Spin polarization of magnetoresistive materials by point contact spectroscopy

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In the strive to find a straightforward method for determining the spin polarization, the analysis of the Andreev reflection process in point contact junctions has attracted much interest. However, the prerequisite for an evaluation of the transport spin polarization in this scheme is the existence of elastic (ballistic or diffusive) transport, which cannot be assumed *a priori*. We therefore also include inelastic processes in our analysis and exemplify that thermal effects can have a significant effect on data evaluation. As ferromagnetic samples with a predicted half metallic behavior and comparably low conductivity we used thin films of the double perovskite Sr_2FeMoO_6 and bulk material of the Heusler compound $Co_2Cr_{0.6}Fe_{0.4}Al$.

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I. INTRODUCTION

Devices that exploit the spin polarization for application in magnetic storage systems or sensors are widely studied. Up to now mostly transition metals with spin polarization $P_0 < 0.5$ have been used. The introduction of half metals, i.e., materials with full spin polarization at the Fermi energy, would significantly improve the performance of such devices. In this prospect a wide range of oxide materials such as CrO_2,[1] pyrochlore $Tl_2Mn_2O_7$,[2] and several compounds of the perovskite family like $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.67}Sr_{0.33}MnO_3$ or Sr_2FeMoO_6 have attracted renewed interest. More recently the class of Mn-based Heusler compounds has been addressed. Yet, it is still difficult to gain reliable information on the value of spin polarization of new promising materials. Deducing it from tunneling experiments implies that good expitaxial growth in multilayer thin films has already been achieved. Even then, this method suffers from the influence of nonideal interfaces. Apart from this, it is desirable to measure the spin polarization prior to the time-consuming development of a tunneling device.

One possibility is to study the spin-dependent suppression of Andreev reflection at a transparent metal/superconductor nanocontact, as proposed by Soulen *et al.*[3] and Upadhyay *et al.*[4] The Andreev reflection process occurs when a single electron with energy below the superconducting energy gap Δ propagates from the metal to the superconductor, and vice versa. At the interface it is transformed into a Cooper pair by reflecting a hole with opposite spin and momentum. For the simplest case of a nonmagnetic metal and matching Fermi surfaces the conductance across the interface for applied voltages $eV < \Delta$ is thus doubled. Due to an imbalance of the current transport for up and down spin electrons, referred to as transport spin polarization P, this effect can be suppressed. Thus analyzing measured $dI/dV(V)$ conductance curves allows, in principle, a determination of P. The extracted transport spin polarization P is not uniquely defined. Its magnitude and sign are not nessessarily reflecting the up and down spin density of states P_0, since P not only depends on P_0 but also on the overlap between the Fermi surfaces of the superconductor and the respective minority and majority surfaces of the metal, as well as the transport regime.[5–8]

Experimentally the anomalies in the linear-response conductance are only observable for coherent transport, i.e., in the limit of either ballistic transport $l_e > a$ (Sharvin limit) or diffusive transport $l_i > a > l_e$. These criteria relate the elastic and inelastic mean free paths of the electron l_e and l_i, respectively, to the contact radius a.

II. MODELS

For both regimes of coherent transport theoretical models have been established, that can be used to simulate the experimental data. In the ballistic regime the Blonder-Tinkham-Klapwijk (BTK) theory[9] can be applied. By employing the Bogoliubov equations at the N/S interface Blonder *et al.* have calculated transmission and reflection coefficients A, B, C, and D as a function of energy E and barrier strength Z. In this framework A denotes the probability of the Andreev reflection proccess to occur while B is the coefficient of ordinary reflection, i.e., an electron being scattered back into the metal. D and C give the transmission probability with and without crossing through the Fermi surface. The current across the interface is then determined by the following equation:

$$I_{NS} \propto \int_{-\infty}^{\infty} [f(E-eV)-f(E)][1+A(E)-B(E)]dE, \tag{1}$$

where f denotes the Fermi-Dirac distribution at a certain temperature. The parameters C and D were eliminated due to the conservation of probability $A+B+C+D=1$ and the correlation of the distribution functions for the incoming and outgoing populations of electron and quasiparticle states, respectively.

