from Hall measurements. The calculated frequencies are those for which $\epsilon = 0$, while the experimental frequencies are those of the reflectivity minima ($\epsilon = 1$). Hence, the experimentally determined frequencies are not exactly the calculated frequencies. Table I has also been plotted as Fig. 3, showing ω_+ and ω_- as functions of the free-carrier concentration.

To give a shift of the surface-plasmon frequency from ω_p to $\omega_p/\sqrt{2}$, the depletion layer must be approximately a wavelength thick or thicker. If it is much less than a wavelength thick, the surface-plasmon frequency lies between ω_p and $\omega_p/\sqrt{2}$. This shift of the plasmon frequency with thickness of the dielectric overcoat has been used by Stanford[11] to study the thickness of AgS films on Ag. Note that our etching data indicate that the depletion layer is of order 0.1 mm thick, or approximately one wavelength thick.

The cutting of the grating also increases the surface roughness and this presumably plays an important role. This is because the incident photon carries less momentum than a surface plasmon of the same energy. However, we are apparently not observing just a change in surface roughness but also a damage layer, because the reflectance minima shift continuously as etching proceeds.

In conclusion we have a very simple model of two coupled harmonic oscillators to explain qualitatively the far-infrared reflectivity of n-type InSb. No attempt was made to include retardation effects or to treat rigorously the plasmon-phonon coupling. Clearly, both must be done for a complete treatment. Ngai, Economou, and Cohen[5] have done a calculation (including retarda-

tion) for a semiconductor bounded by a dielectric for the case where the surface-plasma frequency was high enough (~ 800 cm^{-1}) so that coupling to the phonons could be neglected. It would be interesting to extend this treatment to include coupling to the phonons. Recently Marschall, Fisher, and Queisser[12] have observed surface plasmons in InSb using the grating technique. The free carrier concentration was an order of magnitude larger than ours, so that the plasma frequency was well removed from the LO phonon frequency and no coupling effects were observed. In addition, their gratings were ruled with a diamond which did not create a damage layer.

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Evidence for One-Dimensional Metallic Behavior in K₂Pt(CN)₄Br₀.₃ · (H₂O)n

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Single crystals of $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$ show a Drude-type optical reflectivity for light polarized parallel to the crystal axis. The energy of the plasma edge indicates a metallic density of free carriers. The relatively small conductivity at dc and low frequencies and the photoconductivity at 4.2°K can be understood in terms of a simple model assuming metallic strands interrupted by lattice defects.

We report measurements that give for the first time conclusive evidence for the metallic behavior of a square planar organometallic-complex compound.

Planar complexes containing four ligands arranged on the corners of a square around the metal atom have been known for a long time.[1] They form crystals in which the squares are stacked

in such a way that chains of directly interacting metal atoms are formed.[2] It has been suggested that mixed-valency compounds of this type [for instance $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$] might exhibit one-dimensional metallic properties.[1] The underlying concept is the following: We can think of the mixed-valency compound $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$ ($n \approx 2.3$) as an intermediate between the compounds $K_2Pt(CN)_4 \cdot 3H_2O$ where the platinum is divalent and $K_2Pt(CN)_4Br_2$ where the platinum is tetravalent. In the mixed-valency compound Pt has formally a valency of 2.30. Since no measurable phase range with respect to bromine content exists this is a fixed number.[2] In the crystal the $Pt(CN)_4$ squares are stacked such that linear Pt chains parallel to the tetragonal z axis of the crystal are formed. The Pt-Pt distance is only 2.89 Å.

