Large anisotropy in the paramagnetic susceptibility of SrRuO$_3$ films

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By using the extraordinary Hall effect in SrRuO$_3$ films we performed sensitive measurements of the paramagnetic susceptibility in this itinerant ferromagnet, from $T_c$ ($\sim$ 150 K) to 300 K. These measurements, combined with measurements of magnetoresistance, reveal that the susceptibility, which is almost isotropic at 300 K, becomes highly anisotropic as the temperature is lowered, diverging along a single crystallographic direction in the vicinity of $T_c$. The results provide a striking manifestation of the effect of exceptionally large magnetocrystalline anisotropy in the paramagnetic state of a 4$d$ itinerant ferromagnet.

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The coupling of spin to electronic orbitals yields the ubiquitous phenomenon of magnetocrystalline anisotropy (MCA) in ferromagnets [1]. While the manifestation of MCA below $T_c$ in the form of hard and easy axes of magnetization is well studied, the fact that the strength of the MCA decreases with temperature as a high power of the spontaneous magnetization [2] could give the impression that MCA effects above $T_c$ are at most a weak perturbation. Here we show that the MCA has a significant effect in the paramagnetic state of the 4$d$ itinerant ferromagnet SrRuO$_3$ over a wide range of temperatures – not only is the susceptibility diverging along a single axis at $T_c$, but the difference between the susceptibilities along the different crystallographic axes is noticeable (more than 30%) already at $t \equiv (T - T_c)/T_c = 0.5$.

A paramagnetic susceptibility diverging along only one crystallographic direction has been reported previously for bulk specimens of Cu(NH$_4$)$_2$Br$_4$·2H$_2$O [3], but the anisotropy there was found to be only 2% of the exchange integral $J$ (compared to 20% which we find in SrRuO$_3$). Another report refers to two-dimensional cobalt films, where an anisotropy of 5% was measured [4]. In both cases, the temperature range for which the susceptibility was measured is by an order of magnitude smaller (in units of $T_c$) than in our measurements of the three-dimensional SrRuO$_3$ films.

Measuring the paramagnetic susceptibility in films poses a considerable technical challenge due to the combination of small magnetic moment of the film with large background signal from the substrate. We avoided these difficulties by using the extraordinary Hall effect (EHE) whose signal depends on the film internal magnetization and not on the total magnetic moment of the sample. Therefore, the signal does not diminish with decreasing thickness, neither is it affected by the substrate magnetization.

We study high-quality epitaxial films of the itinerant ferromagnet SrRuO$_3$ ($T_c \sim$ 150 K) with thicknesses in the range of 6-150 nm patterned by photolithography for measurements of resistivity and Hall effect. The unit cell is orthorhombic ($a = 5.53$ Å, $b = 5.57$ Å, $c = 7.85$ Å), and the single easy axis of magnetization is roughly in the $b$ direction [5, 6]. The films are grown by reactive electron beam coevaporation [7] on miscut ($\sim$ 2°) SrTiO$_3$ substrates. This technique produces single-phase films with the [110] direction perpendicular to the surface (as was shown by transmission electron microscopy study of films grown in the same apparatus [8]), so that the $b$ direction is at 45° out of the plane of the film.

The transverse electric field $E_H$ in magnetic conductors originates from both the ordinary (or regular) Hall effect (OHE), which depends on the magnetic induction $B$, and the extraordinary (or anomalous) Hall effect (EHE), which depends on the magnetization $M$:

$$E_H = -R_0 J \times B - R_s J \times \mu_0 M,$$

where $J$ is the current density, $R_0$ is the ordinary Hall coefficient related to the carrier density $n$, and $R_s$ is the extraordinary Hall coefficient whose temperature dependence in the ferromagnetic phase of SrRuO$_3$ has been reported in Refs. [5, 6].

