Structural Studies of Partially Oxidized One-dimensional Bis(oxalato)-platinate Salts Containing Bivalent Cations: $Ni_{0.84}[Pt(C_2O_4)_2]\cdot 6H_2O$

Akiko KOBAYASHI,* Hidetaka KONDO,** Yukiyoshi SASAKI, Hayao KOBAYASHI,†
Allan E. UNDERHILL,†† and David M. WATKINS††

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
†*Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274*
††*School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd, LL57 2UW, U.K.*

(Received October 16, 1981)

Fundamental structure, k_F and $2k_F$ satellite reflections, and electrical properties of $Ni_{0.84}[Pt(C_2O_4)_2]\cdot 6H_2O$ (Ni–OP) were determined. Complex Ni–OP crystallizes in the orthorhombic space group Pccn with cell parameters of $a=14.296(2)$, $b=16.387(3)$, and $c=5.671(1)$ Å and $Z=4$. Ni–OP is essentially isostructural with Mg–OP ($Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$) and Co–OP ($Co_{0.83}[Pt(C_2O_4)_2]\cdot 6H_2O$). The space group of Mg–OP and Co–OP is Cccm. Owing to the change in the space group, there are two independent Pt chains in Ni–OP. X-Ray studies of M–OP (M=Co, Ni) show that there exist strong k_F satellite spots and weak $2k_F$ spots. One M^{2+} cation is vacant per period of the lattice modulation wave of the platinum chain, λ_{2k_F}. The periodic cation defect induces the k_F modulation waves. The $2k_F$ waves do not have a Peierls origin but are induced by the k_F modulation wave. A second order phase transition is observed at about 305 K above which the $2k_F$ spots disappear.

In recent years partially oxidized cyanoplatinates and bis(oxalato)platinate complexes have been attracting much interest because of their quasi-one-dimensional metallic behavior.

The prototype compound $K_2[Pt(CN)_4]Br_{0.3}\cdot 3.2H_2O$ (KCP(Br)) undergoes a gradual transition from a room temperature one-dimensional conductor state to a low temperature insulating state. Observations of a giant Kohn anomaly and a low temperature three-dimensional superlattice have been proposed as evidence for the Peierls transition with this compound. The nature of sinusoidal modulation of the one-dimensional platinum chain has been investigated by many workers through various neutron and X-ray diffuse scattering studies.[1–3]

One-dimensional metallic system is unstable at low temperature and exhibits lattice distortions with a wave number equal to twice the Fermi momentum ($2k_F$). The period of a Peierls distorted cell is determined by the degree of partial oxidation (DPO).[4]

Bis(oxalato)platinate salts have the formula $M_x[Pt(C_2O_4)_2]\cdot yH_2O$ (M–OP). For bivalent cations Mg^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, and Cu^{2+}, $0.81<x<0.84$ and $y\approx 6$.[5–8, 10,11] For monovalent cations NH_4^+, Rb^+, and K^+, $1.6<x<1.81$ and $y=1$—4.

In the present paper, fundamental structure, X-ray satellite reflections (k_F and $2k_F$), and diffuse scattering of Ni–OP are reported together with electrical conductivity measurements and 2nd-order phase transition.

Experimental

Ni–OP was prepared by the method previously reported.[6] A crystal of $0.43\times 0.36\times 0.01$ mm³ was used for data collection. Data were collected on a Rigaku automated diffractometer equipped with a graphite monochromator.

Crystal data:

$a=14.296(2)$, $b=16.387(3)$, and $c=5.671(1)$ Å,

$V=1328.54$ Å³, $Z=4$, $d_{calcd}=2.643$ g cm^{-3}, and $\mu=123.32$ cm^{-1} (Mo $K\alpha$ radiation, $\lambda=0.71069$ Å).

