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著者	Koyano Mikio, Ohara Shigeo, Hara Yoshiaki, Inoue Masasi, Kido Giyuu, Nakagawa Yasuaki
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Magnetotransport Measurements of η-Mo_4O_{11} Crystals Using a Hybrid Magnet*

Mikio Koyano [a], Shigeo Ôhara [a], Yoshiaki Hara [a], Masasi Inoue [a],
Giyuu Kido [b] and Yasuaki Nakagawa [b]

[a] Department of Materials Science, Faculty of Science,
Hiroshima University, Higashi-Hiroshima
[b] Institute for Materials Research, Tohoku University,
Katahira, Sendai

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Synopsis

Magnetoresistance and Hall effect have been measured at 4.2 K using a hybrid magnet up to 26 T for several crystals of quasi-two-dimensional η-Mo_4O_{11} that has a charge-density-wave (CDW) induced nested multiple carrier band structure. The magnetoresistance is exceptionally large and the Hall resistivity shows a unique magnetic field dependence. We have confirmed the existence of characteristic hysteresis phenomena in both quantities when a field-sweep range exceeds a threshold value (~10 T). The hysteresis effects can be related with an effective and magnetic field dependent *irreversible process* for the CDW formation and destruction. We have also found that the hysteresis and quantum oscillations in the magnetotransport are strongly sample-dependent.

I. Introduction

Low-dimensional conductors are of current interest because their strongly anisotropic structure leads to a variety of interesting phenomena, such as the formation of spin-density-wave (SDW) or charge-density-wave (CDW). In particular, monoclinic η-Mo_4O_{11} has a quasi-two-dimensional electronic structure with a high electrical conductivity in the crystallographic bc-plane.[1] By cooling down to liquid helium temperatures two CDW transitions at the characteristic temperatures T_{c1}=105 and T_{c2}=35 K are observed, which are caused by partial nesting of the anisotropic Fermi surfaces of electrons and holes with the nesting vector $Q = 0.23b^*$. It has been shown experimentally that in this material system, both electrons and holes contribute to various transport phenomena that show anomalies at T_{c1} and T_{c2}.[2-5] Recent band calculations using a tight-binding (block-band) method[6] have revealed the existence of both

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electron and hole pockets. Figure 1 shows the schematic two-dimensional Fermi surfaces of combined electron hole pockets at the normal state ($T>T_{c1}$) in the extended Brillouin zone scheme proposed by Canadell *et al.*[6] The electron pockets locate around the Γ point and along the Z-M direction, while the hole pockets situate around the Y and Z points. Nesting of these surfaces by the amount of Q occurs at T_{c1}, but no definite nesting vector is known at T_{c2}.

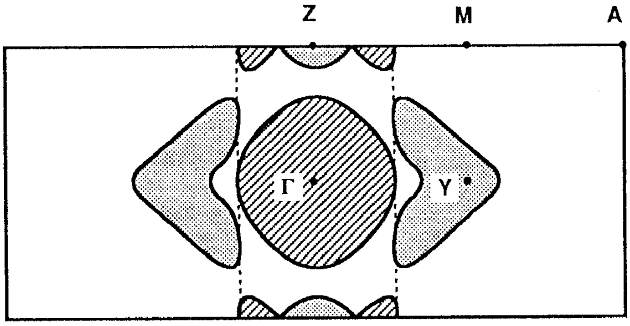


Fig. 1.
Schematic two-dimensional electron and hole Fermi surfaces proposed by Canadell *et al.*[6]

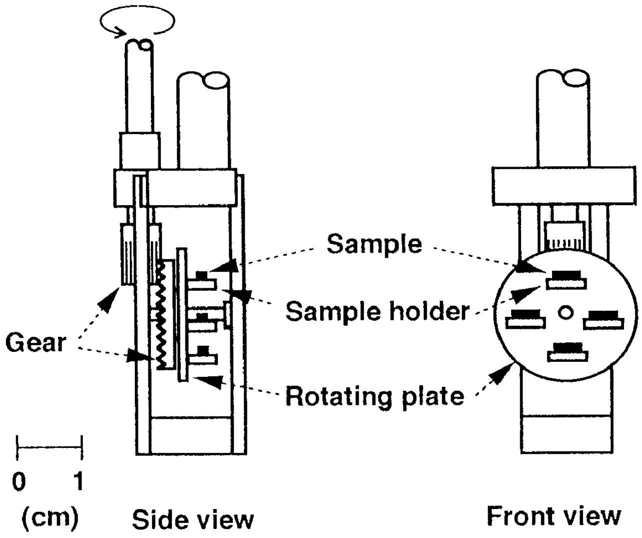
Recently a novel technique, called pulsed-laser induced "Transient Thermoelectric Effect (TTE)" method developed by Sasaki *et al.*,[7] has shown that in the second CDW state ($T<T_{c2}$) there exist two types of electrons and of holes that are responsible for the low temperature transport properties.[8] Moreover, measurements of the magnetoresistance and the Hall effect in pulsed magnetic fields up to 40 T have revealed the appearance of a characteristic hysteresis between up- and down-sweep of magnetic field for peak fields exceeding a threshold value of B_c=10 T, as well as quantum effects such as Shubnikov-de Haas (SdH) oscillations.[9,10] However, the origin of the anomalous hysteresis is yet unknown, for which a tentative model has been recently proposed by Inoue *et al.*[11] Also we should note that these anomalous galvanomagnetic properties are strongly sample-dependent or structure-sensitive to crystal imperfections involved.[12]