To include a transport spin polarization, the model has been extended by separating the current in an unpolarized I_u and fully polarized part I_p for which the Andreev reflection probability A is set to zero.[3,10] The ordinary reflection para-

TABLE I. Normalized differential conductance at $T=0$ in different regimes by Mazin *et al.* (Ref. 11), with $F(s)=\cosh^{-1}[(2Z^2+s)/\sqrt{(2Z^2+s)^2-1}]$ and $\beta=V/\sqrt{|\Delta^2-V^2|}$.

	$\lvert E\rvert<\Delta$	$\lvert E\rvert>\Delta$
ballistic unpolarized	$\frac{2(1+\beta^2)}{\beta^2+(1+2Z^2)^2}$	$\frac{2\beta}{1+\beta+2Z^2}$
ballistic polarized	0	$\frac{4\beta}{(1+\beta)^2+4Z^2}$
diffusive unpolarized	$\frac{1+\beta^2}{\beta}\mathrm{Im}[F(-i\beta)-F(i\beta)]$	$2\beta F(\beta)$
diffusive polarized	0	$\beta F[(1+\beta)^2/2-1]$

meter B for the polarized current is thereby changed due to a renormalization of the probabilities.

Yet, the assumption of $A=0$ is only strictly true for the subgap region. Above the gap evanescent Andreev reflection changes the transparency of the interface, as pointed out by Mazin *et al.*[11] Using the findings of Beenakker,[12] who succeeded in expressing the probability of the Andreev process in terms of the normal state transparency, Mazin *et al.* generalized the BTK approach including the evanescent Andreev reflection amplitude in their calculations. In addition they extended the model from the ballistic to the diffusive transport regime by the introduction of a diffusive region larger than the electronic mean free path, which separates the two sides of the N/S contact in addition to the interface.[11] They interpolate intermediate spin polarizations by treating the fully polarized and unpolarized currents as independent conduction channels. In the analysis of ferromagnet/superconductor junctions by Žutić and Valls this splitting is not introduced *a priori* and the conductivity is expressed as a sum of spin-up and spin-down contributions, with spin dependent reflection coefficients.[5] Calculating the conductance in the latter scheme requires detailed knowledge on the investigated system with concern to variables such as incident angles or Fermi surface mismatch. Variations in these variables can lead to qualitatively different spectra. However, our collected data can be compared well only with those simulated spectra in Ref. 5, which include a small Fermi wavevector mismatch. Since these spectra can also be well described by the ansatz of Mazin *et al.* we therefore restrict our analysis to the approximation of matching Fermi surfaces.

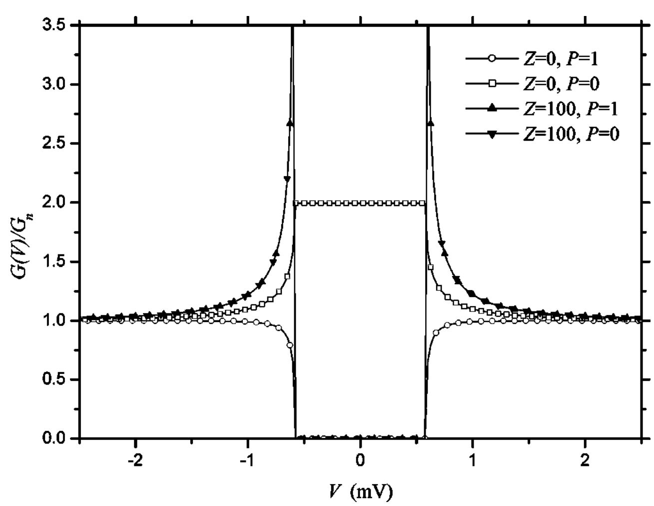

FIG. 1. Calculated normalized conductance at $T=0$ using the model for ballistic transport with the approach by Mazins *et al.* (Ref. 11) for the fully spin polarized conduction channel. The gap value $\Delta=0.58$ of tin is used and different combinations for the two free parameters Z and P are presented.

