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Evidence for a Peierls Distortion or a Kohn Anomaly in One-Dimensional Conductors of the Type $K_2Pt(CN)_4Br_{0.30}\cdot xH_2O$

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A linear superlattice distortion with a period of 6 × 2.88 Å parallel to the platinum chains has been observed at room temperature by x-ray diffuse scattering from the one-dimensional conductor $K_2Pt(CN)_4Br_{0.30}\cdot xH_2O$. This distortion is shown to be sinusoidal and due to shifts of platinum atoms out of their theoretical positions given by structure analysis. From the available information on the electronic band structure, the origin of such a distortion can be attributed either to a dynamic giant "Kohn anomaly" or to a static "Peierls distortion."

INTRODUCTION

Among the few solids which exhibit one-dimensional properties, the "mixed-valence" tetragonal compounds of platinum of the type $K_2Pt(CN)_4Br_{0.30}\cdot xH_2O$ have been the object recently of extensive experimental and theoretical work.[1–15] The origin of this interest is the suggestion, made by Krogmann[1–3] on the basis of the atomic structure, that these compounds might exhibit one-dimensional metallic properties. A characteristic feature of their structure is the presence of columns parallel to the c axis which are built from squares with Pt atoms located in the center and CN groups at the corners (Figs. 1 and 2). The Pt atoms of one such linear stack have a spacing of 2.88 Å, which is only slightly more than the Pt-Pt distance in metallic platinum (2.77 Å).

The electrical conductivity which was found to be up to 10^5 times larger parallel to the c axis than perpendicular to it[13] first confirmed the expected one-dimensional character of the electrical properties; and the conductivity parallel to the platinum chains, which is about $10^2\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at room temperature, is indeed consistent with a metallic band structure.[5,6] Further evidence of a metallic-type behavior at room temperature was obtained by Kuse and Zeller[6] from high-frequency optical measurements.

The origin of such one-dimensional metallic properties can be roughly understood if, following Krogmann[1–3] or Minot and Perlstein,[4] we start from the accepted band structure of the insulator $K_2Pt(CN)_4$ in which the last band, which is completely filled, is produced by the overlap of the platinum d_{z^2} orbitals parallel to the platinum chains of the atomic structure (Fig. 2). The addition of a strong acceptor such as bromine in a limited amount can then be expected to produce a situation in which the d_{z^2} band is partly empty, that is to say, a "one-dimensional metal." Since each platinum atom contributes two electrons to the former filled band and each added bromine removes one of these electrons, the expected metallic band for $K_2Pt(CN)_4Br_{0.30}\cdot xH_2O$ would be $\frac{5}{6}$ full.

This simple picture, which is consistent with the observed electrical properties at room temperature, is nevertheless unable to account for the temperature variation of the electrical conductivity parallel to the c axis which drops to $10^{-12}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at about 20 °K.[5,6] As shown in the two more elaborate models[6,12–14] which have been suggested to explain the electrical properties of these compounds, the real picture can be considerably complicated by typical one-dimensional effects.

Among such typical one-dimensional effects, the possibility of a "Peierls distortion" has not been considered so far in the existing models. As shown by Peierls,[16] if the interaction between electrons is neglected, a "one-dimensional metal" is an unstable structure which should spontaneously undergo a distortion to form a superlattice, which by creation of an energy gap at the Fermi level would split the expected metallic band into filled and empty bands and thus lower the energy (Fig. 3). The obvious reason not to take into account such a possibility can be found in the structure analysis of $K_2Pt(CN)_4Br_{0.30}\cdot xH_2O$ by Krogmann[1,2] which showed that all the platinum sites were equivalent.

It is clear, however, that classical structure analysis is completely unable to detect such a phenomenon precisely because of its necessary one-dimensional character. This ambiguity, and the necessity to obtain more precise information on the disorder which is known to exist in the considered compounds in order to explain their particular properties, has motivated an x-ray diffuse scat-

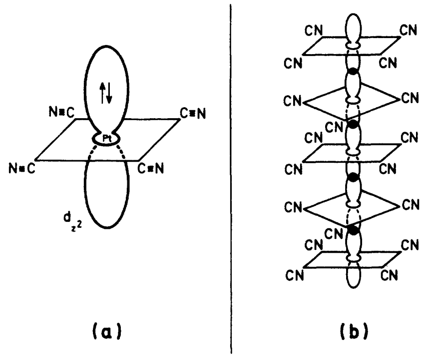

FIG. 1. (a) d_{z^2} orbitals of $Pt(CN)_4^{2-}$ with two electrons. (b) Overlap of d_{z^2} orbitals between stacked complex ions. The ions are staggered to reduce the Coulomb repulsion between ligands [from Minot and Perlstein (Ref. 4)].