In a ligand field picture the metal-metal interaction is given mainly by the overlap of the Pt d_{z^2} orbitals. It has been argued that because of the small Pt-Pt distance the d_{z^2} electrons might delocalize to form a band in one dimension.[1] The d^8 level scheme in the ligand field is such that a partial oxidation of Pt^{2+} into Pt^{4+} corresponds to a partially filled d_{z^2} level or corresponding band.[3] The material thus should exhibit one-dimensional metallic conductivity along the crystal axis. If the Pt-Pt overlap is too small to lead to a delocalization of the electrons, we still may expect a reasonably good conductivity but rather of the hopping type. X-ray data show all Pt sites to be equivalent and favor the metal picture[2] while recently published data on the temperature dependence of the electrical conductivity have been taken as evidence for hopping-type behavior.[4]

This apparent discrepancy may, however, be removed by considering a simple model: In a real crystal the metal chains have interruptions due to lattice defects such as impurities, vacancies, dislocations, etc. which prevent an undisturbed macroscopic current flow. In a steady current flow the charge carriers have either to overcome the interruptions directly or to move to an adjacent strand. If we assume that such a process requires an activation energy, then this results in a thermally activated conductivity at dc or low frequencies even if the strands themselves are metallic. Only at sufficiently high frequencies when the interruptions are short circuited by their capacitance may the metallic character of the strands become evident. This model is supported by our experimental results on the optical, electrical transport, and photo-

conductive properties of $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$ single crystals.

Needle-shaped single crystals with rectangular cross sections of up to 1 mm^2 and a length of 10 mm were obtained by slow cooling of a saturated aqueous solution. For the optical measurements a crystal surface containing the crystal axis was polished. The typical sample size was 0.4×3 mm^2. We have measured the normal reflectivity at room temperature in the spectral range between 5 and 0.5 eV with light polarized parallel ($\vec{E} \parallel \vec{Z}$) and perpendicular ($\vec{E} \perp \vec{Z}$) to the crystal axis. Because of the small sample size and the poor surface flatness the data have to be considered as lower limits for the reflectivity R. Especially in the infrared where the imaging of the light on the small sample becomes diffraction limited, the true values of R may be several percent larger.

Figure 1 shows the highly polarized reflection spectra. In the $\vec{E} \perp \vec{Z}$ polarization the reflectivity is small and essentially wavelength independent. Preliminary measurements showed a high transparency up to 2.2 eV photon energy. For light polarized parallel to the Z axis, in contrast, R is high ($> 85\%$) at small photon energies, drops sharply to virtually zero near 2 eV, and increases slowly with photon energy to a few percent at 5 eV. In this polarization the crystals are opaque throughout the whole spectral range. Preliminary measurements in the energy range 0.5–0.18 eV indicate that for the $\vec{E} \parallel \vec{Z}$ polarization R remains above 70%.

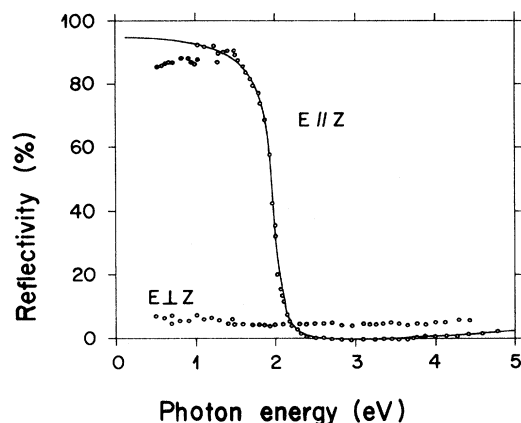We attribute these unusual optical properties

FIG. 1. Reflection spectra of $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$ measured at room temperature with the light polarized parallel ($\vec{E} \parallel \vec{Z}$) and perpendicular ($\vec{E} \perp \vec{Z}$) to the tetragonal optical crystal axis. Open circles represent experimental data. The solid curve is a reflection spectrum calculated from Drude's free-electron theory.

to the presence of charge carriers that are high-
ly mobile parallel to the crystal axis and local-
ized perpendicular to it. The solid line in Fig. 1
represents a reflection spectrum calculated from
the simple Drude theory[5] of free carriers using
the following parameters: $h\nu_p = 2.88$ eV, $\tau = 7.3$
$\times 10^{-15}$ sec, $\epsilon_{ib} = 1.1$, where ν_p is the plasma fre-
quency, h is Planck's constant, τ is the mean
free time of the carriers, and ϵ_{ib} is that part of
the optical dielectric constant which is due to all
other than free-carrier excitations. ϵ_{ib} is as-
sumed to be wavelength independent in the spec-
tral range of interest. This assumption seems
reasonable, since the reflection spectra show no
evidence of interband transitions of sizable inten-
sity below 5 eV.

