Superconducting and dielectric instabilities in $Tl_2Mo_6Se_6$: Unusual transport properties and unsaturating critical field

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The Hall effect of the quasi-one-dimensional compound $Tl_2Mo_6Se_6$ undergoes a progressive transition between an electronlike metallic regime at 300 K and a holelike semimetallic regime just above the superconducting transition ($T_c \approx 6.5$ K). We show that, above ≈ 80 K, the paradoxical transport properties can be explained by an unusual anisotropic electron scattering related to the low dimensionality of the system and to its instability. A spin-density-wave (SDW) or charge-density-wave (CDW) state certainly builds up below ~ 80 K—leading also to a change of regime in the thermopower but not in the conductivity—which is accompanied, at lower temperatures, by a magnetic-field dependence of the Hall coefficient and by a significant transverse magnetoresistance. The superconducting (SC) state therefore arises after the electron spectrum has been partly dielectrized by the CDW (or SDW) condensation, and it involves a very small density of states. A large paraconductivity which we attribute to superconducting fluctuations is detected just above T_c and the transverse upper critical field $H_{c_2}^{\perp}$ does not saturate down to 50 mK, which confirms that we are dealing with a very unusual superconducting state, intricately connected with the other competing instabilities.

I. INTRODUCTION

The interest of the solid-state physics community is more and more often drawn towards compounds whose unusual properties are related to a pronounced anisotropy. Among these compounds $Tl_2Mo_6Se_6$ stands in a remarkable position: It is certainly the inorganic superconductor that has the greatest uniaxial anisotropy—comparable to the most anisotropic organic superconductors—but, unlike most of them, it has very simple crystal and band structures which should encourage theoretical investigations. At room temperature the crystal symmetry is hexagonal[1] (space group $P6_3/m$) and the band structure mainly consists of a wide (≈ 4.5 eV) half-filled quasi-one-dimensional band (the "helix" band)—the electrons being provided by the thallium atoms.[2,3] The presence of a few electrons in a quasi-isotropic overlapping band (the "octahedron" band) was inferred from the stability of the structure which otherwise would be unstable against a Peierls-like distortion. It is worth noticing also that this system is diamagnetic.[4]

These simple features contrast with the many uncommon properties observed in this compound:[5] a relatively high superconducting transition temperature ($T_c \approx 6.5$ K) compared to the very small density of electrons; an extreme type-II behavior with macroscopic penetration depths which imply that the mixed state could be quite different from the Abrikosov-Gorkov picture; a nonmetallic thermopower which seems related to nonclassical scattering mechanisms. Recently it has been shown that an uniaxial stress can induce an insulating ground state with nonlinear effects reminiscent of a charge-density-wave (CDW) or spin-density-wave (SDW) dielectrization.[6] Moreover the superconducting state can coexist with this instability and even seems to take advantage of it before disappearing.

This paper is organized as follows: In Sec. II we present the Hall-effect data obtained for $Tl_2Mo_6Se_6$ and examine the whole "normal-state" properties under this new light; in Sec. III we report upper critical field and magnetoresistance measurements at very low temperatures which show outstanding features. Our analysis of these data allows us to deduce a coherent picture of this very peculiar system which is briefly summarized in Sec. IV. We also outline there the questions that deserve further investigation and could lead to a better understanding of low-dimensional materials.

II. HALL EFFECT AND TRANSPORT PROPERTIES

The Hall voltage measurements were made on two ribbon-shaped crystals approximately 5 mm long in the c direction and about 20 μm thick. To avoid heating effects on the current contacts they were made by evaporating gold around the ends of the crystals before pasting the gold leads (20 μm diam) with silver paint. The Hall voltage was measured perpendicular to the c direction by clasping the sample between two crossed gold leads. Using no silver paint here allows small contact areas to be defined on the two largest opposite faces

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(about 100 μm wide) with minimum perturbation of the current lines. The Hall resistance R_{xy} was measured with an ac bridge working at the frequency of 33 Hz; the current used was less than 1 mA; We determined the thickness of the samples with a scanning electron microscope.

Standard ^{4}He and ^{3}He cryostats have been used with superconducting coils delivering up to 8 and 6 T, respectively. The magnetic field was swept in both directions to eliminate the magnetoresistive contribution which comes from an imperfect alignment of the voltage leads and is noticeable below about 15 K.

A. Results

Our measurements have revealed an unexpected behavior of the Hall effect which is strongly temperature dependent and, below about 30 K, depends also on the magnetic field as it is exemplified in the inset of Fig. 1. Between 30 and 5 K we can extrapolate the Hall resistance derivatives dR_{xy}/dH towards their zero-field limits; the corresponding values of the Hall coefficient R_H are plotted as a function of the temperature in Fig. 1, together with the "high-field" values we have determined for $H=4$ T.

At ambient temperature the Hall constant is only $(-4.2\pm0.5\times10^{-10})$ m^3 C^{-1}; lowering the temperature increases the absolute value of R_H up to a maximum around 80 K where it has been multiplied by about 30. Then R_H goes through zero at 45 K and reaches a positive value of 3.5×10^{-8} m^3 C^{-1} at 10 K.

We shall now discuss these results together with the previous transport data and, as is suggested by this behavior of the Hall effect, we shall consider in turn the high-temperature (80 K $\leq T \leq$ 300 K) and low-temperature ($T_c \leq T \leq$ 80 K) properties of the normal state.

B. Discussion of the normal-state properties

The behavior of the Hall effect clearly indicates that a change of regime takes place around 80 K in $Tl_2Mo_6Se_6$. This is a crucial piece of information for our understanding of this compound and it is quite surprising that it has not been detected earlier. Actually a similar, though less pronounced, upturn toward a low-temperature hole dominated process can be recognized, *a posteriori*, in the thermopower data which are presented again for comparison in Fig. 2. However, as the resistivity does not show any anomaly in the same temperature range, we did not pay much attention to this part of the thermopower data which could be influenced, moreover, by phonon-drag effects.

From another point of view there was some reason to expect, for this compound, another kind of electronic phase transition (other than superconducting) because, as mentioned in Sec. I, the quasi-one-dimensional (quasi-1D) character of its band structure favors a CDW or SDW transition. We shall delay any further discussion about the probability of such a transition but keep it in mind while considering the high-temperature (80 K $\leq T \leq$ 300 K) electronic properties.

1. *The high-temperature transport properties*

Even a quick look at the behaviors of the resistivity, thermopower, and Hall effect, as displayed in Figs. 1 and 2, makes it clear that they are not consistent with the simple quasi-1D-metal model presented in Sec. I. The large thermopower which does not vary linearly with temperature and the strongly temperature-dependent Hall effect are rather reminiscent of semimetallic Bi and Sb. However, we think that this kind of interpretation is not satisfactory either.

Let us consider first the conductivity: Along the c direction ($\sigma_\parallel$) it is about 2×10^6 Ω^{-1} m^{-1} at 300 K and could result from the electrons provided by the Tl atoms (6.4×10^{27} m^{-3}) in a quasi-1D band where their effective mass $m_\parallel$ is approximately the free-electron mass m_e, in accordance with the band-structure calculations.[2] Then the scattering time $\tau_\parallel$ we deduce is about 10^{-14} s and the Hall constant at ambient temperature is satisfactorily accounted for (see the Appendix). In the perpendicular direction the conductivity is at least two orders of magni-

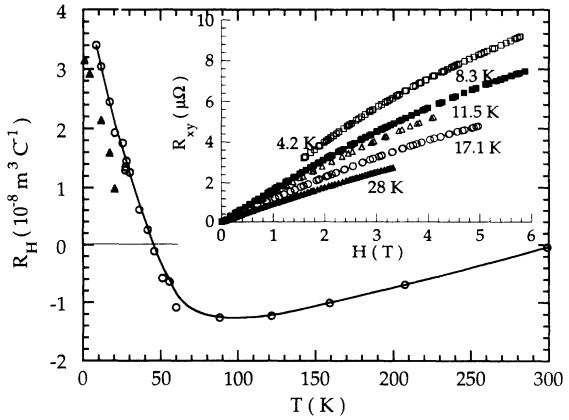

FIG. 1. Temperature dependence of the Hall constant at $H=4$ T (▲) and extrapolated at zero field (○); the solid line is a guide to the eye. The inset shows the magnetic-field dependence of the Hall resistance at low temperature.