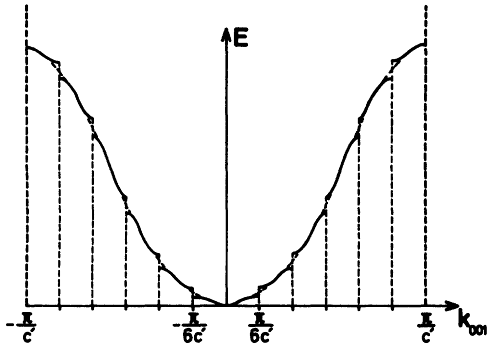

FIG. 3. Distorsion which would arise for a band which is expected $\frac{5}{6}$ full. The gap lowers the energy of the states which are occupied and raises the energy of the empty states so that the result is a net reduction of energy [after Peierls (Ref. 16)].

tering study.

The present paper describes the first direct experimental information on the "disorder" in $K_2Pt(CN)_4Br_{0.30} \cdot xH_2O$ single crystals and a few other related compounds as obtained from x-ray diffuse scattering at room temperature.

EXPERIMENTAL

We used needle-shaped single crystals of about 0.1-mm^2 cross section and a length of about 10 mm. Besides $K_2Pt(CN)_4Br_{0.30} \cdot xH_2O$ crystals, other related compounds such as $Rb_2Pt(CN)_4Br_{0.23} \cdot xH_2O$, $Na_2Pt(CN)_4Br_{0.30} \cdot xH_2O$, and $K_2Pt(CN)_4Cl_{0.32} \cdot xH_2O$ were also briefly examined for comparison. The concentration of bromine or chlorine for each of these compounds was determined by a very careful chemical analysis which gave the values appearing in the formulas just above. The x-ray diffuse scattering was measured by photographic techniques as previously used for ferroelectric crystals[17] and often described improperly as "monochromatic Laue diagrams." All measurements were performed at room temperature.

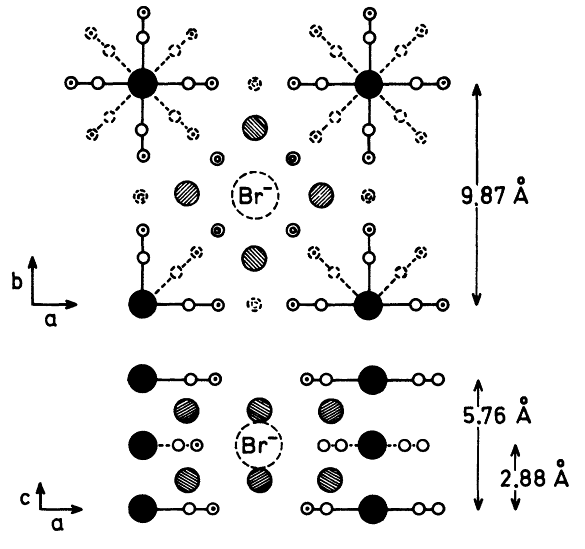

FIG. 2. $K_2Pt(CN)_4Br_{0.30} \cdot 2.3\ H_2O$ unit cell projected along the c and b axes [after Krogmann and Hausen (Refs. 1 and 2)].

The principle of the experimental method is shown in Fig. 4. The primary x-ray beam from a molybdenum anode is first reflected from a lithium fluoride crystal set at the proper angle to select the Mo$K\alpha$ radiation $\lambda = 0.709$ Å for the (200) Bragg reflection, in order to provide a strictly monochromatic beam. In order to avoid the important loss of intensity which would result from tight collimation, the lithium fluoride monochromator is doubly bent to get an approximate point focusing at the level of the photographic plate, providing acceptable resolution with high intensity.

