\vec{K}$ is parallel to the H bond and when it is perpendicular to it. The results were further compared with the deuterated case in order to permit separation of the coherent contribution. The incoherent contribution found in this way for the case of KH_2PO_4 when $\vec{K}$ is parallel to the H bond was measured as a function of the temperature, crossing the Curie point.

Experimental Procedure

The neutron scattering measurements on single crystals of KH_2PO_4 and KD PO were carried out at the ISPRA I cold facility[12], using a 3 m flight path and a two-layer bank of BF_3 counters , with an automatic time-of-flight corrector for the first layer. Single crystals, of KH_2PO_4 and 90% deuterated KD_2PO_4, 0°X cut and 0°Z cut, in the form of plates 25 x 25 mm, were supplied by the Clevite Corp. The KH_2PO_4 crystals were 1.5 mm thick and the deuterated crystals 3 mm thick. The data were corrected for background, sample thickness, air attenuation in the flight path, counter efficiency, and equal monitoring. The inelastic spectra were also corrected for thermal population. The geometrical condition which the momentum exchange $\vec{K}$ is parallel either to the X or Z axis of the crystal was obtained only for the pure elastic scattering. For the inelastic scattering, there was a deviation of up to 35° from the crystallographic axis, as indicated on the time axis of the time-of-flight spectra Fig. 1(a)-(d). A gas flow cryostat permitted measurements between ambient temperatures and -190 for long time runs, with a temperature stability of 1°C.

Results and Discussion

Figs. 1(a)-(d) show the uncorrected KH_2PO_4 and KD_2PO_4 neutron time-of-flight spectra at room temperature, first when the momentum exchange vector $\vec{K}$ is parallel to the X axis and then when it is parallel to the Z axis. The experimental conditions were the same all the four measurements. The corrected data, including population correction, for the energy region 5-30 meV are shown in Fig. 2(a)-(d). The following conclusions can be drawn from a comparison of these four spectra. The fact that the spectra KH_2PO_4 and KD_2PO_4 are almost the same when $\vec{K}||Z$ proves that the main peaks at low energy are coherent peaks coming from lattice modes. Since the shift of the peaks upon deuteration is very small, mostly below the resolution limit, one can assume that the participation of hydrogens in these modes is very small. On the other hand, when $\vec{K}||X$, that is when the momentum transfer is presumably parallel to the hydrogen bonds, there is a striking difference between the spectra of the two crystals. In the low energy region the contribution of inelastic scattering is very small in the case of KD_2PO_4 , whereas in KH_2PO_4 there appear broad peaks of relatively high intensity which seem to be a pure incoherent contribution due to hydrogen displacement along the bond. This broad incoherent contribution, appearing mostly when $\vec{K}$ is parallel to the H bonds, extends from 30 cm^{-1} to 120 cm^{-1} or even to higher wavenumbers. The above observations suggest that the incoherent inelastic component appearing in the KH_2PO_4 spectrum might also be affected by the phase transition, and we therefore measured its behavior as a function of temperature, especially near T_c.

Fig. 3(a) and (b) shows the inelastic spectra of KH_2PO_4, when the momentum exchange vector for the elastic scattering is in the direction of the hydrogen bond, at 135°K and 113°K respectively (T_c = 123°K). The inelastic cross sections in the low wavenumber region are markedly smaller below the

Curie temperature. Fig. 4a shows the corresponding results in the energy range 0-150 cm^{-1}, after correcting for all experimental factors including the population. In order to bring out the characteristic difference between the spectra above and below T_c the ratio between them was plotted (Fig. 4b, full line). A pronounced peak can be seen at 50 cm^{-1}, which may be regarded as the center of the incoherent hand.

In order to obtain improved statistics so as to measure the temperature dependence of the integrated intensity of the above mode, several short runs were taken at various temperatures around the Curie point. These short runs also permit determination of the average change in the Debye Waller factor upon ferroelectric transition, through the behavior of the elastic part of the spectrum. Fig. 5a shows the pure elastic scattering as a function of temperature. The intensity is clearly higher, by $6 \pm 3\%$, below T_c than above it. Fig. 5b shows the integrated inelastic contribution between 48 cm^{-1} and 78 cm^{-1} after correction for the population factor. A decrease of more than 40% occurs on crossing T_c from above. The errors given in both experiments are not only statistical but include estimated systematic errors of the facility due to the long period over which the experiment was performed (weeks). In order to minimize the systematic errors, points were measured above and below T_c at random.