The Drude curve agrees reasonably well with
the measured reflectivity. The striking feature
of the spectrum, the plasma reflection edge at
2 eV, gives rise to a copperlike metallic luster
of the crystals. This visual appearance persists
upon cooling down the crystal to 4.2%, indicating
that the reflection edge and thus the carrier den-
sity remain the same.

We have measured the longitudinal dc conduc-
tivity by a four-probe technique on a series of
crystals with cross sections of typically 0.1 mm^2
and lengths of about 10 mm. We found gold to
give much better contacts than Aquadag.[4,6] In
particular we found that below 78°K for most ex-
perimental conditions the contact resistance of
a gold contact is small compared to the speci-
men resistance. Figure 2 shows a typical result.
The room-temperature conductivity shows a fair
amount of scatter from crystal to crystal but
agrees reasonably well with the results of Beren-
blyum et al.[4] (except that we did not find a small-
er conductivity in thick crystals compared to
thin ones) and is consistently higher than the re-
sults reported by Minot and Perlstein.[6] The
slope of the curve of logσ vs $1/T$ on the other
hand is reproducible and agrees with the results
of Ref. 4. At 78°K we deduce an activation ener-
gy of about 850°K.

Because of the small cross section of the sam-
ples the transverse conductivity could only be
measured in a two-probe arrangement. We ex-
pect the contact resistance to be small compared
to the sample resistance below 78°K and find the
same activation energy as for the parallel resis-
tance and deduce anisotropies $\sigma_{\parallel}/\sigma_{\perp}$ of about 200.

The longitudinal conductivity at $T = \infty$ as ob-
tained from an extrapolation of the low-tempera-
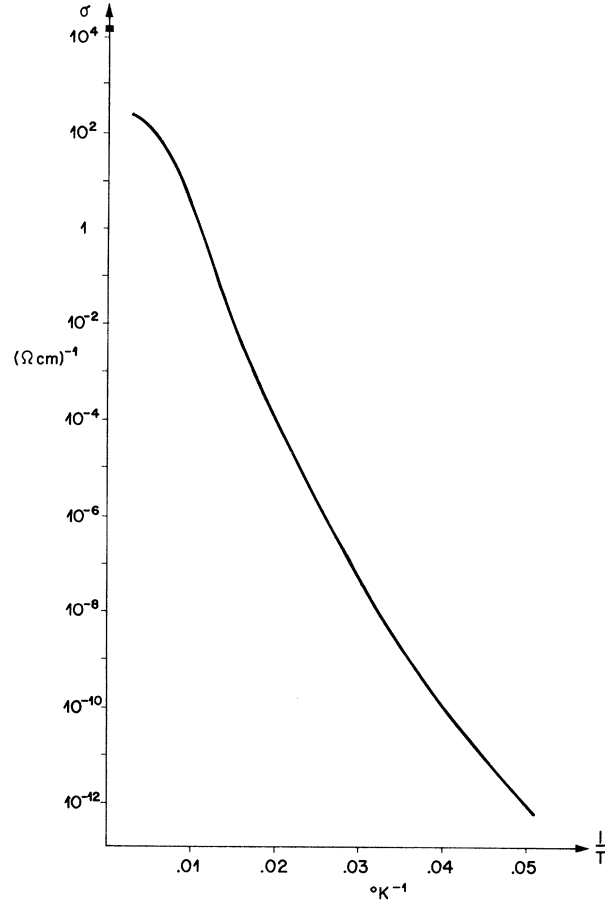ture conductivity in Fig. 2 agrees with the value

FIG. 2. Temperature dependence of the dc electrical
conductivity of a single crystal of $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$
parallel to the c axis. This represents the conductivity
deduced from optical measurements at 290°K and is
approximately equal to the low-temperature dc conduc-
tivity extrapolated to $T \to \infty$.