The x-rays scattered from the sample, which is kept in a given orientation during each exposure, are in the present work measured on a flat camera. The intensity collected on the photographic film corresponds then, point by point, to all general points of reciprocal space which simultaneously

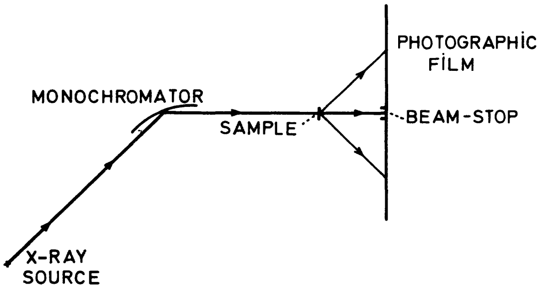

FIG. 4. Schematic view of the experimental setting.

satisfy the relation

$$\vec{Q} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* = 2\pi(\vec{S} - \vec{S}_0)/\lambda \ ,$$

where $\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$, are the reciprocal-lattice parameters, $\vec{S}$ is the unit vector of each scattered beam, $\vec{S}_0$ is the unit vector of the incident beam, and λ is the wavelength. h, k, l are here not restricted to integer values as for usual Bragg diffraction.

Figure 5 shows a vertical section containing the incident beam, the locus of the points $2\pi(\vec{S} - \vec{S}_0)/\lambda$ (Ewald sphere), a reciprocal space as referred to a reciprocal lattice, and the photographic film.

Besides scattering from the acoustic modes (the intensity scattered by phonons is proportional to the inverse of the frequency) due to the Bragg spots which are nearly in a reflecting position and eventually Bragg spots themselves, any type of organized disorder, or phonons of exceptionally low frequency in a limited area of the Brillouin zone, will produce an additional scattering in restricted parts of the photographic film. From the distribution of this scattering, it is then possible to get a direct information on the type of disorder, or low-frequency phonons which are responsible for it.

EXISTENCE OF A ONE-DIMENSIONAL SUPERLATTICE DISTORTION

The scattering pattern shown in Fig. 6 summarizes very concisely the experimental results. Along the most intense layer lines which are visible because of the scattering of the acoustic phonons, and correspond to the distance between successive platinum atoms along the platinum chains parallel to the c axis, one can see pairs of satellite diffuse lines, which correspond in reciprocal space to diffuse sheets perpendicular to the c axis with

$$l = n \pm \tfrac{1}{6}$$

(n = integer). Here, we take as reference, parallel to the c axis of the structure, the Pt-Pt distance ($c' = 2.88$ Å) and not the real unit-cell parameter c which is twice as big, but not relevant for the present work (Fig. 1).

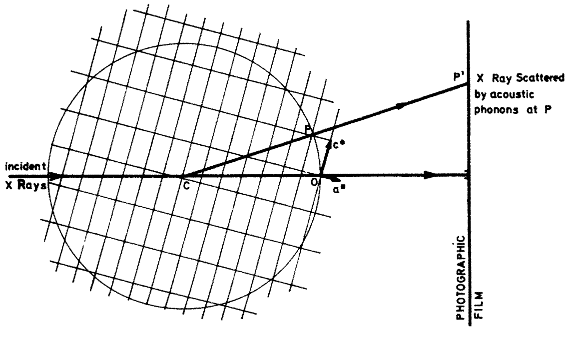

FIG. 5. Vertical section containing the incident beam and showing an example of the relative positions of the Ewald sphere, a reciprocal lattice, and the photographic film. The reciprocal lattice and its orientation has some similarity with the conditions in which the diagram of Fig. 6 was taken, but the magnitude of the reciprocal-lattice constant was multiplied by a factor of 2 for the clarity of the drawing.

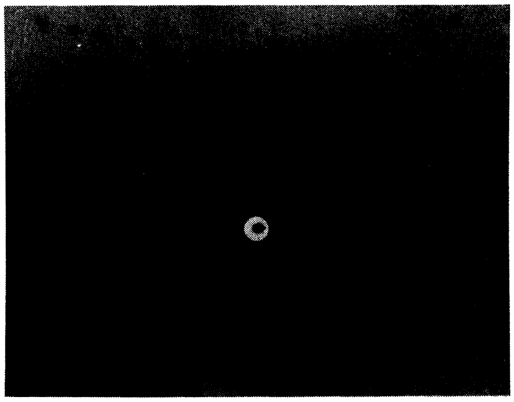

FIG. 6. X-ray diffuse scattering from $K_2Pt(CN)_4Br_{0.30} \cdot x\,H_2O$ with Mo$K\alpha$ monochromatic radiation. The film holder is a flat camera, and the crystal was oriented with its c axis tilted 15° from the vertical, around a horizontal axis.

Several conclusions can be made right away from the observation of such a diagram.

(i) Diffuse sheets perpendicular to the c axis correspond to a one-dimensional periodic structure parallel to the c axis. In other words, we deal with linear objects which are perfectly ordered parallel to the direction of high electrical conductivity but which are, at least partly, disordered relative to each other.