In measurements above $T_c$ we found that a significant Hall effect develops even when the magnetic field is applied parallel to the current which flows along the [110] direction. The temperature dependence of this Hall effect resembles the behavior of the induced magnetization (see Fig. 1). These results indicate that the in-plane field generates a significant out-of-plane component of $M$, resulting in a measurable EHE. This implies that the paramagnetic susceptibility of SrRuO$_3$ films is described by an anisotropic tensor.

For quantitative characterization of the susceptibility anisotropy, we measured the Hall effect as a function of field direction at various temperatures. For each temperature above $T_c$, a small-field limit exists, where the magnetization depends linearly on the field and can be fully described in terms of constant susceptibilities $\chi_a$, $\chi_b$, and $\chi_c$.
\(\chi_b\) and \(\chi_c\) along the \(a\), \(b\), and \(c\) crystallographic directions, respectively \((\mu_0 M_a = \chi_b H_a, \text{ etc.})\). An example of measurements in this limit is shown in Fig. 2 where the EHE resistance \(R_{EHE} = \mu_0 R s M_L / t\), where \(t\) is the thickness of the sample) is shown for two different fields at \(T = 153\) K as a function of the angle \(\theta\) (see inset). The solid curve is a fit obtained by assuming certain values of \(\chi_a\) and \(\chi_b\), based on the equation:

\[
R_{EHE}(H, \theta) = \frac{R_s H}{\sqrt{2t}} (\chi_b \cos \theta - \chi_a \sin \theta).
\]

Figure 2 also demonstrates the relatively small magnitude and different angular dependence of the OHE, which was subtracted from the measured signal \([10]\).

The main result of this Letter is presented in Fig. 3, which shows the temperature dependence of the susceptibilities \(\chi_a\) and \(\chi_b\) (multiplied by \(R_s\)). We see that the susceptibility is very anisotropic throughout most of the investigated temperature range. Particularly, \(\chi_b\) exhibits striking divergence at \(T_c\) while \(\chi_a\) changes moderately. The actual divergence of \(\chi_b\) is even stronger than shown in Fig. 3 since \(\chi_b\) was not corrected for the demagnetizing field (because of uncertainty in the value of \(R_s\)); consequently, the apparent susceptibility in our measurement configuration is only \(\chi_b / (1 + \chi_b / 2)\).

Since the \(c\) direction is in the plane of the film, the EHE measurement could not be used to determine \(\chi_c\) (the insensitivity of EHE to a field component in the \(c\) direction was experimentally confirmed). Therefore, measurements of magnetoresistance (MR) \(\Delta \rho = \rho(H) - \rho(0)\) were employed \([11]\). Based on previous \([12]\) and current results (see inset to Fig. 3), \(\Delta \rho \propto -M^2\) (for a constant direction of magnetization). Thus we can infer the susceptibility behavior along \(a\), \(b\), and \(c\) directions by comparing the MR obtained with fields applied along these directions. The results, shown in Fig. 3 clearly indicate that the induced magnetization along the \(b\) direction grows as \(T_c\) is approached much more rapidly than along the \(a\) or \(c\) directions. The divergence here is less pronounced than in Fig. 3 since for fields applied here the magnetization along \(b\) is sub-linear (but using lower fields would not allow obtaining accurate MR data for the \(a\) and \(c\) directions). The temperature dependence of the MR with \(H \parallel c\) is very similar to the MR with
where \( \alpha \) single-site anisotropy or with MCA may be described microscopically by Heisenberg Hamiltonian. The experimental analysis of the critical behavior given in Ref. [13] does not change much as \( T_c \) is approached \( \Delta J = \Delta D/z \), where \( z \) is the number of nearest neighbors.