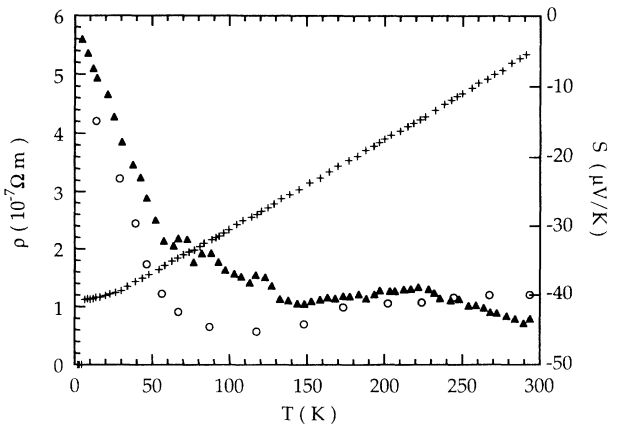

FIG. 2. Temperature dependence of the resistivity (+) and of the thermopower (open circles, see Ref. 5; solid triangles, see Ref. 7).

tude lower: In samples which were not superconducting Mori *et al.*[7] measured $\sigma_{\parallel}/\sigma_{\perp}\approx 200$, whereas in samples similar to ours Armici *et al.*[9] measured $\sigma_{\parallel}/\sigma_{\perp}\approx 1000$. This is compatible with the description resulting from the band-structure calculations and is strongly supported by the IR reflectivity data:[8] For the parallel polarization a well-defined plasma edge is observed which is well accounted for by the half-filled quasi-1D band described above and by a scattering time $\tau_{\parallel}\approx 4\times 10^{-15}$ s; for the perpendicular polarization no plasma edge is observed down to 50 meV which implies $\sigma_{\parallel}/\sigma_{\perp}>400$.

The coherence of this picture makes quite credible these values of the electron concentration, mass and scattering time, as well as the quasi-one-dimensionality of the electronic transport, whereas they cannot be reconciled with a semimetallic picture.

At this point we are faced with the problem of interpreting the high and temperature-independent thermopower. In Ref. 5 we mentioned the possibility of invoking an unusual scattering process leading to a strongly energy-dependent scattering time. We thought it could be related to the scattering of the electrons from the quasi-1D "helix" band toward the isotropic "octahedron band" which should be slightly populated in order to stabilize the structure against a Peierls-like distortion.[2,3] However, it is very unlikely that such a process, which has been proposed by Mott[10] for the transition metals, could explain the thermopower of $Tl_2Mo_6Se_6$.

First, it does not explain why we observe no temperature dependence between 300 and 80 K, as we know today, from our study of the lattice dynamics,[11] that any phonon-drag effect which could mask it, should occur at lower temperatures.

Second, in order to account for the negative thermopower, the scattering time $\tau_{\parallel}$ must *increase* with energy which supposes, in the Mott picture, that the density of states at the Fermi level D_{EF} *decreases* with energy in the upper "octahedron" band: This is most unlikely as this band is quite isotropic and nearly empty.[2]

In several quasi-one-dimensional conductors a high and temperature-independent thermopower has also been observed.[12–14] In some cases it might be explained by a correlation-induced localization in narrow bands,[13] which certainly play no role in the inorganic $Tl_2Mo_6Se_6$ where the conduction band is larger than 4 eV and gives rise to no detectable magnetism.[5]

A main feature of the electronic transport in this kind of compound is its diffusive behavior in the transverse directions as long as the transfer integral $t_{\perp}$ is much lower than $\hbar/\tau_{\parallel}$.[15] Band-structure calculations[2] give $t_{\parallel}\approx 1.2$ eV, which agrees with the optical data,[8] and 7 meV $<t_{\perp}<20$ meV; this is consistent with the anisotropy of the conductivity and upper critical field if this is mainly determined by the anisotropy of the band structure, i.e.:

$$\left[\frac{dH_{c_2}^{\parallel}}{dT}\right]_{T_c}\Big/\left[\frac{dH_{c_2}^{\perp}}{dT}\right]_{T_c}=\varepsilon \quad \text{and} \quad \frac{\sigma_{\parallel}}{\sigma_{\perp}}=\varepsilon^2\approx\left[\frac{t_{\parallel}c}{t_{\perp}\sqrt{3}a}\right]^2$$

for such an open Fermi surface.

At ambient temperature the conductivity and IR reflectivity data[8] give $\hbar/\tau_{\parallel}\approx 0.15$ eV; therefore the transverse transport could become progressively coherent during the cooling down. Nevertheless, as long as we stay within the framework of the scattering time approximation and of the Boltzmann description, this effect should not invalidate the standard expression for the thermopower:

$$S=-\frac{\pi^2 k_B T}{3e}\left[\frac{\epsilon_k''}{(\epsilon_k')^2}+\frac{\tau'(\epsilon)}{\tau(\epsilon)}\right]_{\epsilon=\epsilon_F}. \tag{1}$$

The first term in Eq. (1) gives no contribution if we are dealing with a half-filled one-dimensional tight-binding band; if we include a moderate transverse dispersion the corresponding band term still gives only a minor contribution. Going a step further we have also verified that it cannot be strongly reinforced only by taking account of an anisotropy of the scattering time (see the Appendix). So we are led again to assign to the second term of Eq. (1)—or to the corresponding scattering term in a less restrictive model—the high and temperature-independent value of S. The thermopower of β(BEDT-TTF)$_2$I$_3$ has been analyzed in the same way and the same conclusion has been reached by Mortensen, Williams, and Wang.[14]

Turning now our attention to the Hall effect we could be tempted to explain its temperature dependence by a two-band model in which a pocket of very light electrons is progressively populated during cooling, due to an hypothetical relative shift of the bands induced by some large contraction of the lattice. However, we stress again that we do not see how to introduce such a pocket without recasting completely the calculated band structure which is strongly supported by the resistivity and optical data.

The influence of a diffusive transverse motion on the Hall effect has been investigated by Lyo,[16] Ong, and Portis[17] who found that it could lead only to a slight enhancement (less than a factor of ≈ 5), therefore a transition from a diffusive to a coherent motion should not explain alone the strong temperature dependence observed in $Tl_2Mo_6Se_6$. However, these calculations still involve the scattering time approximation for the longitudinal motion and, within this framework they show that the enhancement factor of R_H is directly related also to the thermopower as long as it can be interpreted in the same framework.

Conversely this analysis strengthens our feeling that the abnormal Hall effect and thermopower are both related to an unusual scattering, the possible sources of which we shall discuss now.

It is well known that in one-dimensional materials undergoing a Peierls transition at T_c we can observe precursory CDW fluctuations up to ambient temperature.[18] It has been claimed that they could be responsible for a significant paraconductivity in the organic conductors;[19] however it is generally admitted that the electronic density of states is hardly affected as long as the temperature is higher than the mean-field transition value T_c^{MF};[20] the smaller the transverse transfer integral $t_{\perp}$, the greater the T_c^{MF}/T_c ratio. As we shall show later it is most likely

that a Peierls type instability develops at low temperature but it seems difficult to assign to T_c^{MF} a value greater than about 80 K. Above this temperature the CDW fluctuations are one-dimensional and if they take a part in the transport properties of $Tl_2Mo_6Se_6$ up to 300 K it should be only *via* a perturbation of the scattering mechanisms. We are here in a field which was very controversial at the beginning of the 1980's and which has been left relatively unexplored since. It is clear that we have not enough experimental and theoretical information to estimate what is the actual importance of the CDW fluctuations and of the diffusive-to-coherent transition for electronic transport in $Tl_2Mo_6Se_6$. Furthermore we cannot totally rule out the possibility that a neighboring band and/or localized states originating from interrupted Mo_6Se_6 chains[3] could enter the scattering mechanisms in a subtle way. Finally we remark that, contenting ourselves with a phenomenological approach, we can reproduce the temperature dependence of the Hall effect with the Boltzmann model by considering a quasi-one-dimensional band and a temperature-dependent anisotropy of an "effective" scattering time mimicking a possible influence of the transverse coherence and of the fluctuations (see the Appendix); however, to explain also the high value of the thermopower we still need τ, or its anisotropy, to be strongly energy dependent, as we have already noted when considering Eq. (1).