In this report we want to focus on the experimental results obtained from ferromagnet/s-wave superconductor junctions and take into consideration the possible influence of heating effects. As we will see later, inelastic processes render it impossible to study differences for intermediate polarization in our case. Following the explanations above, all the subsequent data analysis is performed using the formulations by Mazin *et al.* assuming an s-wave superconductor described by BCS laws. The resulting expressions for the second term in the integrand of Eq. (1):

$$G_{NS}|_{T=0}=1+A(E)-B(E), \tag{2}$$

i.e., the normalized differential conductance at $T=0$ are listed in Table I. A numerical integration of these expressions convoluted with the Fermi-Dirac distribution at finite temperature has to be performed. By varying the values of spin polarization P and barrier strengh Z the experimental results can be simulated. In Fig. 1 the normalized differential conductance curves for two extreme cases in the ballistic regime are shown. For small Z the effect of Andreev reflection dominates, whereas for big values of Z a tunneling spectrum results. Introducing a spin polarization dramatically changes the dI/dV characteristics for low Z, while no change is observed for high Z.

Simulations in the diffusive limit are shown in Fig. 2. Though the shapes of the spectra are different, the typical features of the Andreev reflection process can be seen here as well. In the limit of zero barrier and zero spin polarization an electron will enter the superconductor as a Cooper pair but may diffuse back to the normal metal, reducing the zero bias conductance compared to the ballistic case. For full spin polarization only evanescent Andreev reflection contributions

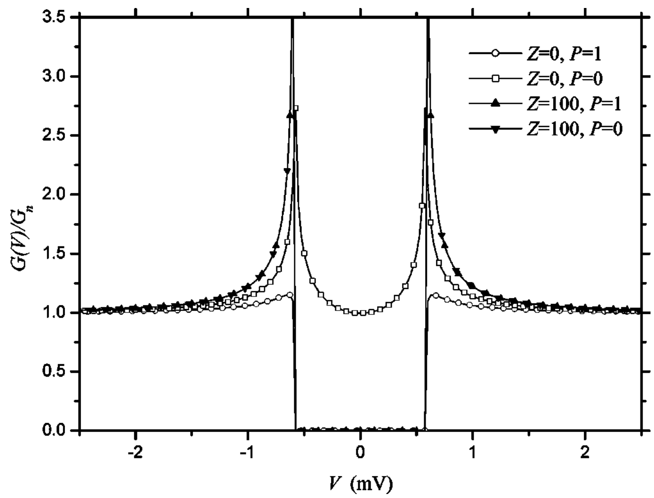

FIG. 2. Calculated normalized conductance at $T=0$ using the model for diffusive transport.

in the subgap region are allowed, and thus the spectra exhibit a strong dependence on the spin polarization. Studying transparent metal/superconductor junctions in the ballistic or diffusive regime therefore should in theory be a decisive method.

Experimentally the limit of ballistic transport can be attained for good conductors especially $3d$ metals in contact with a BCS superconductor. However, for a large number of promising materials, amongst them most metallic oxides, the specific resistivities observed are magnitudes larger. In the case of the widely studied manganites specific resistivities around 100 $\mu\Omega$ cm are observed for single crystals and thin films.[13,14] For Sr_2FeMoO_6 single crystals $\rho\approx$ 200 $\mu\Omega$ cm is found,[15,16] whereas for thin films $\rho\approx$ 500 $\mu\Omega$ cm (Ref. 17) is achieved. Therefore, contacts with such materials are expected to exhibit either diffusive or thermal transport. Due to the strong dependence of the transport regime on contact radius and specific resistivity, i.e., mean free path, a crucial point for the analysis is the detemination of these quantities for each contact. From the bulk conductivity the specific resistivity and thus the mean free path can be estimated. By employing Wexler's formula[18]

$$R_K \approx \frac{4}{3\pi}\frac{\rho l}{a^2} + \frac{\rho}{2a}, \tag{3}$$

which describes the contact resistance R_K with an expression depending on the specific resistivity ρ, the mean free path l and the contact radius a, an approximation for a can be derived. Yet this estimate is very rough for a couple of reasons. For example, Eq. (3) is only true for a perfectly transparent junction, i.e., the influence of a barrier on the contact resistance is not taken into account and also the bulk specific resistivity can be changed at the junction due to the influence of the surface. To improve the approximation the fraction $R_M=\rho/2a$ was identified in previous studies by comparing the T-dependent resistivity of the probed material with the T dependence of R_K.[19] In the case of Sr_2FeMoO_6 and $Co_2Cr_{0.6}Fe_{0.4}Al$ the T dependence in the relevant temperature range is small, so this method cannot be applied here.

