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INCOMMENSURATE LATTICE-INSTABILITY IN K_2SeO_4

M. Iizumi*, J. D. Axe, and G. Shirane
Brookhaven National Laboratory†, Upton, New York 11973

and

K. Shimaoka
Ritsumeikan University, Kyoto 603, Japan

ABSTRACT

Successive phase transformations in K_2SeO_4 at T_i=130K and T_c=93K have been studied by the triple-axis neutron scattering technique. Above T_i a Σ_2 optic phonon branch along $(\xi,0,0)$ shows striking softening and $\omega(\vec{q})$ for $\vec{q}\sim(1/3,0,0)$ tends to zero at T_i. This softening results from a temperature dependent decrease of the interlayer forces with range a/2 and a(a is one unit cell length along the a axis) in the presence of strong and persisting forces with a range 3a/2. The critical scattering above T_i has a maximum at an incommensurate position: $\vec{q}_\delta=(1-\delta)\vec{a}^*/3$ with $\delta\sim0.08$ and peaks at E=0 near T_i. At T_i superlattice reflections appear at incommensurate positions, $\vec{q}_\delta$. The deviation δ decreases with decreasing temperature with an apparently discontinuous jump to δ=0 at T_c. Below this temperature the crystal remains commensurate and is ferroelectric. The incommensurate transition, the simultaneous lock-in of the commensurate phase and the ferroelectricity are discussed using a Landau type expansion of the free energy.

INTRODUCTION

Certain materials exhibit an instability against atomic displacements which are characterized by incommensurate wavevectors.[1] In those materials a phase transition to an incommensurate phase occurs first and in many cases a "lock-in" transformation to a commensurate phase follows. The phase transitions in potassium selenate (K_2SeO_4) are interesting not only because they represent another example of this kind of lattice instability but also because the primary incommensurate atomic

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* Permanent address: Japan Atomic Energy Research Institute, Tokai, Japan.

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displacements induce a polarization wave which becomes the macroscopic polarization in the commensurate phase.[2] This is thus a new type of improper ferroelectric-the incommensurate-commensurate-type improper ferroelectrics.

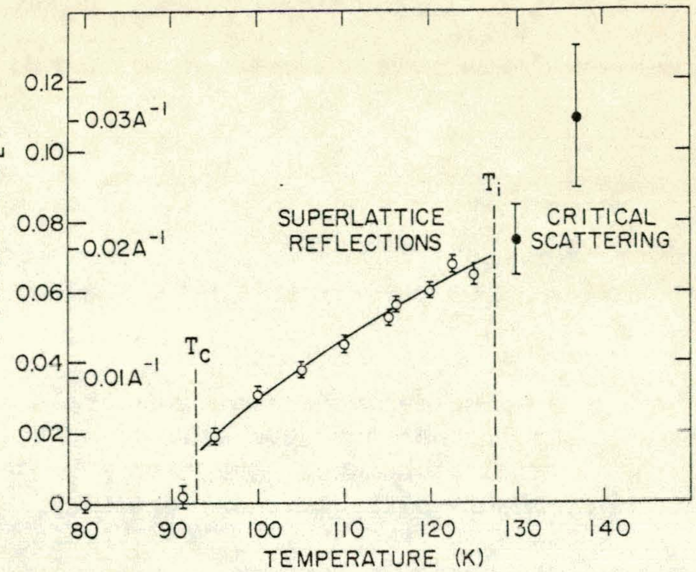

Fig. 1. Temperature change of the deviation δ

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Potassium selenate undergoes two phase transformations at T_i=128K and T_c=93K. Above T_i(P-phase) the crystal structure is orthorhombic with a space group of Pnam.[3] Between T_i and T_c (I-phase) x-ray studies[4] revealed superlattice reflections which are characterized by a wavevector of $\vec{a}^*/3$. The detailed neutron scattering studies[2] disclosed, however, that the superlattice reflections do not appear at exactly $\vec{a}^*/3$ but they are shifted slightly from the commensurate points. The wavevector characterizing the superlattice structure is $\vec{q}_\delta=(1-\delta)a^*/a$ with δ changing with temperature from 0.07 just below T_i to zero at T_c as shown in Fig. 1. Below T_c(F-phase) the superlattice structure