Intensity data were collected with monochromatized Mo $K\alpha$ radiation by the ω-2θ scan technique up to $2\theta=60°$. Corrections were made for the Lorentz and polarization factors. Data revealed systematic extinctions consistent with the orthorhombic space group Pccn. The space group of Mg–OP and Co–OP is Cccm.[5,8] Data were corrected for absorption. Initial locations of the Pt and Ni atoms were assumed from the structure of Co–OP. Positions of the oxalate ligand atoms and independent oxygen atoms coordinated to the Ni^{2+} ion were determined by the standard Fourier and least-squares refinement procedures. Site occupancies of the Ni atoms and four independent oxygen atoms of water molecules were determined by use of the full matrix least-squares program LINUS. Site occupancies are 0.415(6) for Ni, 0.90(4), 0.84(4), and 0.81(4) for the coordinated O atoms, and 1.05(4) for the uncoordinated O atoms. For the three coordinated oxygen atoms, site occupancies are almost equivalent and nearly equal to twice the Ni site occupancy. Discrepancy indexes are $R(|F_o|)=0.050$ and $Rw(|F_o|^2)=0.069$. The weighting scheme used was $w^{-1}=\sigma^2(|F_o|)+c|F_o|^2$, where the value of c is 0.02, as estimated from the fluctuation of intensities of the standard reflections. The atomic coordinates of Pt are (0.25, 0.25, 0.0177). The Z coordinate deviates ≈ 0.1 Å from the $Z=0$ point. This deviation causes the lattice change from C to P. Positional parameters determined from the final least-squares cycle are presented in Table 1. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[12] Calculations were performed on the HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo. $|F_o|-|F_c|$ tables and thermal parameters are kept at the Office of this Bulletin as Document No. 8227.

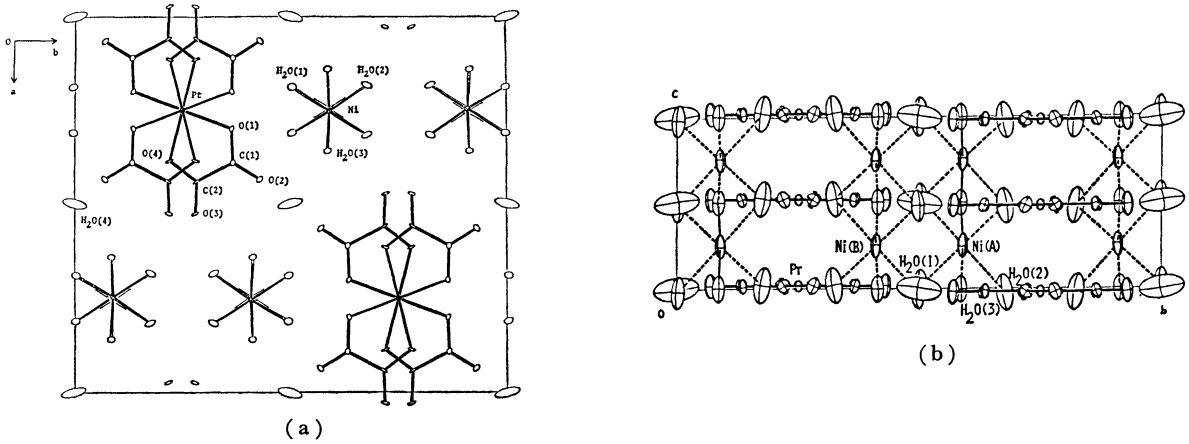
Results and Discussion

Fundamental Structure. The c axis and a axis projections of the structure of Ni–OP are shown in Fig. 1. Bond lengths and bond angles are almost the same as those of Co–OP within 3σ. Slight differences of bond lengths and angles are found in the hexahydrated cations. The main structural difference

**Present address: Systems Development Laboratory, Hitachi Ltd., Ohzenji, Tama-ku, Kawasaki, Kanagawa 215.

Table 1. Fractional coordinates and isotropic thermal parameters ($\times 1000$ for heavy atoms, $\times 100$ for the others, and $\times 1000$ for U_{eq})

Atom	Site occupancy	x	y	z	U_{eq}/Å^2
Pt	1.0	2500	2500	177(1)	18(1)
Ni	0.415(6)	2533(12)	5901(3)	2516(9)	49(2)
O(1)	1.0	299(1)	364(1)	17(2)	25(3)
O(2)	1.0	435(1)	429(1)	19(2)	53(5)
O(3)	1.0	527(1)	280(1)	20(2)	30(3)
O(4)	1.0	385(1)	221(1)	19(2)	24(3)
C(1)	1.0	390(1)	367(1)	18(2)	27(4)
C(2)	1.0	440(1)	284(1)	20(2)	25(4)
$H_2O(1)$	0.90(4)	189(1)	503(1)	21(4)	83(10)
$H_2O(2)$	0.84(4)	184(1)	676(1)	−22(5)	108(13)
$H_2O(3)$	0.80(4)	359(1)	586(1)	−1(3)	59(7)
$H_2O(4)$	1.0	0	500	0	193(29)