Without the possibility to deduce a reliable value for the contact radius a directly from the measured quantities we have to rely on the power of the models and show that the spectra can be interpreted uniquely within one of these pictures. In the discussion of our results we will therefore oppose various approaches.

III. EXPERIMENTAL SETUP AND SAMPLES

We studied the Andreev reflection by point contact spectroscopy (PCAR) on metallic Sr_2FeMoO_6 thin films and polycrystalline $Co_2Cr_{0.6}Fe_{0.4}Al$ with a sharp tin wire $T_C=3.7$ K. The preparation of these samples has been described elsewhere.[17,20] The contact was established by turning a micrometer screw which is driving a lever that moves the wire towards the sample. By a standard four-probe method, I and V across the junction were measured. The differential conductance dI/dV was determined directly by ac lock-in technique at a frequency of 1.7 kHz and a modulation current equal to the stepwidth. The spectra were measured for different temperatures from 1.6 to 4.2 K. We were thus able to take data in the superconducting as well as normal conducting state of tin.

Due to band structure calculations[21] that predict a spin polarization near $P=1$ and its high Curie temperature $T_C=420$ K, Sr_2FeMoO_6 is a promising candidate for magnetoresistive applications. But the half metallic nature of this material has not been confirmed by experimental studies yet. Some evidences of a high spin polarization have been seen in transport measurements of polycrystalline samples, where the observed low temperature MR of about 30% has been attributed to spin-polarized tunneling between adjacent grains.[22]

From the class of intermetallic Heusler compounds we studied $Co_2Cr_{0.6}Fe_{0.4}Al$. On the basis of band structure calculations the composition was optimized in order to obtain full spin polarization in conjunction with a van Hove singularity at the Fermi energy in the majority spin channel. For this material a Curie temperature of 650 K was found and large negative magnetoresistive effects up to 30% at room temperature have been observed in polycrystalline powder solids. As in the case of Sr_2FeMoO_6 it is of great interest to determine the value of spin polarization in this compound to support its potential as a magnetoresistance material.

IV. EXPERIMENTAL SPECTRA AND SIMULATIONS

Figure 3 shows a series of PCAR measurements of one Sr_2FeMoO_6-Sn contact at different temperatures. The contact resistance in this case was 25 Ω. Measurements up to contact resistances of 250 Ω were performed yielding similar results. The specific resistivity measured at similar Sr_2FeMoO_6 thin film samples was of the order of 500 $\mu\Omega$ cm. As a model for this highly resistive material only the diffusive approach comes into question. Simply fitting the depth of the dip in the conductance by adjusting the parameters P and Z does not lead to a satisfying description

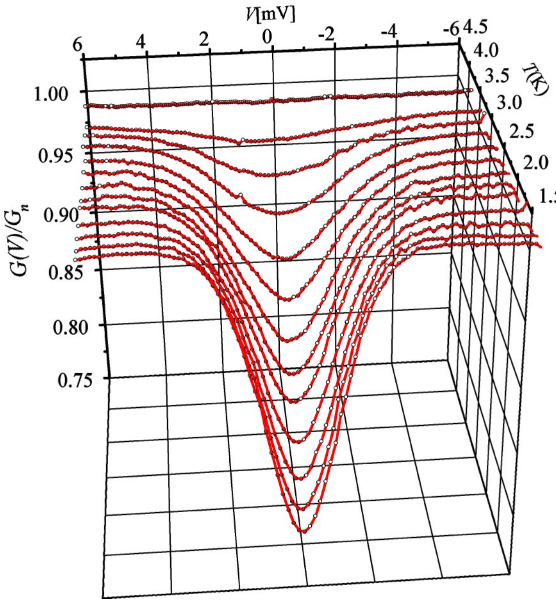

FIG. 3. Measured normalized differential conductance vs. bias voltage for a Sr_2FeMoO_6-Sn contact at different temperatures.