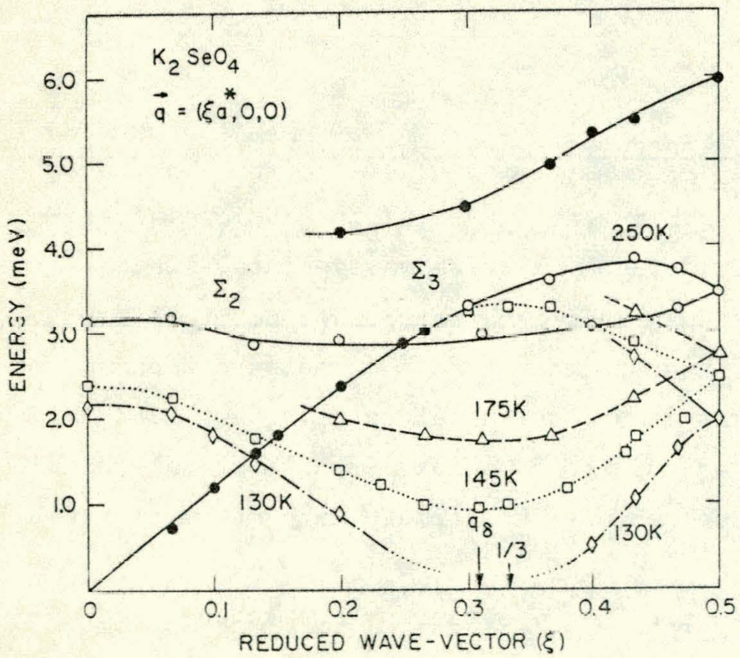

Fig.2. Dispersion relations of transverse modes propagating along [100].

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remains commensurate and shows weak ferroelectricity.[5]

In this paper results of neutron scattering studies on the lattice instability in the P-phase are presented and discussed. All the measurements were made by using triple-axis spectrometers at the Brookhaven High Flux Beam Reactor.

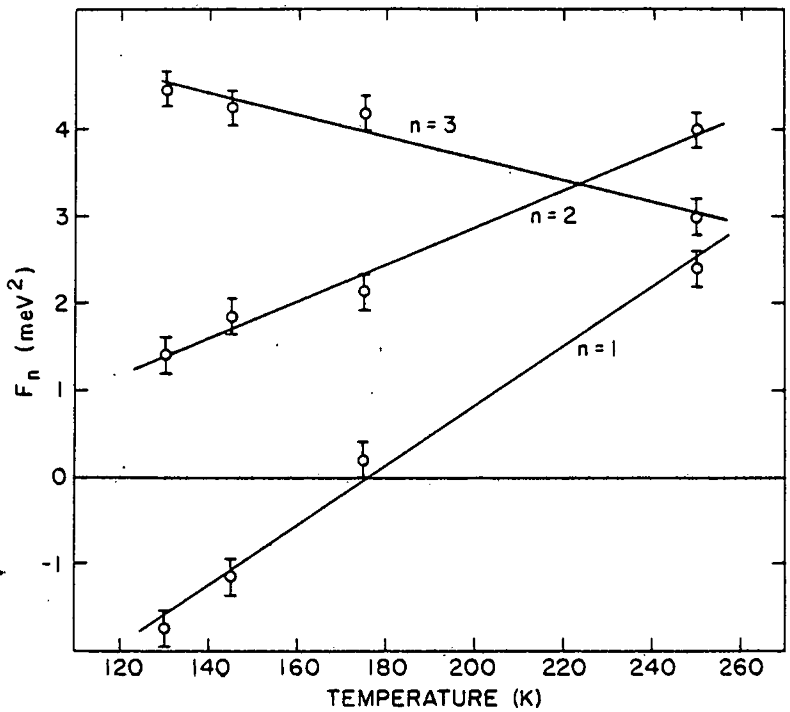

Fig.3. Temperature dependence of the interlayer force constants.

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SOFT MODE DISPERSION RELATION

The dispersion relations for the low-lying transverse modes propagating in the [100] direction were measured at several temperatures and are shown in Fig. 2. The lowest Σ_2 optic branch shows a striking softening towards T_1. The softening is conspicuous around $\xi=1/3$ and extends to a wide range along [100]. Measurements of the dispersion surface in the perpendicular [001] direction shows that the softening is confined to the vicinity of a* axis in the $\vec{q}$-space.

The Σ_2 mode is degenerate at the zone boundary with the Σ_3 acoustic mode. We may, therefore, regard the two branches to be a single branch in the extended zone which is doubled along the a*-axis and in which the instability takes place at $\xi\sim2/3$. In order to characterize the dispersion relation we Fourier analyze it using the relation

$$[\hbar\omega(\xi)]^2 = \sum_n F_n(1-\cos n\pi\xi) \quad (1)$$

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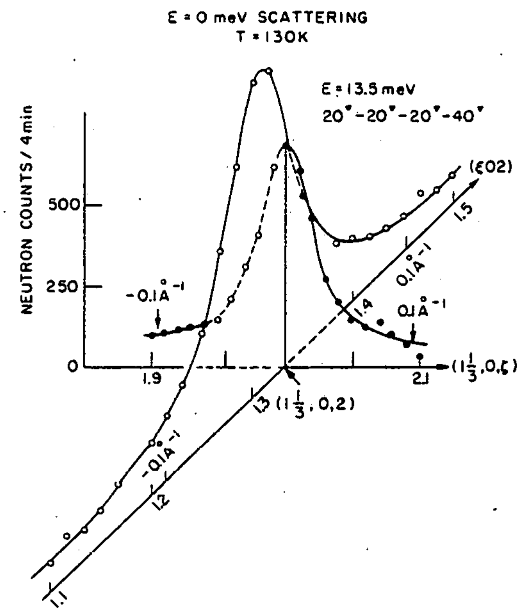

Fig.4. E=0 scattering distribution around (1 1/3,0,2) at 130K.