Since the elastic cross section is proportional to $\exp(-2W) \approx 1-2W$, the method is not very sensitive to changes in U_q at small $|\vec{K}|$ values. Nevertheless, from the jump observed in the elastic data (Fig. 5a), one can estimate that there is a decrease of about 30% in $|U_q|^2$ on going from the nonferroelectric to the ferroelectric phase.

There is a strong indication from the temperature dependence of the inelastic scattering that the incoherent band around 50 cm^{-1} in KH_2PO_4 disappears below T_c. To establish this fact, the ratio of the inelastic neutron cross sections at 135°K and 113°K was calculated, assuming the same frequency distribution but different Debye Waller factors. Using the Zemach Glauber formalism[13], one obtains in the harmonic approximation[14] for one-quantum processes:

$$\frac{d^2\sigma}{d\Omega dt} = \frac{1}{8\pi} \frac{k_i}{k_f} \frac{g(\varepsilon)}{\varepsilon} \frac{1}{e^{\varepsilon/kT}-1} \sum_q (\vec{K}\,\vec{U}_\nu^\lambda)^2 \cdot \sigma_\nu^{inc} \cdot e^{-2W_\nu}$$

and the ratio of the intensities of the same peak at different temperatures is

$$\frac{I_{T_1}}{I_{T_2}} = \frac{[\sum_\nu (\vec{K}\,\vec{U}_\nu^\lambda (T_1)^2]}{[\sum_\nu (\vec{K}\,\vec{U}_\nu^\lambda (T_2)^2]} \frac{e^{-2W_1(T_1)}}{e^{-2W_2(T_2)}} \frac{g_{T_1}(\varepsilon)}{g_{T_2}(\varepsilon)} \frac{e^{\varepsilon/kT_2}-1}{e^{\varepsilon/kT_1}-1}$$

where ε stands for the energy transfer, $g(\varepsilon)$ for the frequency distribution function, and U_ν^λ is the amplitude in normal coordinates of the mode and proton denoted by λ and ν. Using the results of Bacon and Pease[2] for the proton amplitude above the Curie point, and the results shown in Fig. 5a for the change in the average component of the Debye Waller exponent, we obtain with the assumption $g_{T_1}(\varepsilon) = g_{T_2}(\varepsilon)$, the energy dependence as plotted in Fig. 3b (dashed line). It is obvious that the change occurring near 50 cm^{-1} on crossing T_c is much more drastic than in the rest of the spectrum, indicating that this incoherent mode, where the hydrogen displacement is along the hydrogen bonds, disappears in the ferroelectric phase. The abrupt change in the integrated inelastic intensity in Fig. 5b also supports the assumption that in the case $\vec{K}||X$ there is a drastic change in the low frequency spectrum, connected with the inhibition of 50 cm^{-1} mode of motion below T_c.

The characteristics of the 50 cm^{-1} incoherent band found above, namely that in the paraelectric phase it is very broad, its propagation vector coincides with the direction of the hydrogen bond, and that it changes drastically in the ferroelectric phase transition, could be accounted for by either of the following alternatives.

(1) The 50 cm^{-1} level arises from fluctuations in the asymmetry of the double minimum wells, connected with the collective motions of the protons. These fluctuations were assumed to be slower than the tunneling frequency, according to the single particle model of the fluctuating double minimum well[7], or to coincide with it, according to other models[6]. In the ferroelectric phase these collective fluctuations disappear. This is in agreement with the deuteron jumps of the order of 10^{-11} - 10^{-12} sec^{-1} found in NMR experiments on KD_2PO_4 by Schmidt and Uehling[15], which disappear below T_c. The possibility that coupling to such collective motions may explain the broadening of the infrared absorption lines in KH_2PO_4 above T_c, and the narrowing of these lines below T_c, has been suggested elsewhere[10].