of the data. To attribute for the broadening of the spectra in this approach a serial resistance R_s must be introduced. In addition a fraction of the ohmic response is accounted for by allowing a parallel conductivity G_p that does not contribute to the dI/dV anomalies. By adjusting these two parameters a reasonable approximation of the measured data can be obtained if a high spin polarization P is assumed. For a measurement at 1.8 K (see Fig. 4) the best agreement with the experiment was achieved for $R_s/R_k=2$, $G_p/G_n=3.25$, $Z=0$ and $P=0.98$ where R_k denotes the contact resistance and G_n the normal state conductivity. In comparison to this a simulation is shown that has been performed with the same correction parameters but for $P=0$ and a barrier strength $Z=100$ to match the depth of the minimum. It is clear that in this approach a high transport spin polarization is needed to

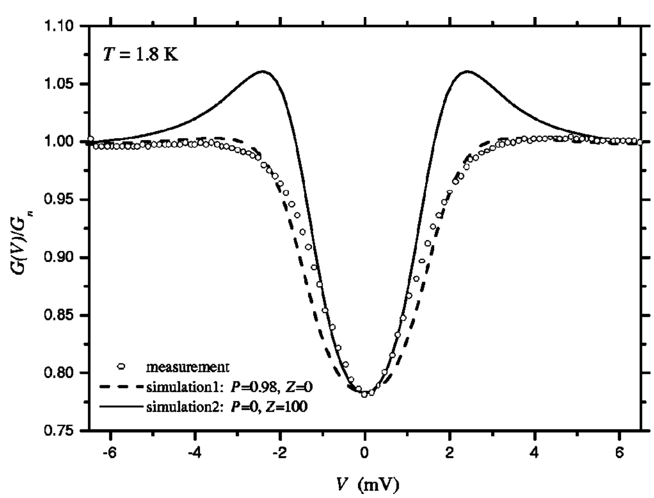

FIG. 4. Experimental data at $T=1.8$ K. The lines are fits with the diffusive transport model for different values of Z and P as indicated in the figure.

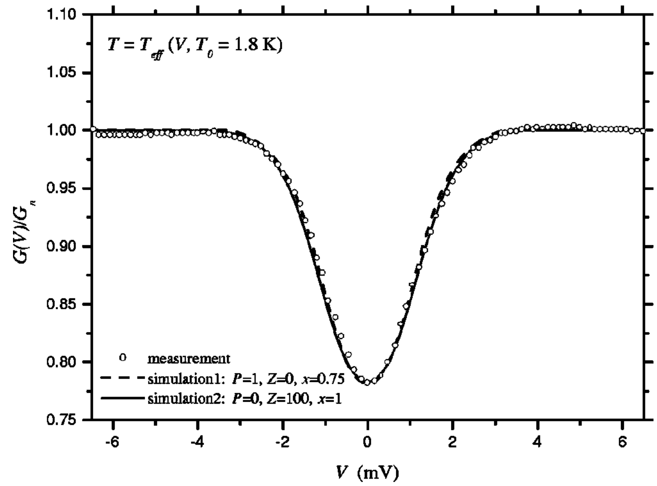

FIG. 5. Experimental data at $T=1.8$ K. The lines are fits with the diffusive transport model that has been extended by the introduction of an effective temperature T_{eff}. The critical temperature $T_{eff}=T_c$ is reached for a voltage of 3.2 mV (3.7 mV) in simulation 1 (simulation 2), i.e., outside the region of nonlinear response.

fit the data. Yet the V-shape of the measured curves are not reproduced well by the simulation. Apart from this, the question how the correction parameters can be interpreted has to be brought up.