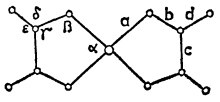
(a) (b)

Fig. 1. The c axis(a) and the a axis(b) projection of the structure of Ni–OP. The disordered cation sites are shown as A and B.

Table 2. Averaged molecular structures of the bis(oxalato)platinate anions

	a/Å	b/Å	c/Å	d/Å	α/°	β/°	γ/°	δ/°	ε/°
A[a]	2.00	1.28	1.55	1.22	82	115	115	126	120
B[a]	2.013(5)	1.26(1)	1.57(2)	1.23(1)	82.7(3)	113.1(4)	115.7(7)	124.5(7)	120.0(7)
C[a]	2.00	1.29	1.54	1.22	83	113	116	124	120
D[a]	2.00(1)	1.30(2)	1.55(2)	1.22(2)	83.6(4)	113.0(9)	115(1)	125(1)	120(1)

a) A: $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$; B: $Co_{0.83}[Pt(C_2O_4)_2]\cdot 6H_2O$; C: $K_2[Pt(C_2O_4)_2]\cdot 2H_2O$; D: $Ni_{0.84}[Pt(C_2O_4)_2]\cdot 6H_2O$.



between Ni–OP and Co–OP (Mg–OP) is in the different space groups Pccn for Ni–OP and Cccm for Co–OP (Mg–OP). This fact indicates that there are two independent Pt chains in Ni–OP.

Within a platinum chain, oxalate ligands are staggered with respect to the ligands located directly above and below them. The staggered angles are approximately 55°. There are two platinum atoms per unit cell in the c-direction with spacing $c'=c/2=$ 2.836 Å. The Ni^{2+} ions are located between the planes containing $[Pt(C_2O_4)_2]^{x-}$ ions and are coordinated by six water molecules with slightly distorted octahedral symmetry. Table 2 shows averaged molecular structures of the anion. The Pt–O distance is 2.00(1) Å on the average. The O–Pt–O angles is 83.6(4)°, the C–O bond distance in the five-membered ring is 1.30(2) Å, and the C–C distance is on the average 1.55(2) Å. The molecular structure of partially oxidized bis(oxalato)platinate complexes with bivalent metal cations (Ni, Co, and Mg) is approximately equal to the molecular structure with $[Pt(C_2O_4)_2]^{2-}$ anion in $K_2[Pt(C_2O_4)_2]\cdot 2H_2O$.[5,8,13] In a cobalt bis(oxalato)platinate salt, a new water site which is not within the Co^{2+} coordination sphere was found. The Ni^{2+} salt also contains this additional water molecule, which was not found in the Mg^{2+} salt. The neighboring Pt chains are linked by hydrogen bonds involving the water molecules. Table 3 compares the bond lengths and angles around each cation in Ni–OP, Co–OP, and Mg–OP.

k_F, $2k_F$ Satellite Reflections. The structure was solved by using intensities of the main reflections. However, characteristic satellite reflections and diffuse scattering are observed on X-ray photographs indi-

TABLE 3. BOND LENGTHS AND ANGLES AROUND THE CATION OF M-OP (M=Ni, Co, Mg) AND BOND DISTANCES FOR THE HYDROGEN BONDING OF WATER MOLECULES