In order to get more information about the mechanism producing the hysteresis, in the present work we have reexamined similar measurements for several crystals under quasi-stationary fields using a hybrid magnet, installed at the Institute for Materials Research, Tohoku University.

II. Experimental

Crystalline samples of η-Mo_4O_{11} were grown by a chemical vapor transport technique with $TeCl_4$ as a carrier gas.[4,5] Since the electrical properties of this material are structure-sensitive as mentioned above, several samples were used to examine the reproducibility. The transverse magnetoresistance and Hall effect were measured at 4.2 K using a dc potentiometric method with a four-probe arrangement, a sample current being applied along the b-axis and a magnetic field along the a*-axis using a hybrid magnet attainable up to 26 T at the moment. In the present experiments, the applied magnetic field was continuously increased at a nearly constant sweep rate (less than 0.6 T/min) up to the ultimate value of 26 T and then decreased to zero. The resistive and Hall voltage measurements were made simultaneously using several sets of digital voltmeters by reversing a sample current to exclude spurious voltages. The magnetic field direction was reversed by rotating a sample mounted on a specially designed manipulator, as illustrated in Fig. 2, where a gear system can rotate simultaneously four samples fixed on a rotating plate.

Fig. 2
Home-made manipulator used for rotating samples in the cryostat for the hybrid magnet.



All the signals were stored by a personal computer for record and analysis. Furthermore, in order to check a hysteresis in the hybrid magnet itself, the magnetoresistance of a copper wire (0.08 mm in diameter) was simultaneously monitored during the field sweeps; as a result, no detectable hysteresis effect in the magnet was observed.

III. Results and Discussion

Figure 3 shows the transverse magnetoresistance $\Delta\rho/\rho_0$ vs magnetic field B for several samples (A,.., G). Since the present field sweep range exceeds far above the threshold field B_c (10 T),$^{10,11)}$ we see clearly a characteristic hysteresis in these curves, where the value of $\Delta\rho/\rho_0$ for up-sweep is always lower than that for down-sweep, as indicated by arrows for representative two samples. We also note that the $\Delta\rho/\rho_0$-B curves are reversible at higher fields, and their magnitudes are quite large ($\Delta\rho/\rho_0$ = 40-200 at 26 T) compared to those of normal metals and semiconductors. These anomalous behaviors, including the magnitude of $\Delta\rho/\rho_0$, together with SdH quantum oscillation, are found to be strongly sample-dependent.