2. *The low-temperature electronic properties*

We underlined above that we have some reason to believe in the main features of the calculated band structure: the room-temperature conductivity agrees with the half-filled "helix" band contribution and the scattering time $\tau_{\parallel}$ deduced from the IR reflectance measurements:[8] $\tau_{\parallel} \approx 10^{-14}$ s, a typical value for the quasi-one-dimensional compounds.[21] The optical data also confirm the one dimensionality of the helix band and its width (≈ 4.5 eV), ruling out a noticeable population of the upper "octahedron" band. The Hall effect at 300 K is also compatible with this description (see the Appendix) although it is much more difficult to interpret at lower temperatures. The band-structure calculations are not sufficiently accurate to fix the occupancy of the octahedron band but a maximum population of 0.1 electron per Tl atom was deduced from experimental estimations of the anisotropy and from the stability of the structure which otherwise would be unstable against any Peierls-like distortion.[2]

Now the experimental landscape is quite different: Our Hall-effect measurements show unambiguously that a change of regime takes place in $Tl_2Mo_6Se_6$ around 80 K, from which we can deduce first, that the high-temperature state anisotropy could be higher than the one we estimate from the upper critical fields H_{c2}, and second, that the octahedron band could be even less populated than proposed in Ref. 2 and the stability of the structure more fragile.

Incidentally the synthesis of large amounts of powder for our neutron experiments[11] gave us the opportunity to observe that superconductivity was favored by a slight deficiency of thallium: We prepared 20 g-powder samples of nominal composition $Tl_xMo_6Se_6$ with x ranging between 1.8 and 2.05, by using the same starting materials and the same procedure including a final annealing at 1100 °C. We monitored the ac susceptibility of the samples down to 1.2 K and detected the superconducting transition only for $x = 1.9$ and 1.95, with an onset at 3 and 7 K, respectively, but the amplitude of the transition was three times smaller in the second sample. This strongly suggests first that the boundary of the superconducting phase stays nearer to $x = 1.95$ than to $x = 1.9$ and second that T_c goes through a maximum just before we leave the superconducting phase.[22]

For $x < 1.9$ the ground state is probably insulating as suggested by the following experiment: A couple of crystals that were annealed for 1 h at 500 °C in a flow of HCl gas displayed a larger resistivity upturn and a lower superconducting T_c than the pristine samples. Although this result calls for confirmation it is a first indication that the removal of a small proportion of Tl atoms favors also the semiconducting low-temperature (LT) phase and that the superconducting instability can coexist with the dielectric instability in a small domain of the $T_c(x)$ phase diagram.

This behavior is very similar to what is observed if a stress is applied to a crystal along the c direction,[6] i.e., T_c first increases slightly and then the SC state disappears abruptly above a 0.6% strain, giving way to a new phase with semiconducting and nonlinear transport properties typical of a CDW or SDW state. Moreover increasing the stress continuously amplifies the low-temperature resistivity upturn which is often hardly visible in the unstrained samples, so much so that for the maximum strain compatible with the existence of the SC phase ($\approx 0.6\%$) the resistivity just above T_c is multiplied by about 20 with respect to its value in zero stress. Finally it is worth noticing that, for such a strain, the change from a metallic to a semiconducting behavior of the resistivity occurs around 80 K, i.e., coincides with the upturns we observed in the thermopower and Hall effect of the unstressed samples.

These results are consistent with the band structure described above and with the buildup of a CDW or SDW instability below about 80 K, favored by an uniaxial stress or a slight reduction of the number of conduction electrons. The mechanism probably involved in the first case is the enhancement of the transverse coupling *via* the c/a ratio which allows the fluctuating distortions to condense at temperatures nearer to the mean-field value T_{MF}; in the second case small variations of the band filling could produce a better nesting of the opposite parts of the Fermi surface and also improve the efficiency of the umklapp electron-electron scattering (the g_3 coupling parameter in the Fermi-gas model[23]) which is relevant only for a half-filled band.

One rather puzzling feature of the transition from the metallic high-temperature (HT) state to the semiconducting LT state is that we cannot detect it in the resistivity of the unstressed samples whereas it appears clearly in the thermopower and Hall effect. Even under stress no abrupt resistivity change marks the transition temperature; the same remark applies to the $M_2Mo_6Se_6$ isotypes

(M = IA metal: Cs, Rb, K, Na) which are semiconducting below about 80 K.[24] This behavior could be explained on the one hand by a large enhancement of the carrier mobility in the same temperature range: Actually the $M_2Mo_6Se_6$ lattice is rather soft[11] and, if the phonon contribution to the electron scattering follows approximately the same temperature dependence as the specific heat, we expect a steep decrease of this contribution below ≈ 80 K. On the other hand we can invoke one-dimensional effects like those put forward in the case of TMTSF-TCNQ,[25] for instance: The transition could be progressive because it takes place in a temperature range where the transverse electronic motion is becoming coherent; moreover, if we have to deal with a CDW or SDW transition, it can be preceded by a wide region of strong fluctuations (see Sec. II B 1).

Obviously our assignment of the low-temperature properties to a CDW or SDW state deserves more direct evidence from diffraction or NMR experiments. Our feeling is that, among these two possibilities, the CDW state is the most likely because the $M_2Mo_6Se_6$ compounds are diamagnetic down to T_c.[4]

Below about 80 K the thermopower and Hall effect of $Tl_2Mo_6Se_6$ increase rapidly and finally become dominated by a hole contribution. This behavior is consistent with the progressive condensation of the CDW or SDW inducing first a pseudogap near $T = T_{MF}$ and then a real gap on a part of the Fermi surface (FS). The geometry and population of the electron and hole pockets which are created by this process depend critically on the wrapping of the unperturbed FS upon which we have only rather crude information. In the following section we shall compare more precisely the normal low-temperature transport properties with the usual two-band model but we can already see a particular difficulty in the description of the Hall effect: As we mentioned above R_H is field dependent below about 30 K; this phenomenon can be related to a low-field to high-field transition for $\omega_c\tau \approx 1$, ω_c being the cyclotron frequency. However, we observe in Fig. 1 that R_H decreases quite linearly from the lowest fields, therefore we think that a main contribution to this effect could arise from the sensitivity of the CDW or SDW to magnetic fields, as in $NbSe_3$,[26] KMo_6O_{17},[27] or the Bechgaard salts $(TMTSF)_2X$,[28] respectively. This is confirmed by the behavior of the magnetoresistance, as presented below.

III. TRANSVERSE MAGNETORESISTANCE AND UPPER CRITICAL FIELD H_{C2}

We have measured the transverse magnetoresistance of a crystal of the same batch and approximately the same dimensions as those used in the Hall-effect measurements. We employed also the same technique to make the current contacts (but the gold leads were soldered with Indium to the gold plated tips of the sample) and the same ac bridge to measure the resistance of the sample with a 10 μA current in the c direction. The voltage contacts were achieved by pasting the gold leads to evaporated gold spots. Preliminary measurements were made in a standard He^4 cryostat, in the field provided by a 0.7-T rotating electromagnet, to check that no anisotropy was detectable in the basal plane. Then we used a He^3 cryostat including a 6-T superconducting solenoid and finally a top-loading dilution refrigerator mounted on a Bitter coil of the Service National des Champs Intenses. Our measurements have been done chiefly by regulating the temperature while sweeping the magnetic field. Even with the lowest speed compatible with a reasonable measuring time the eddy currents induced by the sweep and the vibrations of the Bitter coil prevented us from regulating correctly the temperature below about 50 mK.