	Ni-OP	Co-OP	Mg-OP
M-H_2O(1)	2.13(2)	2.227(8)	2.23(5)
M-H_2O(2)	2.09(2)	2.138(7)	2.13(5)
M-H_2O(3)	2.32(2)	2.259(9)	2.23(5)
H_2O(1)-O(1)	2.78(3)	2.81(1)	
H_2O(2)-O(3)	2.73(2)	2.74(1)	2.75(8)
H_2O(2)-O(2)	2.79(2)	2.81(1)	2.89(8)
H_2O(3)-O(3)	2.82(3)	2.82(1)	2.85(8)
H_2O(4)-H_2O(1)	2.71(2)	2.70(1)	
H_2O(1)-M-H_2O(2)	79(1)	82.0(3)	81
H_2O(1)-M-H_2O(3)	82(1)	82.2(3)	82
H_2O(2)-M-H_2O(3)	88(1)	84.6(3)	83

cating that the lattice is periodically modulated. Extra reflections are located at $\boldsymbol{G}(hkl)+nk_F\boldsymbol{c}^*$ $(n=1,2,\cdots)$ and classified into three groups:

I) k_F Satellite Reflections: Intensities of the k_F satellite reflections are comparatively strong.

Satellites are located near the a* and a*±b* axes. Since some of these are accompanied by very weak 2nd order satellite reflections ($2k_F$ spots), these k_F satellites are considered to be associated with the sinusoidal modulation wave whose displacement vector is parallel to the a and a±b axes, perpendicular to the direction of wave propagation c*. The intensity of the n-th satellite spot of the sinusoidally modulated structure is proportional to the square of the Bessel function $J(2\pi(p\xi+g\eta+r\zeta))$, where (ξ,η,ζ) is the position in the reciprocal space $(\zeta=l+nk_F)$ and $p\boldsymbol{a}/a+q\boldsymbol{b}/b+r\boldsymbol{c}/c$ is the amplitude vector of the modulation wave (see Figs. 2, 3, and 4).†††

In addition to this, strong k_F satellite reflections are observed at low 2θ-values which appear not to originate from the sinusoidal modulation of lattice.

II) $2\boldsymbol{k}_F$ Satellite Reflection: There are two kinds of $2k_F$ satellites.

(IIa) The 2nd order satellites originating from the transverse modulation wave with a wave vector k_F as shown in Fig. 2, which are observed around the a* and a*±b* axes.

(IIb) Satellite reflections which are weaker than k_F spots observed around the c* axis. This corresponds to a modulation satellite in Co-OP. Since these spots are observed around the c* axis, the amplitude vector of modulation may be nearly parallel to c*, which is parallel to the wave propagation vector. This is, therefore, a longitudinal modulation wave (see Figs. 2 and 4).

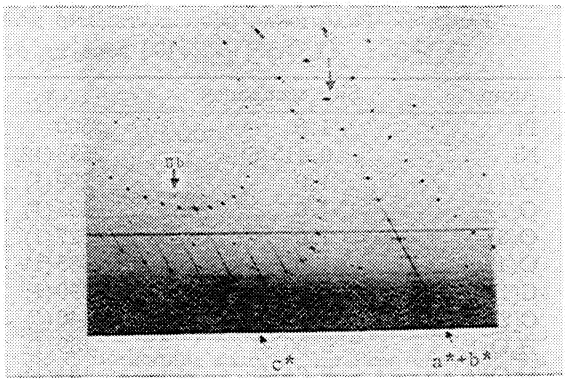


Fig. 2. Weissenberg photograph of the zero layer of the a-b axis of Ni-OP.
I and IIb satellite spots are shown.

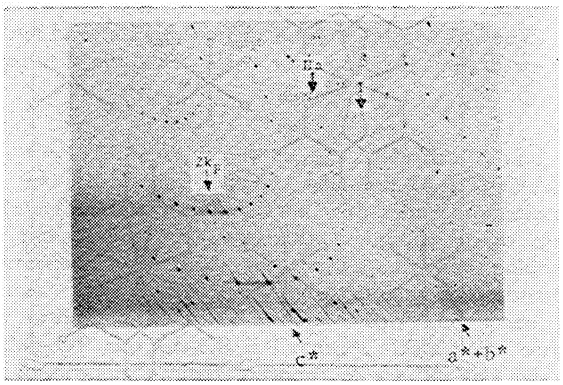


Fig. 3. Weissenberg photograph of the first layer of the a-b axis of Ni-OP showing I and IIa satellite spots and the $2k_F$- diffuse scattering (III).