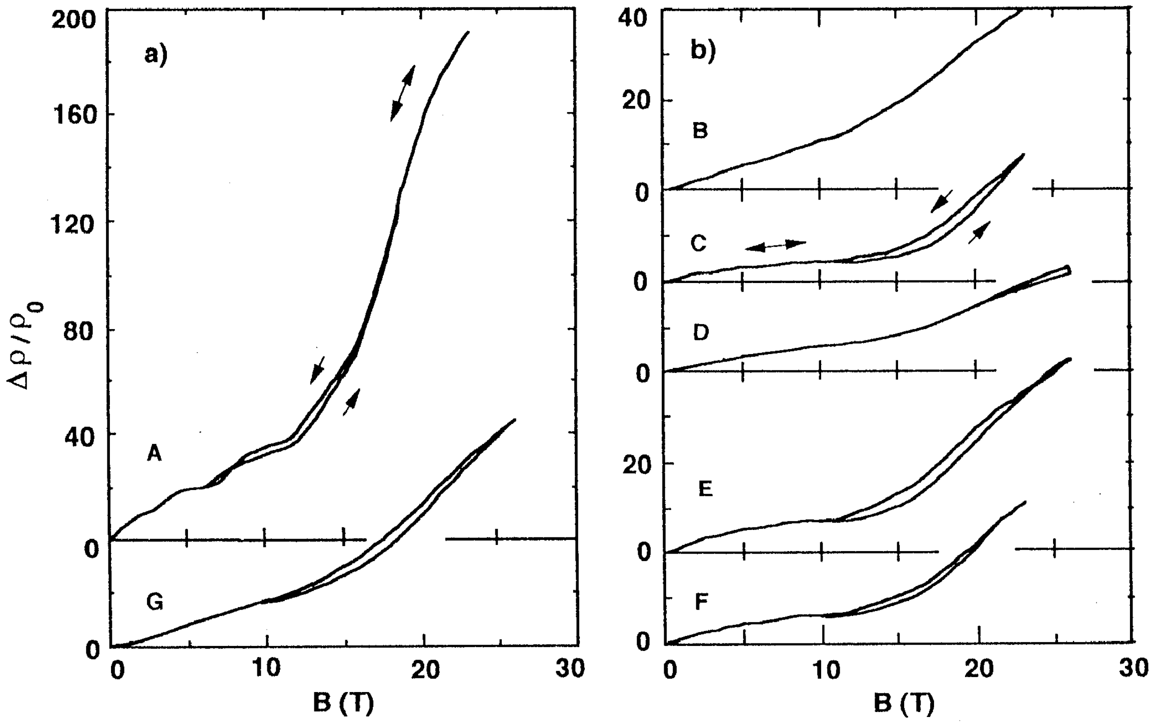


Fig. 3. Transverse magnetoresistance vs magnetic field for various samples (A-G); arrows mark the field-sweep direction.

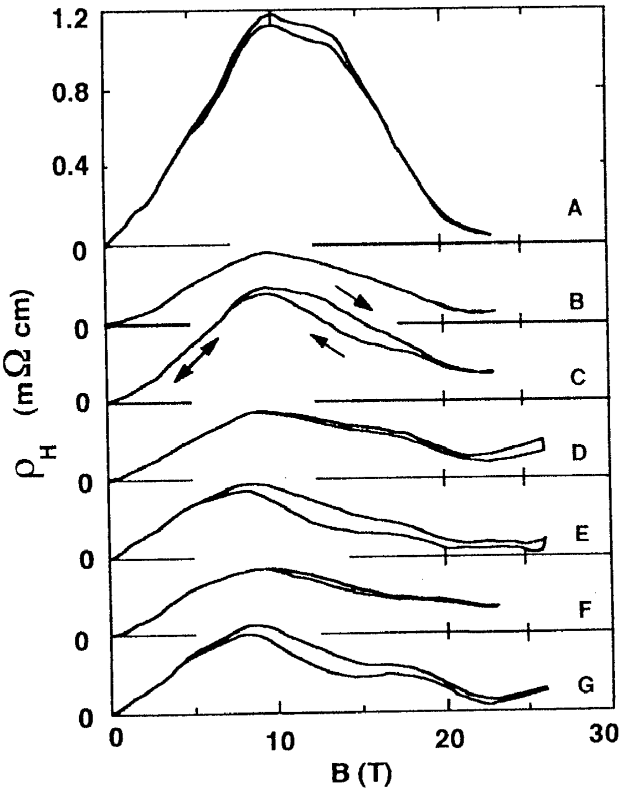


Fig. 4.
Hall resistivity vs magnetic field for various samples (A-G) ; arrows mark the field-sweep direction.

As in the $\Delta\rho/\rho_0$–B curves, the Hall resistivity ρ_H vs B curves exhibit similar characteristic hysteresis, as shown in Fig. 4, where the value of ρ_H for up-sweep is always larger than that for down-sweep, as indicated by arrows for a typical sample C. With increasing B the positive Hall resistivity is increased, peaking at 8-9 T, and decreased to near zero, showing further some oscillatory behaviors at higher fields. We see that these Hall data are also sample-dependent. However, the present experimental results taken under quasi-stationary magnetic fields are in good agreement with those taken using a pulse magnet up to 40 T.[9,10] It is further of interest to study whether the Hall resistivity exhibits a sign reversal from positive to negative at much higher fields due to counterbalance between electron and hole contributions.