A. Transverse magnetoresistance

A summary of our results is presented in Fig. 3 where the temperature dependence of the resistivity below 15 K is plotted for different values of the field.

As we shall show below, the amplification by the magnetic field of the low-temperature resistivity upturn cannot be attributed solely to orbital effects. Actually the field dependence of the resistivity follows a H^2 behavior only at high fields ($H \geq 10$ T). The curvature of the $\rho(H)$ curves becomes negative at lower fields where they join the end of the superconducting transition (Fig. 4). Therefore we propose to process these data in the following way: At each temperature we extrapolate the H^2 behavior down to $H = 0$ and obtain a value $\rho_0(T)$. Then we express the resistivity as $\rho(H,T) = \rho_s(H,T) + \beta H^2$, where $\rho_s(H,T)$ is a term tending towards $\rho_0(T)$ when $H \rightarrow \infty$ (see inset in Fig. 3), and define the magnetoresistance as

$$\frac{\Delta\rho}{\rho} = \frac{\rho(H,T) - \rho_0(T)}{\rho_0(T)} = \frac{\rho_s(H,T) - \rho_0(T)}{\rho_0(T)} + \alpha H^2 . \quad (2)$$

This asymptotic value $\rho_0(T)$ is plotted in Fig. 3 where it appears clearly that the major part of the resistivity upturn comes from this contribution.

We shall consider first the α coefficient in Eq. (2) which is approximately constant $[= (2.3 \pm 0.15) 10^{-4}\ \mathrm{T}^{-2}]$

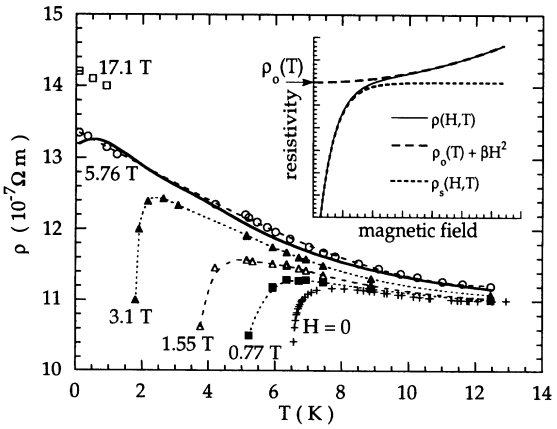

FIG. 3. Temperature dependence of the resistivity in different transverse magnetic field; the solid line represents the $\rho_0(T)$ values defined by Eq. (2). All the lines are a guide to the eye. The inset illustrates our decomposition of the magnetoresistance which leads to Eq. (2).

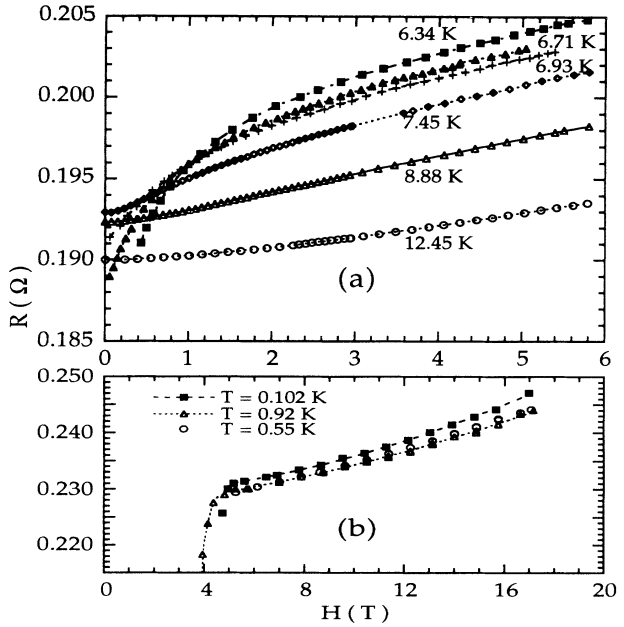

FIG. 4. The magnetic-field dependence of the resistivity in low field at $T \geq T_c$: (a), and in high field at $T \ll T_c$: (b).

within the temperature range where high-field data are available, i.e., between 0.1 and 1 K.

It is tempting to ascribe this term to an orbital origin and to compare it with that derived from a two-band model.[29] Then we find that the measured values of σ and R_H are only compatible with α if this results from a high-field nonsaturating behavior, typical of a compensated metal.[30] The carrier concentration would be $n = p = \approx 3 \times 10^{20}$ cm^{-3}, the holes having a much higher mobility ($\nu \approx 0.2$ m^2/V s) than the electrons ($\mu \approx 10^{-3}$ m^2/V s). In view of the complexity of the system we are dealing with, this model is certainly too crude. In particular it supposes that we have well-defined electron and hole pockets; such a FS could result from the opening of a CDW or SDW gap in the middle of the quasi-1D helix band, however, the absence of anomaly in the conductivity, and the absence of discontinuity in the Hall effect and thermopower, indicate that the dielectric instability cannot condense completely and leads only to a pseudogap and a fluctuation regime.

Alternatively, if we suppose that the Fermi surface of the normal state is still an open one, made of two slightly warped planes at $\pm k_F$, the existence of a magnetoresistance is difficult to explain. Anisotropic scattering[31] or superconducting fluctuations[32] have been put forward in the studies of the (TMTSF)$_2X$ family.[33] We think like Jacobsen *et al.*, and Chaikin[31] that it could be associated with the precursor of the spin-density-wave transition which takes place at lower temperature in (TMTSF)$_2$PF$_6$ or which is induced by higher fields in (TMTSF)$_2$ClO$_4$. The case of $Tl_2Mo_6Se_6$ is still more complicated because we are here in the range of temperature where a transition is taking place; moreover the field dependence of R_H and the major nonorbital contribution to the magnetoresistance $\rho_0(T)$ are signs of the sensitivity of this transition to the magnetic field. Therefore our decomposition of the magnetoresistance illustrated by Eq. (2) should be only considered as a first phenomenological attempt to disentangle its various constituents.

We shall turn our attention to the contribution which does not follow an H^2 law—the first term in the right side of Eq. (2)—and we present its field dependence at different temperatures in Figs. 5 and 6.

One way to rationalize this unusual effect is to consider that $\rho_0(T)$ is the normal value of the resistivity and that the proximity of the superconducting phase induces a supplementary conductivity which is reduced by a transverse magnetic field; in other words a paraconductivity associated with superconducting fluctuations.

In this case current theories,[34] applied to low-dimensional materials, predict a crossover between a 3D behavior near to T_c [$\varepsilon = (T - T_c)/T_c \ll 1$] and a 2D or 1D behavior for $\varepsilon \gg 1$, corresponding to a transverse correlation length $\xi_\perp$ greater or smaller than the distance d between the conducting planes (2D) or chains (1D), respectively. If the main contribution to the fluctuation conductivity is the regular one calculated by Aslamazov and Larkin[35] (AL) it should follow a $\varepsilon^{-1/2}$ law within the 3D regime and decrease more rapidly within the low-dimensional regime [$\Delta\sigma \propto \varepsilon^{-\eta}$ with $\eta > \frac{1}{2}$ (Refs. 32 and 36)]. The situation is more complicated if one has to include the "anomalous" fluctuation conductivity derived by Maki and Thompson[37] (MT), which results from the scattering of the normal excitations by the superconducting fluctuations; as illustrated by Hikita and Suzuki in $YBa_2Cu_3O_y$ this contribution can reduce the effective exponent η of the power law.[38,39]