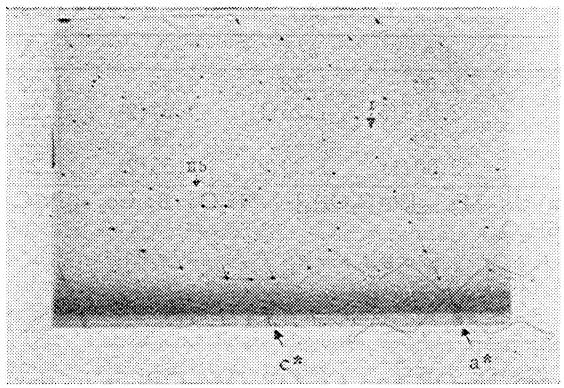


Fig. 4. Weissenberg photograph of an *h0l* reciprocal layer showing I and IIb satellite spots.

III) $2k_F$-Diffuse Scattering: This is the X-ray diffuse scattering distributing around the c* axis (see Fig. 3). As indicated by Braude *et al.*,[9-10] this scattering appears to be based on the low-frequency longitudinal lattice vibration with the Peierls origin. However, temperature dependence of the $2k_F$ diffuse scattering must be investigated in order to elucidate its origin.

The X-ray diffraction pattern described above suggests that the superstructure of Ni-OP is very complicated. The displacive periodic antiphase model of Bertinotti[14] suggests that the superstructure is formed by displacements of the oxalate ligands from the Pt

†††A. Bertinotti *et al.*[14] proposed a displacive periodic antiphase model for Co-OP. They found two kinds of satellite reflections. One appears for each $l=2n$ at h, k, $l\pm1/2M$ where $h+k=2n+1$ and the value of M is 3.25, and the other appears at h, k, $l\pm1/M$ where $h+k=2n$. The former corresponds to k_F spots and the latter to $2k_F$ spots. For Ni-OP, the extinction rule is more complicated and there are weak reflections which are not in accord with it.

atom in the transverse direction and that these displacements form the antiphase domain with the period $2M$.

The coexistence of $2k_F$ and k_F spots is a common feature of one-dimensional bis(oxalato)platinate complexes with bivalent cations. However, in general, the origin of $2k_F$ spots in bis(oxalato)platinate complexes with univalent cations will be a Peierls instability of the Pt chain.

Cation Distribution. In one-dimensional bis(oxalato)platinate complexes with bivalent cations, the relationship between the degree of partial oxidation (DPO) and the $2k_F$ value is as follows: DPO$=2(1-x)$, $k_F=\pi x/c$, and $2k_F'=2\pi/c-2k_F=(2\pi/c)(1-x)$. In the crystal lattice $2k_F'$ and $2k_F$ are equivalent. The wavelength of the $2k_F'$ (or $2k_F$) wave is $\lambda_{2k_F'}=c/(1-x)$. For example, when x is 0.84, $\lambda_{2k_F'}$ is $6.3c$ and $\lambda_{k_F'}$ is $12.6c$. The structure of bis(oxalato)platinate complex indicates that two cation sites exist within a tunnel. The arrangement of $[M(H_2O)_6]^{2+}$ is shown in Fig. 5. These cations cannot occupy both sites A and B (see Fig. 1b) due to a strong cation-cation Coulomb repulsion. If the cation sites are 50% occupied, each chain of $[M(H_2O)_6]^{2+}$ ions will be an ordered array of alternating vacant and occupied M sites. However, with 42% occupancy, one M^{2+} cation is vacant per one period of the $2k_F'$ wave of the platinum chain $\lambda_{2k_F'}$. Therefore, the cation site has a period of $\lambda_{k_F'}$.

This model satisfactorily explains the fact that k_F reflections are commonly observed with the bivalent bis(oxalato)platinate complexes but that they are not observed in the univalent complexes. The k_F spots are stronger than the usual $2k_F$ spots observed in the modulation structure. The presence of periodic cation defects will result in deformation of the surrounding structure. The neighboring cations and $[Pt(C_2O_4)_2]$ anions will move to fill up the vacancy and this produces modulation waves with a period of $\lambda_{k_F'}$. This may be the origin of k_F modulations.***

In one-dimensional systems, the origin of $2k_F$ waves and the lattice distortion are generally considered to have a relation to the Peierls instability. However, Braude *et al.*[10] from X-ray diffraction patterns proposed that $2k_F$ spots in Co–OP have a non-Peierls origin. In the bivalent bis(oxalato)platinate complexes, there exists a strong k_F lattice distortion, which has no direct relation to the Peierls instability.