(ii) From the fact that the intensity of the diffuse sheets increases with increasing scattering vector $S = 2\sin\theta/\lambda$ parallel to the c axis, it can be stated that the origin of the diffuse scattering is due to a distortion involving displacements of atoms out of their theoretical positions determined by classical structure analysis and parallel to the c axis. This excludes diffuse scattering due directly to a superlattice arising from nonstochiometry, that is to say, a particular local arrangement of bromine or water molecules.

(iii) The satellite diffuse sheets are not visible around the layer lines which correspond to the true lattice parameter $c = 5.76$ Å, but only around those corresponding to a periodicity $c' = \frac{1}{2}c = 2.88$ Å. The atoms involved in the distortion must consequently, in the average theoretical structure, be separated by that same distance of 2.88 Å parallel to the c axis.

(iv) Satellite diffuse scattering is well known to arise from sinusoidal distortions.[18] From the dis-

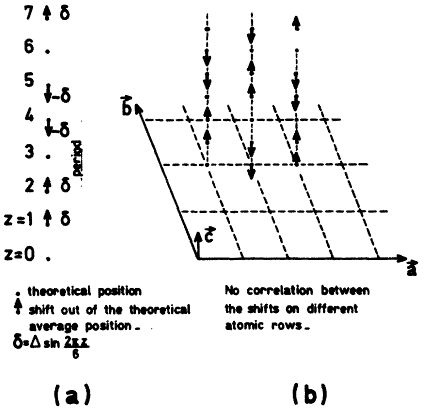

FIG. 7. Schematic representation of the type of distortion (a) along one platinum chain and (b) different platinum chains, perpendicular to a square lattice. Each chain is distorted, but without correlation between neighboring chains. In the figure, for simplicity, we have only considered the cases in which two out of six platinum atoms are not displaced, but any phase difference in the term $\Delta \sin \frac{2}{6} \pi z$ between parallel chains is possible.

tance of the satellite to the layer line, we get displacements out of the theoretical average positions which along the c axis vary as

$$\Delta \sin \tfrac{2}{6} \pi z \ ,$$

where z labels the successive atoms and Δ is the amplitude of the distortion. This gives us rows of atoms located at the extremity of a vector $\vec{r} = z\vec{c}\,' + \vec{\Delta} \sin (2\pi z/6)$, where $c' = \frac{1}{2} c = 2.88$ Å [Fig. 7(a)].

If, for different parallel chains of that type, we have either different possible values of Δ distributed at random or a random-phase origin in the term $\sin \frac{2}{6} \pi z$ [Fig. 5(b)], the superlattice 6×2.88 Å will appear as one dimensional and give diffuse sheets. The mean structure, on the other hand, as determined by classical diffraction methods and which corresponds to the same term $z\vec{c}\,'$ for all equivalent rows of atoms, is unchanged.

The existence of a linear sinusoidal distortion parallel to the c axis and with a superperiod of 6×2.88 Å is thus established with $K_2Pt(CN)_4Br_{0.30} \cdot xH_2O$ crystals. From the width of the diffuse sheets (full width at half-maximum), we can furthermore evaluate the coherence length of such distorted chains which is found to be larger than 400 Å.

The difficulty is now to determine directly from the x-ray data which atoms are involved, and the diagram of Fig. 6 alone is unable to provide that information. This is why other related compounds have also been examined.

If a linear superlattice arising from nonstochiometry and involving the bromine ions or water molecules was already excluded above there are further reasons which indicate that neither these atoms nor the CN groups can be at the origin of the diffuse scattering. (i) The mean spacing, parallel to the c axis, which is needed between successive atoms is 2.88 Å while all the former atoms have sites which correspond to a period of 5.76 Å. (ii) If the bromine atoms were involved, the substitution by chlorine which has a scattering factor half of that of bromine, should decrease the intensity by a factor of 4. No such change is observed experimentally on the diffuse scattering from $K_2Pt(CN)_4Cl_{0.32} \cdot xH_2O$.

It is more delicate to decide whether the distortion involves the potassium atoms or the platinum atoms because the K-K distance, as well as the Pt-Pt distance, parallel to c is 2.88 Å. There we rely entirely on the comparison between isomorphs.

If the alkaline atoms were involved, the substitution of potassium by sodium, as in $Na_2Pt(CN)_4Br_{0.30} \cdot xH_2O$, should decrease the intensity of the diffuse scattering by a factor 2.5. Again, no change of that kind is observed experimentally.