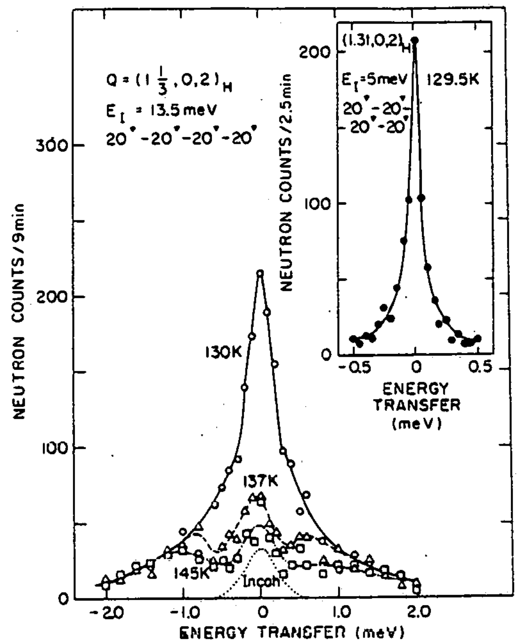

Fig.5. Energy spectrum of the critical scattering at several temperatures. Inset shows a result obtained by a better energy resolution.

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in which the coefficients F_n correspond to fictitious effective force constants coupling planes in the crystal separated by a length equal to na/2. Sets of force constants obtained are shown in Fig. 3 as a function of temperature. The force constants beyond n=3 are insignificant and are not shown in the figure. The force constant between nearest neighbor "planes" F_1 decreases linearly with decreasing temperature and changes sign at about 175K. F_2 is larger than F_1 and also decreases as the temperature is lowered. In contrast, the force constant between the third neighbor "planes" F_3 is strong and increases slightly with decreasing temperature. At temperatures just above T_i F_3 becomes a predominant component which characterizes the softening of the phonon energy around $\xi=2/3$. Notice that F_3 alone produces a phonon instability at $\xi=2/3$. The presence of F_1 and F_2 displaces the minimum from the commensurate point. This simple picture explains how the incommensurate instability develops in K_2SeO_4.

CRITICAL SCATTERING

As shown in Fig. 4, as the transformation temperature is approached from above, the well-defined phonon sidebands disappear and very near T_i the critical scattering is peaked at $\Delta E=0$. If the incoherent scattering is subtracted, there is no central peak at $T\geq 145K$, but there is weak evidence for a three-peak structure at 137K, and the unusual width of the wings of the scattering closer to T_i also suggest the presence of more than one relaxation time. A high resolution scan of the critical scattering (see inset of Fig. 3) revealed no detectable energy width. Fig.5 shows the distribution of the E=0 critical scattering in reciprocal space, and clearly shows the incommensurate nature of the instability.

INDUCTION OF SPONTANEOUS POLARIZATION

Below T_i the Σ_2-type lattice distortion $Q(\vec{q}_\delta)$ characterized by the wavevector q_δ develops. Due to an interaction term[2]

$$F_{int} = A\ Q^3(\vec{q}_\delta)\ P_z(\vec{q}_{3\delta}) \qquad (2)$$

in the free energy expansion, the secondary lattice distortion with amplitude $P_z(\vec{q}_{3\delta})$ representing a long wavelength displacement wave with an associated polarization and characterized by a wavevector $\vec{q}_{3\delta}= 3\delta(\vec{a}^*/3)$ is induced. As $q_{3\delta}$ becomes zero together with δ at T_c, the polarization wave transforms to the spontaneous polarization. The interaction term (2) also provides a driving force for the incommensurate-commensurate phase transition. A more detailed account of the phase transformations and the excitations of the low temperature phase will be published elsewhere.

REFERENCES

1. J. D. Axe, this Proceedings.
2. M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, to be published, Bull. Am. Phys. Soc. 21, 292 (1976).
3. A. Kálmán, J. S. Stephens, and D. W. J. Cruickshank, Acta Cryst. B26, 1451 (1970).

4. K. Shimaoka, N. Tsuda, and Y. Yoshimura, Acta Cryst. A<u>28</u>, Suppl. 187 (1972).

5. K. Aiki, K. Hukuda, H. Koga, and T. Kobayashi, J. Phys. Soc. Japan <u>28</u>, 389 (1970).