Origin of the $2k_F$ Wave. In order to elucidate the origin of $2k_F$ satellite spots (IIb) and the relationship between $2k_F$ and k_F spots, we examined temperature dependence of X-ray diffraction spots. In Fig. 6 Weissenberg photographs at 295 K (6a) and 305 K (6b) are shown. The $2k_F$ spots disappear at 305 K, although the k_F spots are visible in this temperature range. In the bivalent complexes, the k_F spots are stronger than the $2k_F$ spots. Since periodic cation defects are the origin of k_F modulation, k_F spots can be thought to have no strong temperature dependence. From the X-ray diffraction experiments at high temperatures and the phase transition theory applied to K_2SeO_4 by Iizumi *et al.*,[15] the $2k_F$ wave may be considered to be induced by the primary k_F lattice distortion wave.†††

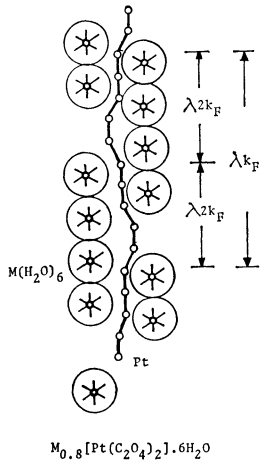


Fig. 5. The schematic arrangement of $[M(H_2O)_6]^{2+}$ is shown.
The cation is octahedrally surrounded by six water molecules. One M^{2+} cation is vacant per one period of the $2k_F$ wave of the platinum chain λ_{2k_F}. The cation site has a period of λ_{k_F}.

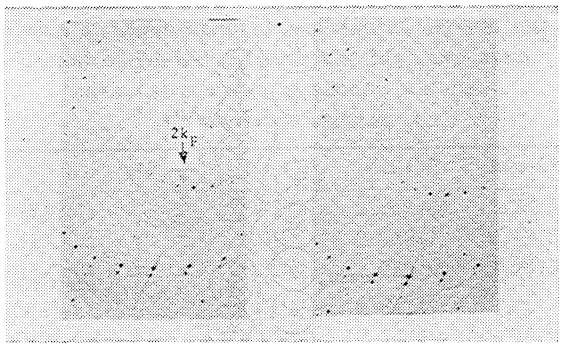
Electrical Resistivity Measurements. Results of the electrical resistivity study are shown in Fig. 7. DC resistivity was measured by use of the four probe method. Measurements were made on several specimens along the needle axis parallel to the Pt chains of crystal. Electrical contacts were made by four 0.025 mm gold wires attached with aquadag. The conductivity at room temperature is 5 $(\Omega\cdot cm)^{-1}$ and dI_NR/dT^{-1} diverges at about 305 K. This result agrees well with that of Watkins *et al.*[6] The anomaly at 305 K is in good agreement with the temperature at which the $2k_F$ spots begin to vanish. Therefore, this phase transition temperature corresponds to the temperature at which the secondary lattice distortion wave

***The k_F modulation is not simple since there are two types of k_F spots. However, the presence of transverse modulation spots suggests that k_F modulations contain a transverse sinusoidal component.

†††When there exists a lattice distortion wave with a wave vector $\boldsymbol{q}$ in the crystal, the atomic displacement is written as $\boldsymbol{u}=Q(\boldsymbol{q})\exp i\boldsymbol{q}.\boldsymbol{r}$. According to the phase transition theory applied to K_2SeO_4 by Iizumi,[15] the free energy of the modulated system is written as:

$$V^{(1)}Q(\boldsymbol{q}_1)^2 + V^{(2)}Q(\boldsymbol{q}_2)^2 + \cdots V^{(n)}(\boldsymbol{q}_1,\boldsymbol{q}_2)Q(\boldsymbol{q}_1)^{n-1}Q(\boldsymbol{q}_2), \quad (1)$$