$\sigma = 1.2 \times 10^4$ Ω^{-1} cm^{-1} derived from the optical da-
ta using the formula[5]

$$\sigma = \pi\tau\nu_p^2.$$

This is predicted by our model of interrupted
metallic strands. The actual high-temperature
conductivity does not extrapolate to the optical
conductivity for reasons outside our model. The
reproducibility of the activation energy and the
fact that $\sigma_{\parallel}$ and $\sigma_{\perp}$ have the same activation ener-
gy suggest that at an interruption of the conduct-
ing strand the electron jumps to an adjacent
strand rather than crossing the interruption di-
rectly and remaining in the same strand. If this
is correct, then the measured anisotropy $\sigma_{\parallel}/\sigma_{\perp}$
of the conductivity is merely given by the aver-
age number of undisturbed Pt ions along the
chain. The intrinsic anisotropy may be much
higher.

We have found $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$ to be a

good photoconductor along the crystal axis at 4.2°K. For both polarization directions of the incident light the spectral dependence of the photocurrent shows structure related to the spectral dependence of the optical properties, in particular to the highly polarized reflection edge at 2 eV. However, the photocurrent per absorbed power is roughly independent of the photon energy and persists at least down to photon energies of 0.6 eV. We thus conclude that the photoconductivity is only indirectly connected to the optical properties in the visible and near infrared region and that the light supplies the energy for the electrons to overcome the interruptions in the conducting strands. Further details will be published in a forthcoming paper.

One might object that ionic conduction in the compound is conceivable, since the crystal structure is rather open and only a fraction of the potassium and bromine sites are occupied.[2] Furthermore, the compound was reported to decay under the action of an electric current.[2] We have passed a total charge of 2 A h through a crystal of $0.6 \times 0.4 \times 8$ mm^3 size (i.e., about 10^3 elementary charges per atom) and did not find any significant change in the electrical resistance nor visual appearance of the crystal. We believe that the effect reported in Ref. 2 was thermal. Ionic conductivity would lead to electrolytic effects at much smaller charges, and

we may safely assume that the dc conductivity is electronic.

In conclusion we have shown that $K_2Pt(CN)_4Br_{0.3} \cdot (H_2O)_n$ has a one-dimensional metallic conductivity in the 10^{14}-Hz region. This is the first direct evidence for metallic behavior in a square planar organic-complex compound. The dc and low-frequency conductivity and the photoconductivity at low temperature can be understood in terms of a simple model assuming metallic strands interrupted by lattice defects.

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Acoustic Paramagnetic Resonance in a Dense Magnetic Insulator

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The first observation of acoustic paramagnetic resonance in a dense magnetic system (RbMnF$_3$) is reported and a theory proposed which correctly predicts the shape of the observed line.

We report the observation of acoustic paramagnetic resonance (APR) in a dense magnetic insulator and propose a theory, valid in the high-temperature limit $(T \gg T_N)$, which correctly predicts the shape of the observed APR line. The experiment was carried out at 293 K utilizing 1.1-GHz longitudinal phonons propagated along the [110] axis of a single crystal of the dense cubic paramagnet RbMnF$_3$. RbMnF$_3$ becomes antiferromagnetic at $T_N = 82$ K. The acoustic absorption as a function of magnetic field exhibits a characteristic square-root shape and includes contributions from both positive and negative frequencies.

Although electron paramagnetic resonance studies are routinely carried out in both dilute and dense paramagnetic systems, APR has been observed heretofore only in dilute magnetic systems.[1,2] Theoretical estimates of APR in dense paramagnetic systems such as RbMnF$_3$ have been previously made.[2,3] Such dense magnetic systems are characterized by strong dipole-dipole coupling and large exchange forces. Since both dipolar and exchange forces are strongly dependent upon interatomic distance, a periodic lattice vibration resulting from the propagation of an ultrasonic wave might be expected to induce