To compare our data with these theoretical results we have plotted in Fig. 7 the excess conductivity $\Delta\sigma$ as a function of ε, taking $\Delta\sigma = \rho(H,T)^{-1} - \rho_0(T)^{-1}$, to be consistent with our conception of the normal resistivity. The transition temperature we used in this plot is $T_c = 6.54$ K corresponding to the middle of the resistive transition. The zero-field paraconductivity, as it appears on Fig. 7, roughly agrees with the above theoretical picture: A

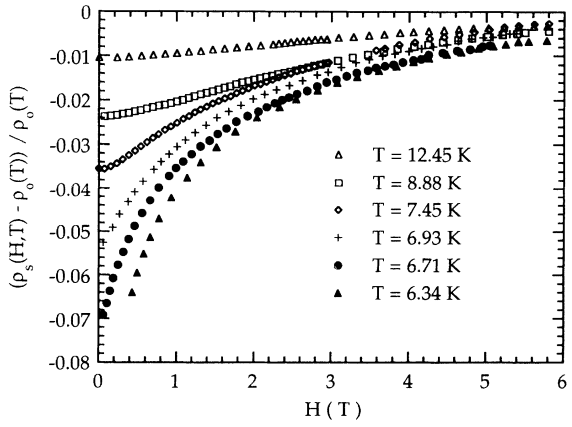

FIG. 5. The magnetic-field dependence of the nonorbital contribution to the transverse magnetoresistance, i.e., $\Delta\rho/\rho - \alpha H^2$, as defined by Eq. (2), in low field at $T \geq T_c$.

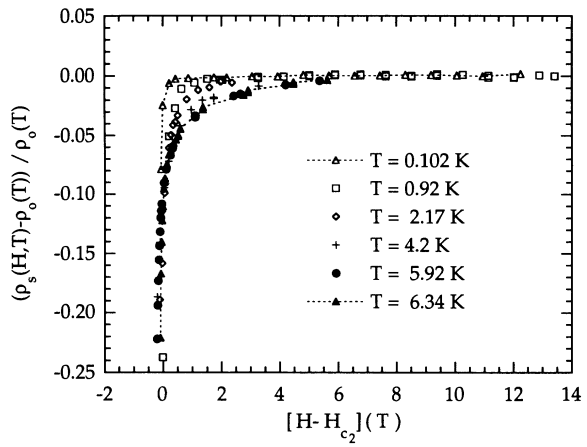

FIG. 6. The magnetic-field dependence of the nonorbital contribution to the transverse magnetoresistance, i.e., $\Delta\rho/\rho-\alpha H^2$, as defined by Eq. (2), in high field at $T \leq T_c$.

crossover occurs between two power laws with, respectively, $\eta \approx 0.3$ below and $\eta \approx 0.45$ above $\varepsilon \approx 0.1$.

The AL contribution to the paraconductivity in a quasi-one-dimensional superconductor has been calculated by Schulz *et al.*[32] using a model system of a square array of parallel conducting chains with the possibility of electron tunneling between adjacent chains. They obtain in the 3D regime

$$\sigma_{\parallel}^{3D} \approx \frac{e^2\pi^{3/2}}{8\sqrt{2}d_{\perp}^2\hbar k_F}\left[\frac{T}{T_F}\frac{\theta}{T_F}\right]^{-1/2}\left[\frac{T}{B}\right]\varepsilon^{-1/2}, \quad (3)$$

where $d_{\perp}$ is the distance between the chains; T_F and k_F are, respectively, the Fermi temperature and electron momentum, θ represents the finite electron lifetime broadening of the Fermi distribution ($k_B\theta \approx \hbar/\tau$; τ being the electron scattering time). B is related to the crossover temperature between 1D and 3D regimes, it is given approximately by $k_B B \approx 2\pi^2 t_{\perp}^2/k_B\theta$ but it has been used as an adjustable parameter by Schulz *et al.*, owing to its strong dependence on the approximate forms employed for the integrals involved in the derivation of Eq. (3). Finally it is also supposed that we are dealing with a tight-binding band.

This formula cannot account for the excess conductivity in $Tl_2Mo_6Se_6$ if we neglect the perturbation of the 1D helix band by the CDW (or SDW) instability. Actually, taking $E_F \approx 2$ eV, $k_F = \pi/c$, $d_{\perp} = a$, and $\tau \approx 10^{-14}$ s we obtain at $T = 7.2$ K ($\varepsilon \approx 0.1$): $\sigma_{\parallel}^{3D} \approx 2\times 10^7$ (T/B) $\Omega^{-1}\,m^{-1}$, which is about 50 times greater than our experimental estimation (Fig. 7) if we take $B \approx 7$ K (which would imply a mean-field transition temperature $T_c^0 \gtrsim 13$ K). We are faced with an even larger discrepancy if we take, instead of Eq. (3), the formula corresponding to the 1D regime.

Therefore our results could agree with the fluctuation conductivity model proposed by Schulz *et al.* only if we have to deal with a much narrower but still quasi-one-dimensional band, which seems quite contradictory if this new band structure results from the opening of a CDW (or SDW) gap. Another possibility is to abandon the strong fluctuation picture stemming from the quasi-one-dimensional model above, owing to the fact that the transverse coherence length $\xi_{\perp}^0$ is much larger than $d_{\perp} = a$, and to turn to the usual 3D model. In this case the (AL) excess conductivity is given by[34]

$$\sigma_{3D}^{AL} = \frac{1}{32}\frac{e^2}{\hbar\xi^0}\varepsilon^{-1/2}, \quad (4)$$

which gives at most $10^4\ \Omega^{-1}\,m^{-1}$ when $\varepsilon = 0.1$, taking for ξ^0 the shortest coherence length:[5] $\xi_{\perp}^0 = 25$ Å. So our data are just situated halfway between the two extreme models. This situation could be interpreted naively as if the SC state retained some one-dimensional character after the partial dielectrization of the electron spectrum.

Finally we shall notice that this paraconductivity is of the same order of magnitude as in $YBa_2Cu_3O_y$ (Ref. 39) and leads to a very similar behavior of its field dependence $\sigma(0)-\sigma(H)$ as shown in Fig. 8.

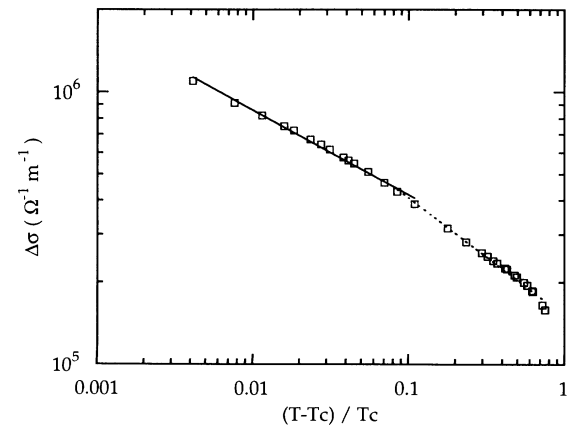

FIG. 7. The excess conductivity $\Delta\sigma = \rho(T)^{-1} - \rho_0(T)^{-1}$, according to the definitions used for Eq. (2), as a function of $\varepsilon = (T-T_c)/T_c$. The straight lines are power-law fits with exponents $\eta = 0.31$ and 0.45, below and above $\varepsilon \cong 0.1$, respectively.

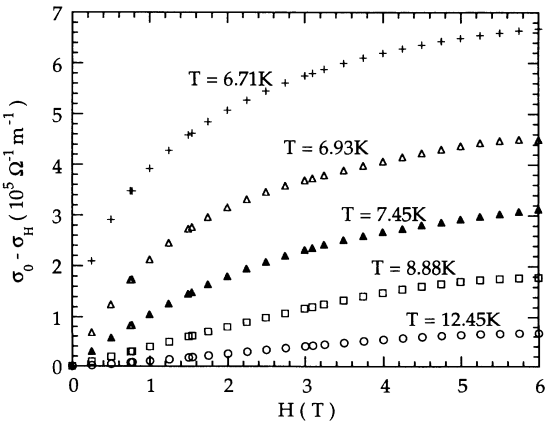

FIG. 8. The magnetoconductivity $\rho(0,T)^{-1} - \rho_s(H,T)^{-1}$ as a function of the magnetic field; $\rho(0,T)$ is the conductivity in zero field and $\rho_s(H,T)$ is the conductivity in transverse field, as defined in Eq. (2).