where $V^{(n)}$ is the n-th energy factor, $Q(\boldsymbol{q}_1)$ is the amplitude of a primary lattice distortion which is characterized by the wave vector $\boldsymbol{q}_1$, and $Q(\boldsymbol{q}_2)$ is the amplitude of a secondary lattice distortion which is induced by the translational invariance, $(n-1)\boldsymbol{q}_1+\boldsymbol{q}_2=\boldsymbol{G}$, where $\boldsymbol{G}$ is a reciprocal-lattice vector or zero. Since the k_F spots in these bivalent bis(oxalato)platinate complexes are stronger than the usual $2k_F$ spots originating from the Peierls modulated lattice, the k_F wave can be regarded as the primary lattice distortion wave. Then the secondary lattice distortion wave is induced from the third energy term $(Q(\boldsymbol{k}_F)^2—Q(-2\boldsymbol{k}_F))$, whose wave number $\boldsymbol{q}_2$ is equal to $2\boldsymbol{k}_F$.



(a) (b)

Fig. 6 Weissenberg photograph of zero layer of diagonal axis a+b of Ni–OP at 295 K(6a) and 305 K(6b) are shown.
The exposure time of Cu $K\alpha$ radiation was 24 h. $2k_F$ spots (IIb) are visible at 295 K and vanish at 305 K.

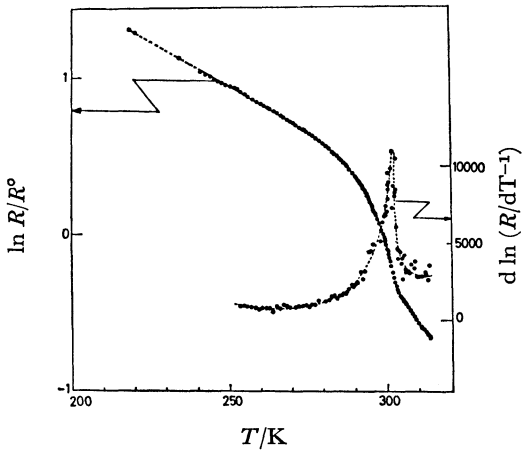


Fig. 7. The electrical resistivity measurements of Ni–OP is shown.
$dI_N R/dT^{-1}$ diverges at about 305 K. This anomaly corresponds to the temperature at which $2k_F$ spots are vanishing.

vanishes.

In order to understand lattice distortion waves of bis(oxalato)platinate complexes in crystal, precise structural studies and theoretical considerations on superstructures must be performed.

One of us (AEU) wishes to acknowledge the support of NATO (Grant No. 016-81).

References

1) R. Comès, M. Lambert, H. Launois, and H. R. Zeller, *Phys. Rev. B*, **8**, 571 (1973).
2) C. F. Eagan, S. A. Werner, and R. B. Saillant, *Phys. Rev. B*, **12**, 2036 (1975).
3) J. W. Lynn, M. Iizumi, and G. Shirane, *Phys. Rev. B*, **12**, 1154 (1975).
4) K. Krogmann, "One-Dimensional Conductors," ed by J. Ehlers, K. Hepp, and H. A. Weidenmüller, Springer-Verlag, Berlin (1975).
5) A. J. Schultz, A. E. Underhill, and J. M. Williams, *Inorg. Chem.*, **17**, 1313 (1978).
6) D. M. Watkins, A. E. Underhill, and C. S. Jacobsen, *J. Chem. Phys. Solids*, in press.
7) A. E. Underhill, D. M. Watkins, and C. S. Jacobsen, *Solid State Commun.*, **36**, 477 (1980).
8) K. Krogmann, *Z. Anorg. Allg. Chem.*, **358**, 97 (1968).
9) A. Braude, A. Lindegaard-Anderson, K. Carneiro, and A. S. Petersen, *Solid State Commun.*, **33**, 365 (1980).
10) A. Braude, A. Lindegaard-Andersen, K. Carneiro, and A. E. Underhill, *Synth. Metals*, **1**, 35 (1979/1980).
11) A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, **9**, 429 (1980).
12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. VI.
13) R. Mattes, and K. Krogmann, *Z. Anorg. Allg. Chem.*, **332**, 247 (1964).
14) A. Bertinotti, C. Carcaillet, G. Jehanno, and R. Saint-James, *J. Phys. Lett. (Paris)*, **39**, L-37 (1978).
15) M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, *Phys. Rev. B*, **15**, 4392 (1977).