The anisotropy \( \Delta J \) (or \( \Delta D \)) can be estimated from the susceptibilities in the mean-field region, which are expected to follow the Curie-Weiss \( 1/(T - T^\text{MF}) \) law (with different mean-field transition temperature \( T^\text{MF}_c \) for each direction), if Pauli paramagnetism and diamagnetism can be neglected \[12\]. We cannot fit \( R_s \chi_a \) or \( R_s \chi_b \) as a function of temperature because the temperature dependence of \( R_s \) is unknown. However, the ratio \( \chi_b/\chi_a \) does not depend on \( R_s \), and fitting the data to the expression \( (T - T^\text{MF}_c)/ (T - T^\text{MF}_{c,b}) \) converges to the values \( T^\text{MF}_c = 123 \pm 2 \) K, \( T^\text{MF}_{c,b} = 151 \pm 1 \) K for 165 K < \( T < 300 \) K (see inset in Fig. 4). From these values we find an anisotropy of \( J_b - J_a \approx 0.2 J_{\text{avg}} \) or \( D_b - D_a \approx 0.2 J_z \). This result is almost thickness-independent from 6 to 150 nm (the data presented above are from a 30-nm film).

To examine whether the paramagnetic anisotropy is consistent with the ferromagnetic anisotropy we performed magnetization measurements below \( T_c \). However, noting that the easy axis of the magnetization, which is along the \( b \) direction close to \( T_c \), changes its orientation as the temperature is lowered (by a maximum of 15° at zero temperature) \[21\] and considering that additional factors become significant when the magnetization is large, the most we can expect is an order-of-magnitude agreement between the paramagnetic and the ferromagnetic anisotropy.

Using a SQUID magnetometer which measures the whole magnetization vector we estimated the ferromagnetic anisotropy by measuring the rotation of the \( \langle 101 \rangle \) plane by up to \( \sim 20° \) at \( H = 5 \) T (see Fig. 5) almost without change of magnitude \[22\]. This behavior can be described by an anisotropy energy, \( E_{\text{anis}} = K \sin^2 \theta \), with a weakly-temperature-dependent anisotropy constant \( K \) whose low-temperature value is \( (1.2 \pm 0.1) \times 10^7 \) erg/cm\(^3\).

The large anisotropy constant (compared to \( 5 \times 10^5 \) erg/cm\(^3\) in Fe \[23\], \( 8 \times 10^6 \) erg/cm\(^3\) in Ni \[24\], and \( 4 \times 10^6 \) erg/cm\(^3\) in hcp Co \[25\]) is probably a result of the reduced symmetry (orthorhombic) \[26\] and the large spin-orbit coupling \[27\] through which the spin direction is affected by the crystal structure.

To relate the ferromagnetic anisotropy with Eqs. \[11\] and \[12\], we note that at low temperature the exchange aligns the spins along a single direction, thus the experimental observation that the exchange splitting in SrRuO\(_3\) does not change much as \( T_c \) is approached supports the relevance of such a treatment to SrRuO\(_3\).

Since \( T_c \propto J \), anisotropic exchange results in a different effective \( T_c \) for each spin component. Consequently, only the susceptibility along the direction with the largest \( J \) diverges at the actual \( T_c \) \[18\]. Single-site anisotropy yields the same critical behavior \[18\], with an effective \( J = \Delta D/z \), where \( z \) is the number of nearest neighbors.
ergy cost of magnetization rotation from the $b$ direction toward the $a$ direction by an angle $\theta$ in the case of anisotropic exchange is $\Delta E = zNS^2(J_b - J_a)\sin^2\theta$, where $N$ is the number of spins per unit volume. A similar result is obtained in the case of single-site anisotropy. Considering that the zero-temperature magnetization is 1.4$\mu_B$ per Ru ion, and calculating $J$ according to the relation $J = 3k_BT_c^{MF}/2zS(S+1)$ we obtain $J_b - J_a \approx 0.1J_{avg}$. This result is in reasonable agreement with $J_b - J_a \approx 0.2J_{avg}$ extracted from the anisotropic susceptibility.

Finally we would like to note that while it is common to use the EHE as an indicator of magnetization, it is seldom used for a quantitative analysis of magnetic behavior. In this work we presented a striking example of the latter, by performing sensitive measurements of the zero-field-limit magnetic susceptibility in thin films of SrRuO$_3$, which allowed us to gain microscopic insight into the effect of MCA in the paramagnetic state of a $4d$ itinerant ferromagnet.

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