(2) The 50 cm^{-1} mode does not describe pure hydrogen motions, but is connected with some very anharmonic lattice mode, probably a collective phase-correlated motion of PO_4 groups with hindered rotations, corresponding to the degrees of freedom of torsion. These motions stop entirely in the ordered phase.

It is interesting that a 50 cm^{-1} band was detected recently in the infrared absorption spectra of KH_2PO_4 by Arefév et al.[16]. These authors suggest the mode to be of a "Cochran's ferroelectric" type, which should tend towards zero frequency on approaching T_c. However, they could not check this

because of experimental difficulties, especially with the cooling of the samples. From our inelastic measurements we could not check whether the 50 cm^{-1} band, actually follows this behavior because of the broad character of the band, which is certainly connected with over-damping of this frequency.

Recently, quasi-elastic scattering of cold neutrons has been measured by Blinc et al.[17] for sample temperatures as high as 145°C. Within the resolution of our spectrometer we could not detect any quasi-elastic scattering at room temperatures, even with $\vec{K}$ in the hydrogen bond direction. A broadening of $E = 0.1$ meV for $K^2 = 5\ A^{-2}$ would have been detected.

Acknowledgement

The authors wish to thank Dr. I. Pelah (Soreq Nuclear Research Center, Israel) and Dr. H. Meister (Ispra) for many enlightening discussions on this topic in the past years.

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Figure Captions

Fig. 1: Neutron time-of-flight scattering spectra of single crystals at room temperature. The angles indicated are the angles between the momentum transfer vector $\vec{K}$ and the relevant axis;
(a) KH_2PO_4, $\vec{K}||Z$; (b) KH_2PO_4, $\vec{K}||X$
(c) KD_2PO_4, $\vec{K}||Z$; (d) KD_2PO_4, $\vec{K}||X$

Fig. 2: Corrected data of Fig. 1 for the energy region 5-30 meV

Fig. 3: Neutron time-of-flight spectra of KH_2PO_4 single crystal with $\vec{K}||X$ at temperatures above and below $T_c(123^oK)$
(a) 135^oK (b) 113^oK

Fig. 4: (a) Corrected spectra of Fig. 3
(b) Ratio of the corrected intensities $I[135^oK]/I[113^oK]$ (full line), and the calculated ratio (dashed line).

Fig. 5: Temperature dependence of the neutron scattering in a KH_2PO_4 single crystal with $\vec{K}||X$
(a) elastic; (b) integral inelastic between 48 cm^{-1} and 78 cm^{-1}.