B. The transverse upper critical field

We defined the upper critical field $H_{c_2}^{\perp}$ at the point where the resistivity is 90% of the normal resistivity: At low temperature there is no serious ambiguity upon the normal resistivity we should use; as shown in Fig. 9 it corresponds to the plateau above the transition and is equivalent to $\rho_0(T)$ defined in the previous section. We notice also that the resistive transition is quite narrow here, so taking 50% of $\rho_0(T)$ instead of 90% hardly changes the values obtained for $H_{c_2}^{\perp}$. Above about 2 K this kind of plateau is missing, due to the unusual magnetoresistance analyzed in Sec. III A (see Figs. 4–6); therefore, to be consistent with this analysis, we have chosen $\rho_0(T)$, determined above, for the normal resistivity.

The temperature dependence of $H_{c_2}^{\perp}$ we obtain this way is displayed in Fig. 10. It is characterized by a continuous increase down to the lowest temperatures (50 mK), which is quite extraordinary. We should emphasize that this positive curvature would be still more pronounced if we take $H_{c_2}^{\perp}$ at 50% of the normal resistivity and also if we take for this a lower value, like for instance the zero-field resistance at a temperature slightly above T_c. To compare our data with that of Lepetit *et al.*,[40] obtained on an early sample whose T_c was only 5.55 K, we present them all on a $h_{\perp}^{*}(t)$ plot, where $t=T/T_c$ and h^* is the critical field normalized by the slope $dH_{c2}/dt)_{t=1}$, in order to minimize the influence of a different purity.[41] In this way we see that the same initial curvature is already present in the first data (inset in Fig. 10).

A positive curvature of the critical-field curve is not very exceptional: it has been observed in many different materials,[42] among which the quasi-1D superconductors, the Chevrel phases and the quasi-2D high-T_c's; however, up to now, this behavior was always followed by the usual low-temperature saturation. Among the explanations proposed a very few could lead to such a delayed saturation and apply to $Tl_2Mo_6Se_6$: One, which has been developed by Gabovich and Shpigel,[43] is based upon a

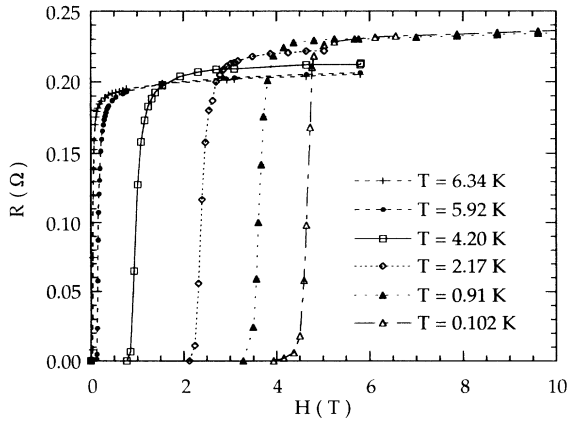

FIG. 9. Typical magnetic-field dependence of the resistivity in the neighborhood of the superconducting transition.

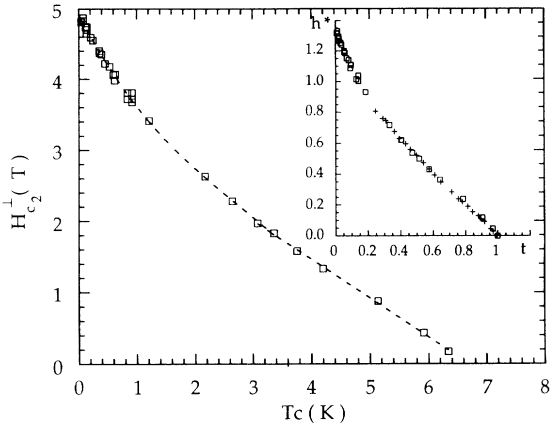

FIG. 10. Temperature dependence of the transverse upper critical field $H_{c_2}^{\perp}$; the insert shows a normalized plot $h_{\perp}^{*}(t)$, where $t=T/T_c$ and h^* is the critical field normalized by $dH_c/dT)_{t=1}$; the crosses are the results of Lepetit *et al.* (Ref. 40).

partial dielectrization of the electron spectrum; it leads also to a saturation when $T\rightarrow 0$, at least as long as the quasiclassical approximation is valid, i.e., until the penetration depth $\lambda(T)$ is much less than the cyclotron radius $r_c=mv_F/eH$. However, $Tl_2Mo_6Se_6$ has macroscopic penetration depths[5] and even if we take for the electron mass and Fermi velocity the values corresponding to the helix band [$v_F\approx 7.3 10^5$ m/s (Ref. 44) and $m\approx m_e$] the above condition is not satisfied ($r_c\approx 4.1$ μm for $H=1$ T). Moreover, when $T\rightarrow 0$ we are faced with another complication which has been raised by Tešanović and co-workers:[45] When $\hbar\omega_c$ becomes greater than k_BT Landau quantization should be taken into account which leads, in the extreme limit where a single Landau level is occupied, to the possibility of a new superconducting state favored by the magnetic field. This quantum limit can be approached if v_F is very small, consequently an enhancement of H_{c_2} in $Tl_2Mo_6Se_6$ could result from this effect if the SC state is determined by a Fermi surface where the CDW (or SDW) instability has induced a partial gapping—as emerges from our analysis of the thermopower and Hall-effect measurements (Sec. II B). Therefore we see that, through the two different mechanisms involved in these models, the dielectrization of the Fermi surface could contribute to the nonsaturation of $H_{c_2}^{\perp}$, especially since this dielectrization seems to be favored also by the magnetic field (Sec. III A).

In quasi-one-dimensional systems another mechanism has been proposed recently,[46] which could lead to the reentrance of the superconducting phase in strong magnetic fields: When ω_c becomes larger than the transverse coupling $t_{\perp}$ the electronic motion can be localized in planes parallel to the magnetic field, which suppresses the orbital frustration of the order parameter. However, in $Tl_2Mo_6Se_6$ the low-temperature value of $t_{\perp}$ seems too large for this mechanism to be effective.

IV. CONCLUSION

From the data we have presented here we can sketch the behavior of the conduction electrons in $Tl_2Mo_6Se_6$ as follows: Coming from the thallium atoms ($\approx 6.3\times 10^{27}/m^3$) they occupy a half-filled (≈ 4.5 eV) quasi-one-dimensional band at room temperature; their scattering cannot be accounted for by the Boltzmann model unless we introduce a strongly energy-dependent scattering time and allow for a temperature dependence of its anisotropy. This unusual scattering could be related to the building up of the CDW (or SDW) instability that emerges timidly below about 80 K. The existence of this instability, which has been revealed unambiguously by our Hall-effect measurements, sheds a new light on the properties of $Tl_2Mo_6Se_6$. In particular it provides a strong confirmation of our low-field magnetization measurements[5] from which we deduced that a very small density of states was left at the Fermi level before the superconducting transition takes place ($D_{EF}\approx 0.5$ states/eV molecule).

A theoretical description of such a frustrated (despite the high uniaxial anisotropy that should favor it) dielectric instability is needed. Bad nesting conditions due to the hexagonal symmetry could make condensation difficult or, conversely, a slight reduction of the band filling or an uniaxial stress could improve nesting. The usual transport properties of $Tl_2Mo_6Se_6$ call for a new microscopic approach of the electron scattering, which could benefit our understanding of many other highly anisotropic materials.