The impossibility to measure the potential exactly at the tip position can cause a contribution of the bulk resistivity to the measured voltage for a highly resistive material. This motivates the parameter R_s. In addition a possible contribution of thermal transport has not been discussed up to now. We thus have to take into consideration that the electrons can loose coherence by scattering inelastically. Therefore, they do not contribute to the energy conserving processes discussed by BTK, and we include them with the parameter G_p in the simulation. Another consequence is that the dissipation of energy in the contact region will cause local heating effects. For the problem of RI^2 heat that is generated by a current in the constriction a classical theory[23] has been developed in the limit of thermal transport. It can be used in the present case to calculate the effective temperature in a steady state at the contact region:

$$T_{eff}=\sqrt{T_0^2+\frac{U^2}{4L}}. \tag{4}$$

It depends on the fraction of the voltage drop $U=xV$ that leads to heating of the constriction and the Lorentz number L determining the heat conduction. The temperature measured far away from the contact $T_0=T(V=0)$ is then replaced by Eq. (4) in the simulation, and the gap is varied as a function of T_{eff} according to the BCS theory. With these modifications the V-shape of the measured curves can be reproduced very well. Due to temperature rise for increasing bias voltages V the typical gap structures become heavily smeared. This effect is so strong that it can lead to a total suppression of the characteristical peaks in the conductivity even for $P=0$, $Z>0$, though the effective temperature is below the critical temperature within the nonlinear region. In Fig. 5 it

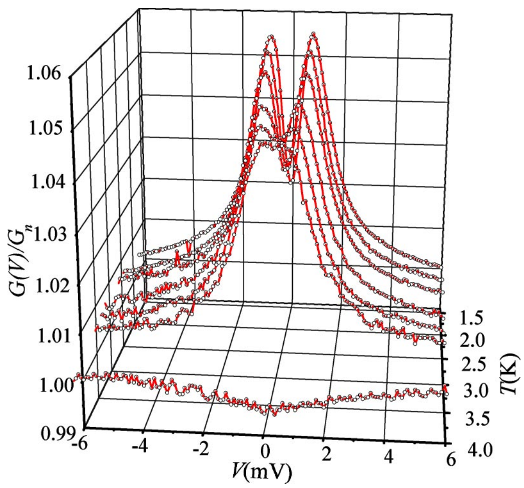

FIG. 6. Measured normalized differential conductance vs. bias voltage for a $Co_2Cr_{0.6}Fe_{0.4}$Al-Sn contact at different temperatures.

becomes obvious that now both cases—namely, no barrier, full spin polarization, and strong barrier, no spin polarization—are equally suited to describe the data. In view of the simplifications of the model tiny differences in the simulation cannot be considered to be decisive. Therefore, no conclusion can be drawn about the value of P with this kind of experiment in the case of a highly resistive material such as Sr_2FeMoO_6.

In comparison to the Sr_2FeMoO_6 samples the studied intermetallic Heusler compound $Co_2Cr_{0.6}Fe_{0.4}Al$ has a lower specific resistivity of $\rho = 90\ \mu\Omega$ cm. Since transport measurements of these polycrystalline samples exhibit a large contribution of carrier scattering at grain boundaries,[20] the obtained value of ρ does not nessessarily reflect the specific resistivity of individual crystalline grains which we analyze by PCAR.

A series of spectra at variable temperature is presented in Fig. 6. The contact resistances in these experiments varied between 1 and 20 Ω. In contrast to the previous measurements on Sr_2FeMoO_6 only a small broadening of the spectra is observed. This reflects a smaller serial resistance due to the higher conductivity as compared to the double perovskite.

Simulating the data with the ballistic model for fixed temperatures (as an example, see Fig. 7) yields $P = 0.49 \pm 0.01$ and $Z = 0$. However, it is possible that the assumption of ballistic transport is not justified and heating occurs. In this case the diffusive limit is appropriate. Following the diffusive approach, as discussed above, leads to $P = 0.06$ and $Z = 0$ instead (see Fig. 8). Thus again the value of the transport spin polarization depends strongly on the ansatz chosen for simulation of the spectra. Since the quality of the simulations is not significantly different in both cases a non-ambigous determination is not possible.