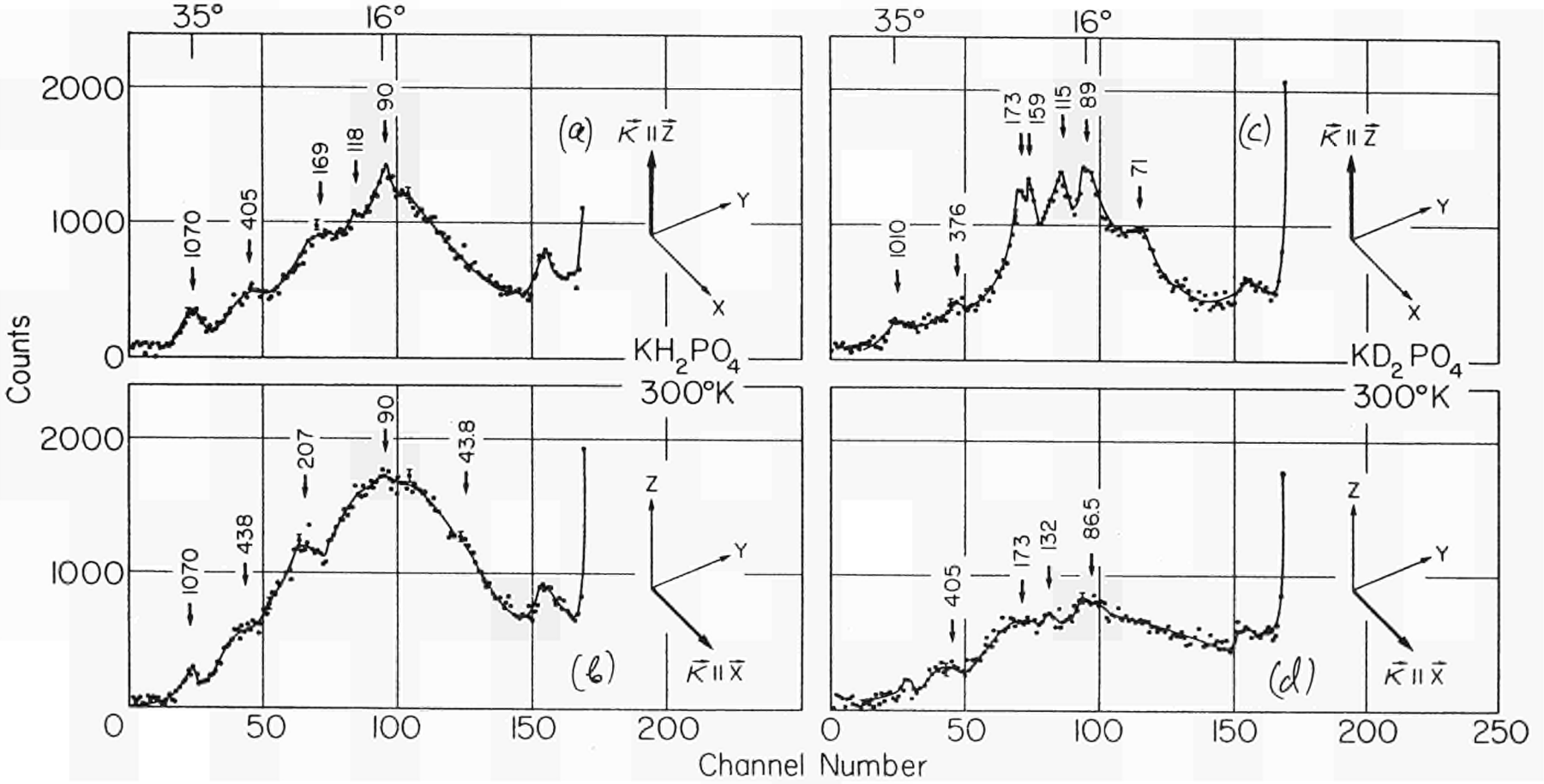
35°
16°
2000
1000
0
Counts
(a)
$\vec{K} \parallel \vec{Z}$
1070
405
169
118
90
Y
X
KH_2PO_4
300°K
(b)
$\vec{K} \parallel \vec{X}$
1070
438
207
90
43.8
Z
Y
(c)
$\vec{K} \parallel \vec{Z}$
1010
376
173
159
115
89
71
KD_2PO_4
(d)
$\vec{K} \parallel \vec{X}$
405
173
132
86.5
0
50
100
150
200
250
Channel Number