Lowering the temperature below 10 K seems to make $Tl_2Mo_6Se_6$ enter a domain where the CDW (or SDW) instability coexists with the superconducting instability: This phenomenon is not very surprising today because it is reminiscent of what has been observed in many low-dimensional compounds including $NbSe_3$, $Ba(Pb,Bi)O_3$, $Li_{0.9}Mo_6O_{17}$,[48] $(Lu_{1-x}Se_x)_5IrSi_{10}$,[49] and the $(TMTSF)_2X$ Bechgaard salts. However, it is particularly remarkable here because of the very high-T_c/D_{EF} ratio we get and which seems to result from this coexistence. A theoretical treatment of this phenomenon in $Tl_2Mo_6Se_6$ requires more information on the nature of the dielectric instability; this would entail difficult diffraction and NMR experiments as we are dealing here with a small density of electrons which are only partially condensed.

In the same temperature range we have shown that superconducting fluctuations can give rise to a sensible paraconductivity which does not follow current models. The application of a transverse magnetic field tips the scales in favor of the dielectric instability, at least when the temperature is not too low, because below about 1 K it seems that the superconductivity is less and less affected by the field: The positive curvature of the $H_{c_2}^{\perp}(T)$ curve down to 100 mK or less is certainly the most striking behavior of this compound among many other unusual ones. It makes $Tl_2Mo_6Se_6$ a valuable illustration of the recently revisited problem concerning the compatibility of superconductivity with high magnetic fields.[45,46]

ACKNOWLEDGMENTS

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APPENDIX

We take the magnetic field and the current in the z and x directions, respectively.

Within the framework of the Boltzmann model and admitting that the electron motion is coherent (bandlike) in all directions, the Hall coefficient of a metal can be written

$$R_H=-\frac{4\pi^3}{3}\frac{\Im_7}{\Im_1\Im_2} \tag{A1}$$

with

$$\begin{aligned}
\Im_1&=-\int\tau\frac{\partial f_0}{\partial E}\left[\frac{\partial E}{\partial k_x}\right]^2 dV\ ,\\
\Im_2&=-\int\tau\frac{\partial f_0}{\partial E}\left[\frac{\partial E}{\partial k_y}\right]^2 dV\ ,\\
\Im_7&=\int\tau\frac{\partial f_0}{\partial E}\frac{\partial E}{\partial k_x}\Omega\left[\tau\frac{\partial E}{\partial k_y}\right]dV\\
&=-\int\tau\frac{\partial f_0}{\partial E}\frac{\partial E}{\partial k_y}\Omega\left[\tau\frac{\partial E}{\partial k_x}\right]dV\ .
\end{aligned} \tag{A2}$$

We use here the formalism introduced by Davis.[47]

Ω is the operator: $(\partial E/\partial k_y)(\partial/\partial k_x)-(\partial E/\partial k_x)(\partial/\partial k_y)$; these relations also suppose that $E(\mathbf{k})$ and $\tau(\mathbf{k})$ are even functions of k_x, k_y, and k_z. f_0 is the usual Fermi distribution function in zero field and $-e$ is the charge of the electron.

1. Constant-scattering-time approximation

To simplify the description we shall replace the hexagonal structure by a tetragonal one and we consider a quasi-one-dimensional tight-binding band:

$$\begin{aligned}
E(\mathbf{k})&=2\Sigma^{\parallel}t_{\parallel}\cos(k_x c)\\
&\quad+2\Sigma^{\perp}t_{\perp}[\cos(k_y a)+\cos(k_z a)]\ ,
\end{aligned} \tag{A3}$$

where $\Sigma^{\parallel}$ and $\Sigma^{\perp}$ hold for the signs $+$ or $-$; in our case they are both $-$.[2] The current flows in the high conductivity direction c, i.e., $t_{\parallel}\gg t_{\perp}$.

Then $\Im_7$ reduces to

$$\Im_7=-\hbar^2\tau^2\int\frac{\partial f_0}{\partial E}v_y^2\frac{\partial^2 E}{\partial k_x^2}dV \tag{A4}$$

with $v_y=(1/\hbar)(\partial E/\partial k_y)$.

We approximate $\partial f_0/\partial E$ by a δ function at E_F and $|\partial E/\partial\mathbf{k}|$ by $|\partial E/\partial k_x|$, which can be considered as a constant over the Fermi surface. The same approximations being used for $\Im_1$ and $\Im_2$, we obtain for a Brillouin zone limited by $k_y=\pm(\pi/a)$, $k_z=\pm(\pi/a)$, and $k_x=\pm k_c^F$:

$$R_H=\frac{\Sigma^{\parallel}\pi a^2 c}{e\tan(k_c^F c)} \quad \text{in SI units}, \tag{A5}$$

which is often used as

$$R_H=\frac{\Sigma^{\parallel}}{ne}\frac{k_c^F c}{\tan(k_c^F c)},$$

where n is the number of electrons per unit volume. The same expression is obtained for a hexagonal lattice.

According to this formula, if the quasi-1D band is half-filled we have $R_H=0$. The value we measured at room temperature $R_H\approx -4.2\times10^{-10}$ m^3/C would correspond to a band filling of 0.83 electron instead of one per Mo_3Se_3 unit. As discussed in Sec. II B 1 the number of conduction electrons could be only $\approx 0.95/Mo_3Se_3$ but not much lower. However, the approximations used in the derivation of (A5) could easily account for this discrepancy, particularly the constant-scattering-time approximation which is reconsidered below.

2. Anisotropic scattering time

The aim of these calculations is only to show that the anisotropy of the scattering time can sensibly influence the Hall coefficient. As we have no information on what this anisotropy could be we shall take for it a simple analytical form that allows a description of various behaviors and leads to straightforward integrations; we take

$$\tau=\frac{k_y^2+k_z^2}{A^2}+\frac{k_x^2}{B^2}. \tag{A6}$$

Keeping the same other approximations we obtain three contributions for $\Im_7$:

$$\mathcal{H}_1=\hbar^2\Sigma^{\parallel}\int \tau v_y^2\frac{\partial\tau}{\partial k_x}dS,$$

$$\mathcal{H}_2=-\frac{\hbar}{|v_x^F|}\left[\frac{\partial^2 E}{\partial k_x^2}\right]_F\int \tau^2 v_y^2 dS, \tag{A7}$$

$$\mathcal{H}_3=\hbar^2|v_x^F|\int \tau v_y\frac{\partial\tau}{\partial k_y}dS,$$

where v_x^F is the Fermi velocity. Then $\Im_1$ and $\Im_2$ become

$$\Im_1=-\hbar|v_x^F|\int\tau\,dS \quad\text{and}\quad \Im_2=-\frac{\hbar}{|v_x^F|}\int\tau v_y^2 dS. \tag{A8}$$

After integration over the Fermi surface we obtain

$$R_H=-\frac{4\pi}{e}(\Re_1+\Re_2+\Re_3)$$

with

$$\Re_1=\Sigma^{\parallel}\frac{\tau_0 a^2}{4k_c^F\pi^2}\left[\frac{2\tau_0+\beta/A^2a^2}{K^2}\right],$$

$$\Re_2=\frac{\Sigma^{\parallel}a^2c}{8\pi^2\tan(k_c^F c)}\frac{(\alpha/A^4a^4+\beta\tau_0/3a^2A^2+2\tau_0^2)}{K^2}, \tag{A9}$$

$$\Re_3=\Sigma^{\perp}\frac{t_{\parallel}}{t_{\perp}}\frac{c}{2\pi^4}|\sin(k_c^F c)|\frac{(\gamma/A^4a^4+2\pi^2\tau_0/A^2)}{K^2}$$

with

$$K=\tau_0+\frac{2\pi^2}{3a^2A^2};\quad \tau_0=\frac{(k_c^F)^2}{B^2};\quad \alpha=\frac{128\pi^4}{45}-\frac{8\pi^2}{3}+3;$$

$$\beta=4\pi^2-3;\quad \gamma=\tfrac{2}{3}\pi^4+\pi^3-6\pi.$$

Replacing the tetragonal structure by the hexagonal one would certainly change a little the coefficients α, β, and γ.