This leaves us with a linear sinusoidal distortion, with a superperiod of 6×2.88 Å due to shifts of the platinum atoms out of their theoretical positions given by structure analysis. This corresponds exactly to the "Peierls distortion" which could be expected in order to split an energy band which is $\frac{5}{6}$ full into filled and empty bands as explained in our Introduction.

Further evidence in that direction is provided by the diffuse scattering from $Rb_2Pt(CN)_4Br_{0.23} \cdot xH_2O$. Once more, there is no change in the intensity of the diffuse scattering. If the alkaline atoms were involved, the rubidium compound should show an intensity increase of more than an order of magnitude compared to the sodium compound due to the very different scattering factors. The fact that the distortion is due to the platinum atoms is thus clearly established. More important for the interpretation is that the superperiod of the distortion is changed for the rubidium compound, where it is found to be 8×2.88 Å. If we consider the composition of the rubidium compound, we find out that we have now one bromine atom for every four platinum atoms (and not three as in the potassium compound) and following our Introduction a d_{z^2} band which if metallic would be this time $\frac{7}{8}$ full. The experimental superperiod of 8×2.88 Å due to the platinum atoms is then again in exact agreement with the expected superperiod as due to a "Peierls distortion."

CONCLUSION

Despite all the experimental evidence which has been collected in favor of a direct observation of a

"Peierls distortion" in the one-dimensional conductors of the type $K_2Pt(CN)_4Br_{0.30} \cdot xH_2O$, we are nevertheless left with one intrinsic difficulty of all x-ray scattering experiments, that is, the impossibility of determining whether the scattering is elastic or inelastic. The sinusoidal distortion which is observed is indeed consistent with a longitudinal wave. According to the relative magnitude of the interaction between electrons, of the electron-phonon coupling, and of the energy which can be gained by the opening of a real gap at the Fermi level, the same phenomenon occurring at $2k_F$ can either lead to a dynamic "Kohn anomaly" or a static "Peierls distortion." A sharp minimum of the energy in a longitudinal phonon branch for the wave vector $\pi/6c'$, as expected for an enhanced[19,20] one-dimensional Kohn anomaly (Fig. 8), could also account for the observed diffuse scattering (the scattered intensity is proportional to $1/\omega^2$). (See *note added in proof.*)

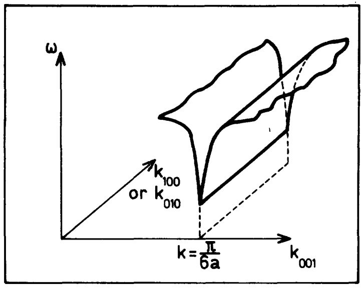

FIG. 8. Schematic picture of a one-dimensional Kohn anomaly occuring for $k = \pi/6c'$.

If we finally consider the crucial problem of the electronic band structure and its suggested metallic character, it is obvious that no definite information can be obtained from the present new results. Even if the "Peierls distortion" is static, which would apparently favor a semiconductor-type band structure, the possibility of a metallic behavior is still open. The difficulty lies in the composition of the compounds we have considered, which is never precisely what is needed to get the observed superperiod but only close to it (0.30Br instead of 0.33 for the potassium compound, 0.23Br instead of 0.25 for the rubidium compound). If the compositions given by chemical analysis are reliable, there are sufficient electrons left which might be responsible for metallic properties.

X-ray diffuse scattering experiments performed at low temperatures which are now in progress, and neutron inelastic scattering experiments which are planned in the near future, should be able to determine whether the reported sinusoidal distortion is static or dynamic and how it varies with temperature, but, as shown above, a better knowledge of the true composition is also of central importance.

Note added in proof. While this paper was in press, B. Renke *et al.* [Phys. Rev. Lett. 30, 1144 (1973)] reported inelastic neutron scattering results showing such a giant Kohn anomaly.

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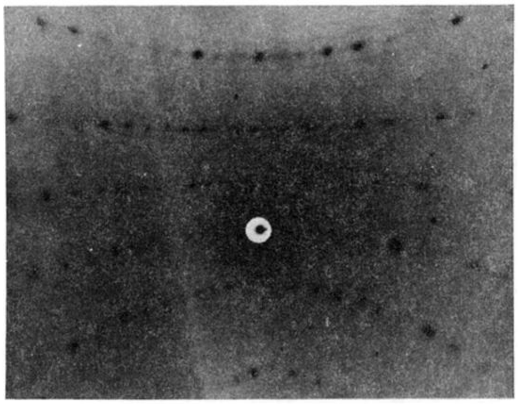

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