Fig. 1

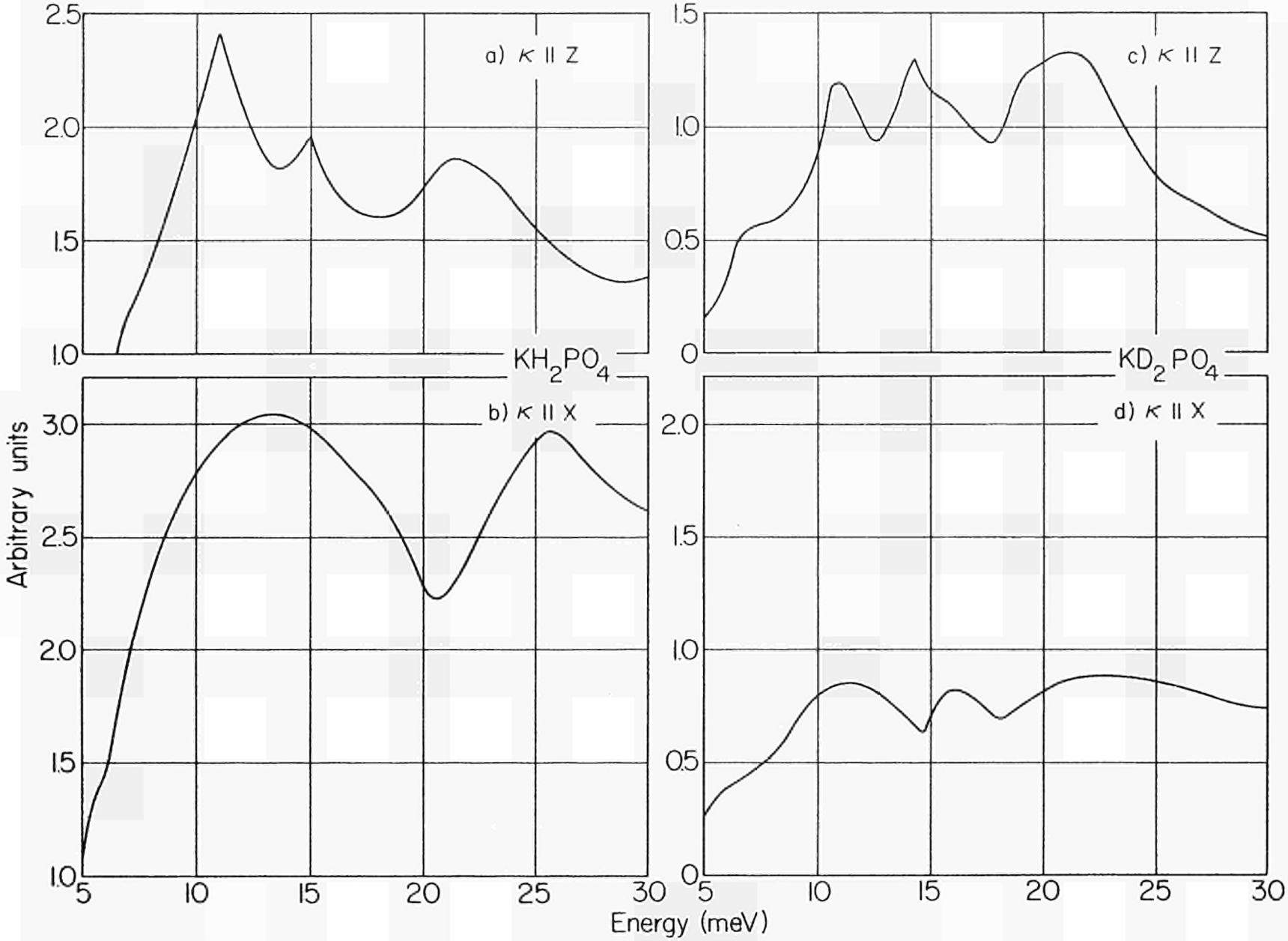
a) κ II Z
c) κ II Z
KH2PO4
KD2PO4
b) κ II X
d) κ II X
Arbitrary units
Energy (meV)
2.5
2.0
1.5
1.0
0.5
0
3.0
5
10
15
20
25
30