The typical behavior of R_H as a function of A, given by (A9), is displayed in Fig. 11 for $\tau_0=10^{-13}$ s and $t_{\parallel}/t_{\perp}=100$, together with the three contributions in (A9). For $0.8<k_c^F/k_{1/2}<1$ the k_c^F dependence of R_H can be neglected ($k_{1/2}$ is the k_x value for the half-filled 1D band: $k_{1/2}=\pi/2c$). The behavior of R_H for $\tau_0=10^{-14}$ s is shown in Fig. 12 including also the case where $t_{\parallel}/t_{\perp}=1000$. In Fig. 13, we show that when R_H is not too great it is proportional to $t_{\parallel}/t_{\perp}$ and otherwise only depends on $\tau_{\max}/\tau_0$, $\tau_{\max}$ being the maximum value of τ on the Fermi surface, given according to (A6) by $\tau_{\max}=\tau_0+2\pi^2/a^2A^2$.

We see in this figure that for $t_{\parallel}/t_{\perp}\sim1000$ the Hall coefficient changes from about -4×10^{-10} m^3/C (the room-temperature value) to -10^{-8} m^3/C (the minimum value at ~60 K) by only changing $\tau_{\max}/\tau_0$ from 1.01 to 1.04. Therefore this model shows that a very small variation of the scattering time over the Fermi surface is able to explain a strong temperature dependence of R_H in a quasi-one-dimensional compound.

Moreover, we have to note that this slight variation of τ is obtained by allowing for a very anisotropic **k** dependence as given by Eq. (A6) ($A/B\approx10$ for $\tau_0=10^{-14}$ s).

The scattering time which is involved in the dc conductivity is

$$\tau_\sigma=\frac{1}{\mathcal{A}}\int\tau\,dS,$$

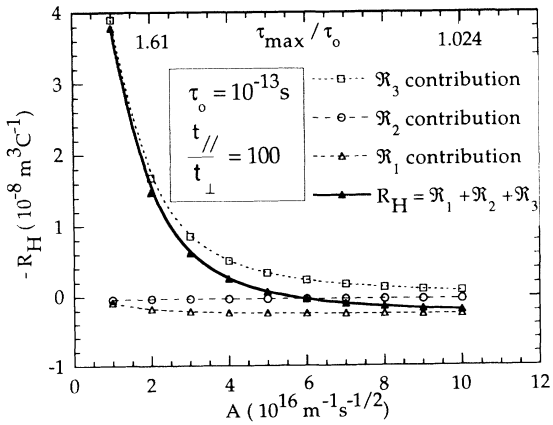

FIG. 11. The dependence of the Hall effect as a function of the A parameter which describe the anisotropy of the scattering time according to Eq. (A6) (solid line); the corresponding values of $\tau_{\max}/\tau_0$ are given on the upper abscissa axis. The contributions $\Re_1$, $\Re_2$, and $\Re_3$ (multiplied by $4\pi/e$) are defined in Eq. (A9) (dotted lines); the parameters used in this calculation are $\tau_0=10^{-13}$ s, $t_{\parallel}=100t_{\perp}$.

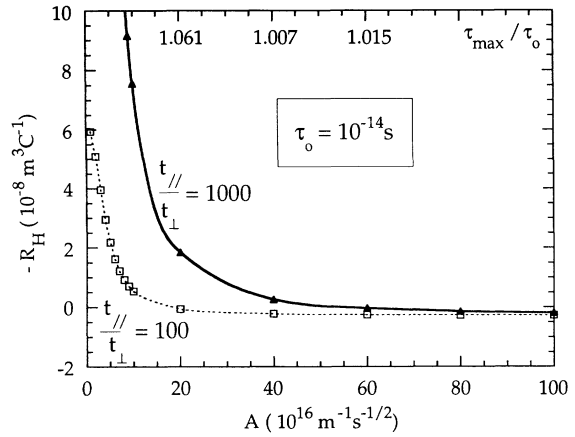

FIG. 12. The dependence of the Hall effect as a function of the A parameter calculated with $\tau_0 = 10^{-14}$ s and $t_\parallel/t_\perp = 100$ (dotted line) or 1000 (solid line).

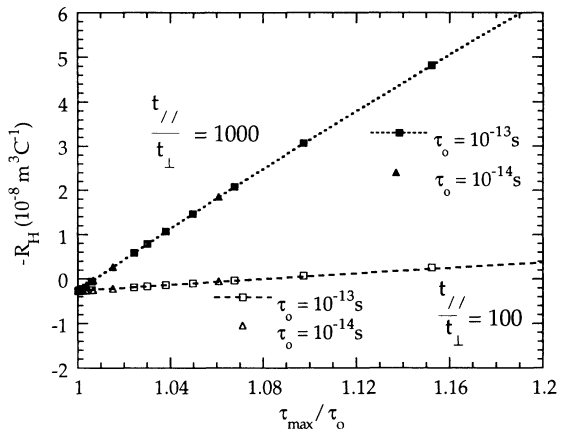

FIG. 13. The dependence of the Hall effect as a function of the anisotropy parameter τ_{max}/τ_0 for $t_\parallel/t_\perp = 100$ (open symbols) or 1000 (solid symbols).

where $\mathcal{A}$ is the area of the Fermi surface; the optical scattering time deduced from the plasma edge is

$$\tau_\sigma = \frac{1}{\mathcal{A}} \frac{\int \tau^2 dS}{\int \tau\, dS} .$$

In our model we obtain

$$\tau_\sigma = 3\tau_{max} - 2\tau_0$$

and

$$\tau_{op} = \frac{1}{5}\left[\frac{38\tau_0^2 - 96\tau_{max}\tau_0 + 63\tau_{max}^2}{3\tau_{max} - 2\tau_0}\right] .$$

For $\tau_{max}/\tau_0 \simeq 1.04$ these scattering times only differ from τ_0 by about 12%, which is quite difficult to detect experimentally.

3. The thermopower

Within the same model we obtain the thermopower from the standard relation

$$S = \frac{-\pi^2 k_B^2 T}{3e}\left[\frac{\partial \log\sigma(E)}{\partial E}\right]_{E_F} \qquad \text{(A10)}$$

with the conductivity $\sigma = (e^2/\pi h^2)\Im_1$.

Straightforward calculations give

$$S = \frac{\pi^2 k_B^2 T}{3e}\left\{\frac{\cos(k_c^F c)}{2t_\parallel \sin^2(k_c^F c)} + \frac{\tau_0}{K(k_c^F c)t_\parallel \sin(k_c^F c)} + \frac{2\pi^2}{3a^2}\frac{1}{KA^3}\left[\frac{\partial A}{\partial E}\right]_{E_F}\right\} .$$

For a nearly half-filled band the first term is negligible, the second one is about

$$S_2 = \frac{\pi^2 k_B^2 T}{3e}\frac{2}{\pi t_\parallel [3(\tau_{max}/\tau_0) - 2]}$$

with $t_\parallel \approx 1$ eV and $\tau_{max}/\tau_0 \approx 1$, this term give $S_2 \approx -5$ μV/K at 300 K. Then the third term is approximately

$$S_3 = \frac{\pi^2 k_B^2 T}{3e} 3\left[\frac{\tau_{max}}{\tau_0} - 1\right]\frac{1}{A}\left[\frac{\partial A}{\partial E}\right]_{E_F} .$$

If the temperature dependence of R_H is due to the variation of τ_{max}/τ_0, this effect will lead to a S_3 contribution which is approximately independent of the temperature. However, to account for the large constant experimental value we need to have $-(1/A)(\partial A/\partial E)_{E_F}$ as large as 150 eV^{-1}. Such a sensitivity of the scattering anisotropy seems very difficult to account for. However, a CDW (or SDW) instability is able to develop in $Tl_2Mo_6Se_6$ and this kind of instability depends critically on E_F: In the temperature range where it gives rise to significant fluctuations it certainly affects very effectively the scattering mechanisms.

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