We have analyzed the oscillatory components of the SdH oscillations in the observed $\Delta\rho/\rho_0$– and ρ_H–B curves in a semiempirical way. The observed resistive or Hall voltage $V(B)$ at a magnetic field B is expressed as the sum of an oscillatory component $V(B)^{\mathrm{osc}}$ and a background $V(B)^{\mathrm{bg}}$; $V(B) = V(B)^{\mathrm{osc}} + V(B)^{\mathrm{bg}}$, where the background component can be evaluated by a successive smoothing (or averaging) procedure.[13] In Fig. 5 are shown the oscillatory components in the a) magnetoresistance and b) Hall resistivity plotted against the magnetic field for sample G. One notes that these oscillatory components are also irreversible for up- and down-sweeps of the magnetic field, as marked by arrows, thus the maximum or minimum positions being slightly different each other.

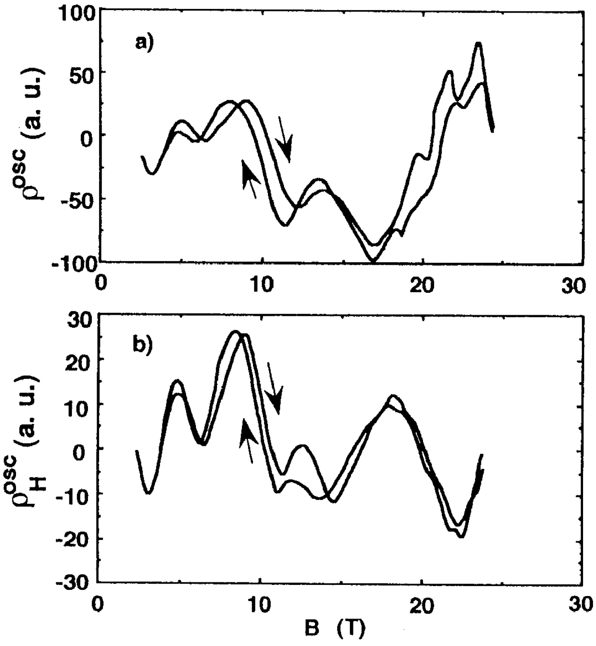


Fig. 5.
Oscillatory components in the a) magnetoresistance and b) Hall resistivity for sample G with up- and down-sweeps.

Figure 6 shows the integer plots for the inverse of the magnetic fields corresponding to the maxima (indicated by solid circles) or minima (open circles) in the oscillatory components of the ρ^{osc}- and ρ_H^{osc}-B curves for sample G (Fig. 5). As can be seen, the integer plots show almost straight lines at higher fields $B > 10$ T, which indicates that the observed oscillations are the SdH oscillations.

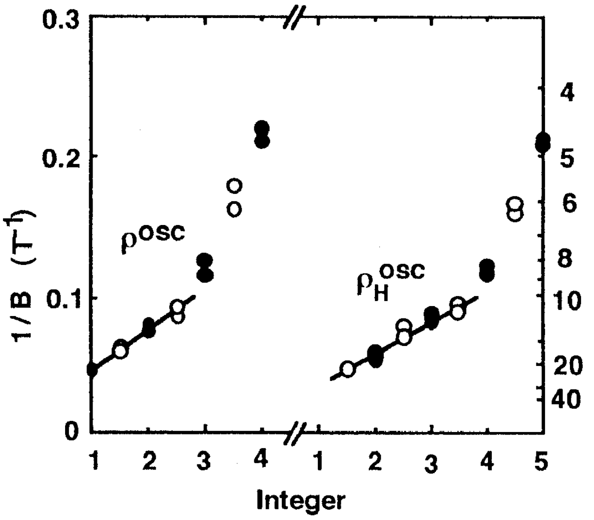


Fig. 6.
Integer plots for the inverse of the magnetic fields corresponding to the maxima (indicated by solid circles) or minima (open circles) in the oscillatory components of the ρ^{osc}- and ρ_H^{osc}- B curves for sample G.

The fundamental frequencies observed in the high field region $B > 10$ T are evaluated to be 38 T for the component ρ^{osc} and 45 T for ρ_H^{osc}, while similar data obtained in the low field region give three kinds of frequencies (4.5, 7.5, 16 T).13) The appearance of such a large frequency (38-45 T) above B_c (=10 T) is very interesting, which in turn suggests the existence of an additional Fermi surface that is formed newly above B_c.