Fig. 2

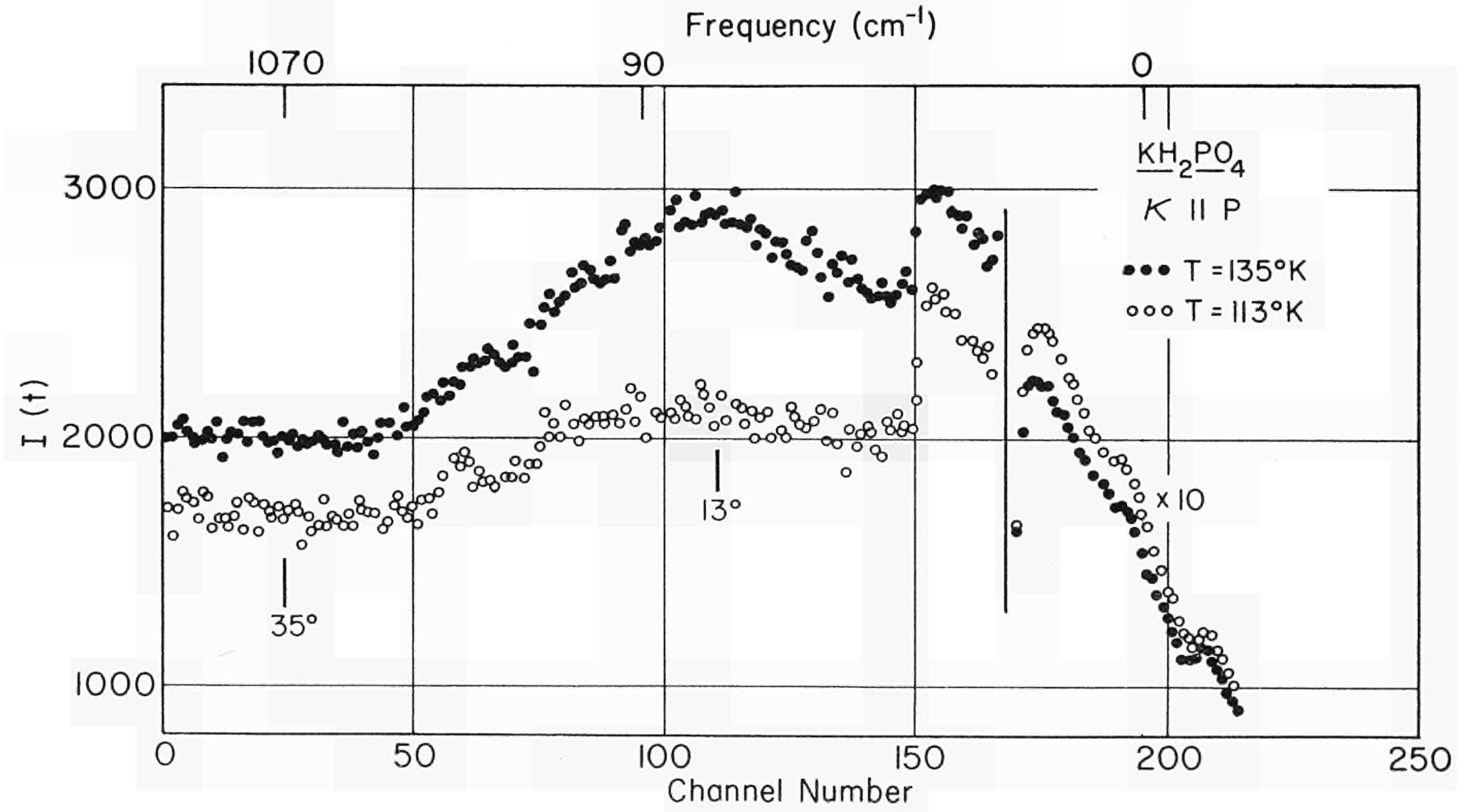
Frequency (cm⁻¹)
1070
90
0
KH2PO4
K II P
T = 135°K
T = 113°K
3000
2000
1000
I (t)
35°
13°
x 10
0
50
100
150
200
250
Channel Number