The low value observed in the latter case is smaller than expected from the observation of a strong ferromagnetism and a large magnetoresistive effect in this Heusler compound. Since the PCAR method is sensitive to a thin surface layer determined by the mean free path of the conduction electrons, a degraded surface layer can be the reason for

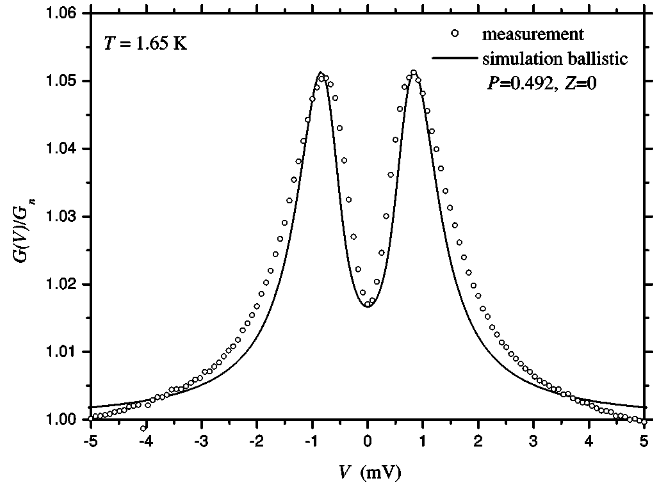

FIG. 7. Experimental data at $T = 1.65$ K with a simulation in the ballistic limit. A small contribution of parallel conductance $G_p/G_n = 0.1$ and a serial resistance $R_s/R_k = 0.8$ were used to simulate the data.

these discepancies. Yet it is not clear up to now if this has to be attributed to intrinsic material properties such as the existence of surface states destroying the spin polarization in a thin layer or if it is caused by extrinsic changes of the surface such as oxidation or adsorption.

V. CONCLUSION

In order to investigate the transport spin polarization we realized point contacts between a superconducting tip and a ferromagnetic material. We observed dI/dV anomalies commonly attributed to coherent transport and simulated the measured spectra using existing models for the suppression of Andreev reflection by spin polarization. In these models the temperature is a fixed parameter. However, inelastic processes can lead to a temperature increase in the contact region. Using a classical model describing the temperature rise

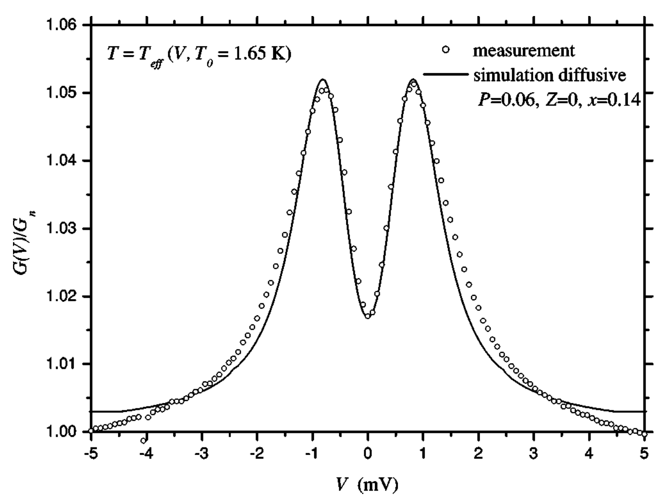

FIG. 8. Experimental data at $T = 1.65$ K with a simulation in the diffusive limit for T_{eff}. The critical temperature $T_{eff} = T_c$ is reached for a voltage of 4.5 mV.

in a small constriction we introduced an effective temperature in the simulations. This effective temperature determines the quasiparticle distribution function and the BCS value of the superconducting gap. With these modifications we could simulate the spectra with much smaller values of the transport spin polarization.

It has been shown that for Sr_2FeMoO_6 the spectra are most likely dominated by thermal transport due to its high specific resistivity. In this case it is impossible to decide whether the observed dI/dV characteristics are caused by a fraction of coherent transport exhibiting the effect of Andreev reflection suppression or just the result of a strongly broadened spectrum dominated by electron tunneling at the effective barrier Z. For $Co_2Cr_{0.6}Fe_{0.4}Al$ the dI/dV anomalies can be clearly attributed to coherent transport. Here the ballistic and diffusive model yield a comparable description of the data but the different simulations again lead to incompatible values of the tansport spin polarization. To justify the use of one approach further studies are needed for the Heusler compounds, especially with respect to mean free path of the charge carriers and surface effects.

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