As shown above, all the magnetotransport properties are sample-dependent or structure sensitive. To characterize each sample in terms of measurable quantities, we have plotted the total (or apparent) Hall mobility μ_H ($=R_H/\rho$) against the resistivity at 4.2 K and zero field $\rho(0)$, where the observed Hall coefficient R_H is strongly field-dependent since the Hall voltage is varied with magnetic field B (Fig. 4). Figure 7 summarizes the results obtained at three fixed fields (2, 10, and 23 T) for the present samples (marked by A, B, ..., G). As reported earlier,12) there is no appreciable difference in the crystallographic quantities like lattice spacings, but the electronic difference is noticeable, as evidenced from Fig. 7. In particular, we note that the Hall mobilities obtained at low magnetic field are decreasing function of $\rho(0)$, which is thus regarded as a good parameter to specify the sample quality. A high Hall mobility sample may have less crystal imperfections, while a low Hall mobility one may involve a number of crystal imperfections, such as excess oxygen atoms or oxygen vacancies produced during the crystal growth, which may lead to the changes in the carrier concentration, scattering mechanism, the size of the Fermi surfaces, or the degree of nesting.12)

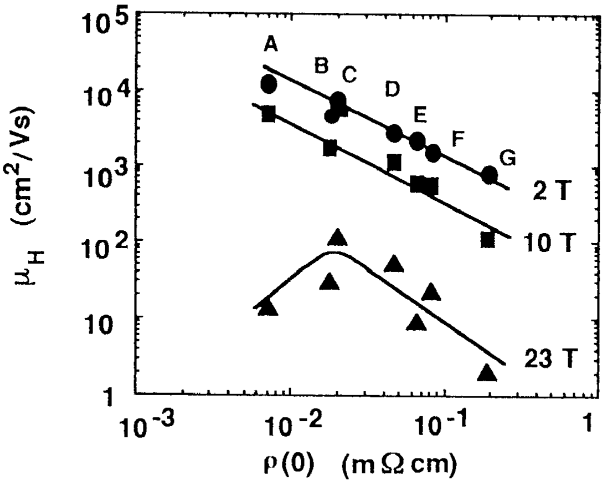


Fig. 7.
Total or apparent Hall mobility measured at three fixed magnetic fields plotted against the resistivity at zero field for various samples (A-G).

At first sight one may suppose that the appearance of a unique hysteresis is due to any "magnetic-field induced band inversion" of electron and hole bands in the CDW states of this material, as in semimetal $Bi_{1-x}Sb_x$ alloy,[14] whose g-value is very large (g ~100). But the g-value of η-Mo_4O_{11} is expected to be small (g ~ 2.3), and therefore even if the band inversion could occur, the threshold field would be much higher (100-1000 T) since the Fermi energies of electron and hole bands are estimated to be 10 meV,[11] which is in contrast to the actual value of B_c=10 T. So the band inversion may be unlikely in our material system. Instead, it appears that the CDW condensation formed below T_{c2} (=35 K) may be responsible for the origin of the hysteresis.

Based on the band model for η-Mo_4O_{11} proposed by Canadell *et al.*[6] and the experimentally determined transport properties, we have proposed a possible CDW-induced band modification of this material.[11] The basic idea is that after the second CDW transition at T_{c2}, at least four different types of carriers (two types of electrons and of holes)[8] are remaining in small carrier pockets, as a consequence of incomplete nesting of their Fermi surfaces. In addition, the carriers that are condensed into the CDW are characterized by a CDW-band with an energy gap Δ_2 at the Fermi level (in case of the second CDW transition). Here, only thermally over the gap activated carriers are able to contribute to the conduction. This model is based on the following assumptions. At an appropriate high magnetic field, the Zeeman-splitting of the above bands is comparable to the Fermi energies and the CDW-gap Δ_2, which leads to a significant magnetic field dependence of the Fermi energies of the up-and down-spin bands. Moreover, the energy gap Δ_2 depends not only on temperature, but varies also with the applied magnetic field. One may suppose that at a certain critical field the gap vanishes completely (i.e., a magnetic field driven destruction of the CDW state). Finally, within this model the hysteresis is assumed to be caused by a magnetic field induced *irreversible process* of the formation and destruction of CDW condensate. The results of the numerical simulation with the model described above are in good agreement with the experiments.[11)] However, in this model the Hall resistivity becomes negative at higher fields $B > 20$ T, in contrast to the observations; thus more refined model including quantum effect must be considered.

In summary, we have confirmed the appearance of the characteristic hysteresis effects in both transverse magnetoresistance and Hall effect under quasi-stationary magnetic field sweep up to 26 T, which can be attributed to the magnetic field induced *irreversible process* of the formation and destruction of CDW condensate formed below T_{c2}=35 K. It is still uncertain whether the Hall resistivity changes its sign from positive to negative at much high fields $B>$ 30 T. In order to get more insight into the microscopic mechanism of these anomalous behaviors, detailed measurements of the band parameters, like effective masses and g-values, transport measurements at much higher fields, as well as theoretical consideration, are required.

Acknowledgments

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