Fig. 3

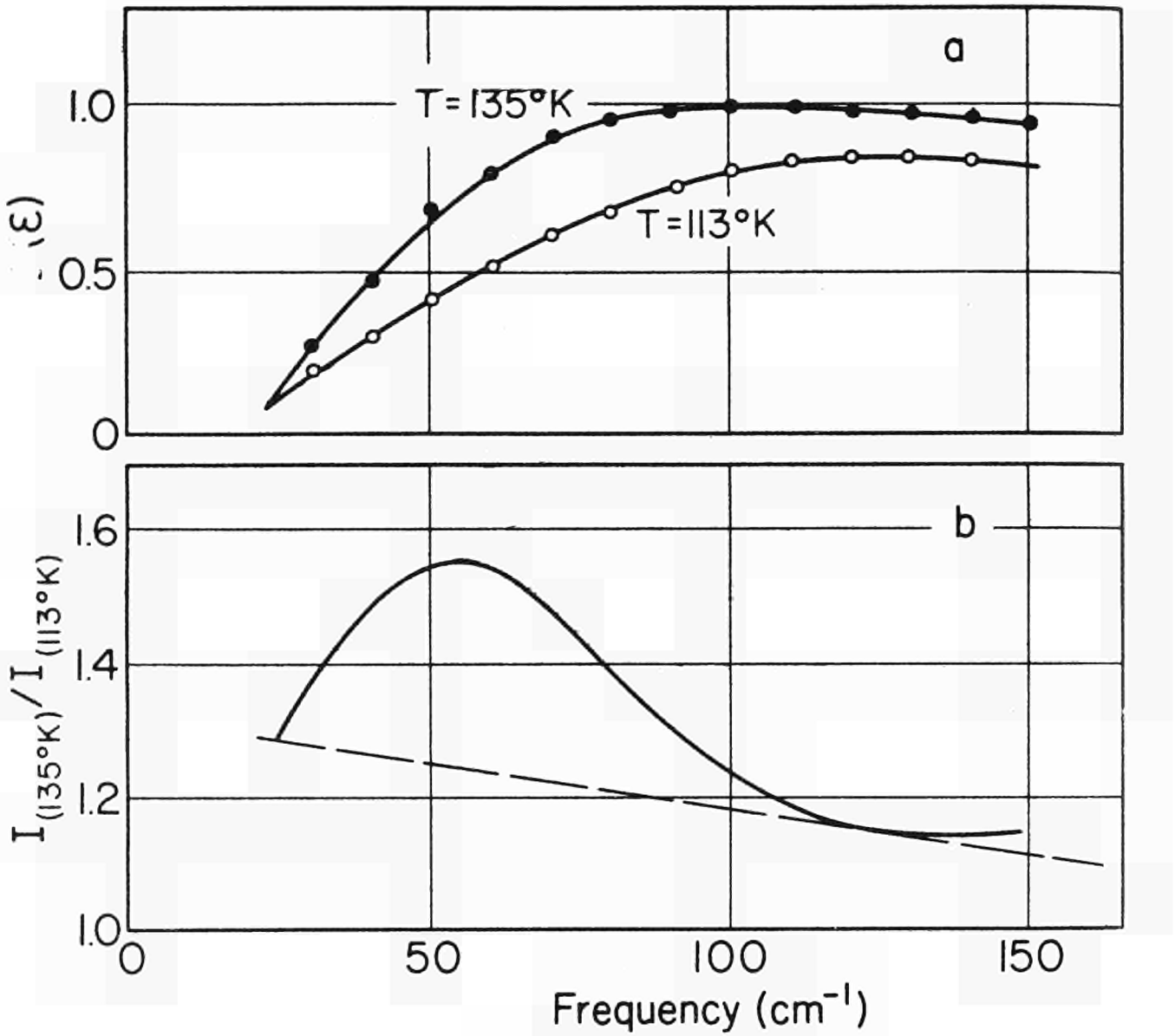
a
T = 135°K
T = 113°K
1.0
0.5
0
ε''
b
1.6
1.4
1.2
1.0
$I_{(135°K)} / I_{(113°K)}$
0
50
100
150
Frequency (cm^{-1})

Fig. 4

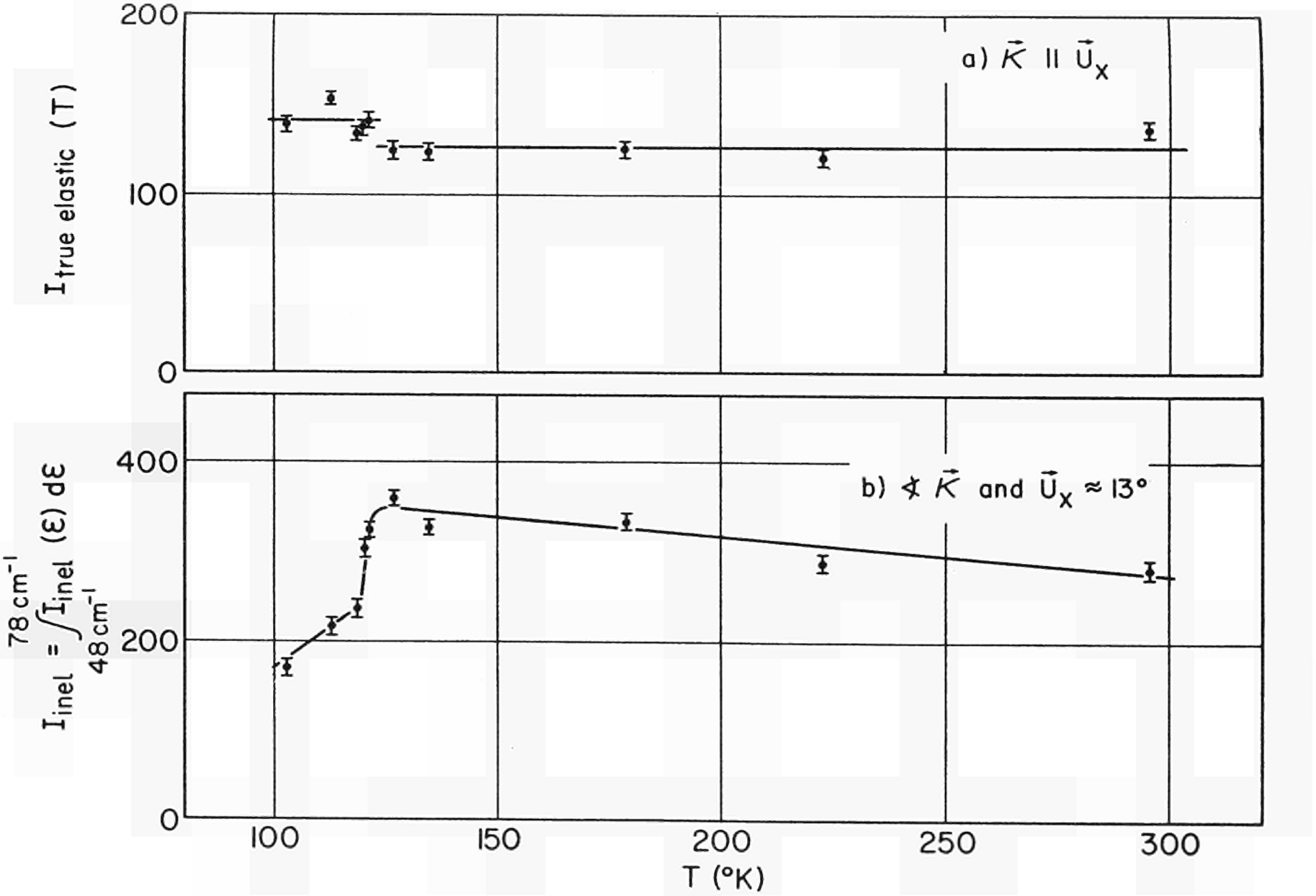
200
100
0
$I_{true\ elastic}$ (T)
a) $\vec{K}$ ∥ $\vec{U}_x$
400
200
0
$I_{inel} = \int_{48\,cm^{-1}}^{78\,cm^{-1}} I_{inel}(\varepsilon)\, d\varepsilon$
b) ∢ $\vec{K}$ and $\vec{U}_x \approx 13°$
100
150
200
250
300
T (°K)

Fig. 5

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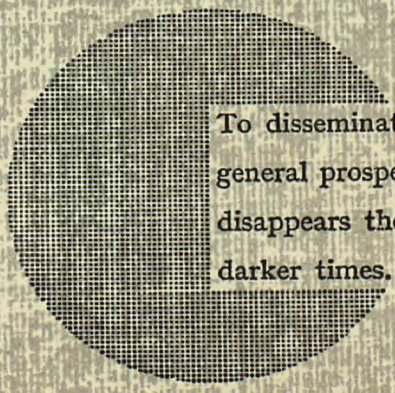

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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