Exchange Model of Zero-Bias Tunneling Anomalies*†

JOEL A. APPELBAUM‡
Department of Physics and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois
(Received 31 August 1966)

An exchange model for zero-bias tunneling anomalies previously proposed by the author is examined in greater detail. The tunneling Hamiltonian is derived microscopically and its connection with the one proposed by Anderson is indicated. The interference scattering derived from the model is shown to be capable of explaining the magnitude and the temperature T and voltage V dependence of the anomalous conductance $G(V, T)$ found by Wyatt and by Rowell and Shen in A–(oxide A)–B junctions. Here A is a transition metal, such as Ta or Nb, and B a simple metal, such as Al. (Both metals are always in their normal state.) In addition, the dependence of $G(V, T)$ on magnetic field H is studied in detail. Finally, the interpolated forms for $G(V, T, H)$ previously given are replaced by more exact numerically evaluated curves.

I. INTRODUCTION

ANOMALOUS behavior centered at zero-voltage bias has been observed in the I-V characteristics of a number of tunnel junctions. This behavior was first identified by Hall, Racette, and Ehrenreich[1] in their study of p-n tunnel junctions composed of III-V compounds. These semiconductors exhibited a dip in the conductance centered on zero bias. The dip varied with dopant, concentration, temperature, and the III-V semiconductor used. Studies of p-n junctions composed of Si and Ge were later performed by Logan and Rowell,[2] who found a peak in the conductance for large dopant concentrations and a dip at low dopant concentration. They found that the conductance peak at zero voltage varied with temperature as $\ln(k_BT/E_0)$ and that away from zero voltage the conductance peak varied as $\ln[(k_BT+|eV|)/E_0]$. Further studies of p-n tunnel junctions of the III-V type and those composed of lead salts by Williams and Shewchun[3] found different types of anomalous behavior, some of which could be interpreted as logarithmic anomalies in the resistance.

Anomalies not restricted to semiconductor junctions were first observed by Wyatt[4] in tunnel junctions composed of normal metals separated by oxide barriers. The anomalies Wyatt found were peaks in the conductance with logarithmic temperature and voltage dependence similar to those found by Logan and Rowell. Recently Rowell and Shen[5] have published an extensive table of normal-metal tunnel junctions which exhibit similar anomalous conductance peaks of widely varying size. In addition, they have found enormous anomalous behavior in tunnel junctions composed of Cr which is best exhibited as a peak in the resistance. In the case of Cr the anomaly is so large as to completely obliterate any background that might be present; traces of the anomaly persisted even to room temperatures. In all other cases the anomalies were observable only in the temperature region $T<10$°K. Anomalies as large as a factor of 10 change in the resistance were reported by Shewchun and Williams for the p-n junctions, while for normal-metal junctions the effect varied from 20% to less than 1%.

A number of theoretical attempts have been made at explaining the anomalies in the p-n tunnel junctions. The original interpretation[1] of the III-V tunnel junctions attributed the anomaly to the polar interaction between the tunneling electron and optical phonons. Various other attempts[6] to attribute the anomaly to structure in the density of states caused by an electron-phonon interaction have been proposed. All these mechanisms have been extensively analyzed recently by Mahan and Duke,[7] who concluded that proper treatment of screening removes the singularities found in the density of states in previous calculations. They also go on to invalidate the original polaron-formation argument advanced by Hall, Racette, and Ehrenreich.

For the normal-metal junctions the original explanation offered by Wyatt was that the anomaly was due to a logarithmic singularity in the density of states of the transition metals used as one of the components of the junction. No microscopic explanation was advanced, however, for this assumption. Kim[8] has proposed an explanation based on a mechanism whereby conduction electrons spin-flip-scatter from one side of the junction to the other, with the spin recoil taken up by conduction electrons on either side of the junction. He finds that anomalies with the correct voltage

* This work was supported in part by the National Aeronautics and Space Administration, Grant No. NsG-352.
† Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.
‡ National Aeronautics and Space Administration, Predoctoral Fellow. Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.
[1] R. N. Hall, J. H. Racette, and H. Ehrenreich, Phys. Rev. Letters 4, 456 (1960); R. N. Hall, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 193.
[2] R. A. Logan and J. M. Rowell, Phys. Rev. Letters 13, 404 (1964).
[3] J. Shewchun and R. M. Williams, Phys. Rev. Letters 15, 160 (1965); R. M. Williams and J. Shewchun, *ibid.* 14, 824 (1965).
[4] A. F. G. Wyatt, Phys. Rev. Letters 13, 401 (1964).
[5] J. M. Rowell and L. Y. L. Shen, Phys. Rev. Letters 17, 15 (1966).
[6] L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela 5, 1411 (1963) [English transl.: Soviet Phys.—Solid State 5, 1026 (1963)].
[7] G. D. Mahan and C. B. Duke, Phys. Rev. 149, 705 (1966).
[8] D. J. Kim, Phys. Letters 18, 215 (1965).

and temperature dependence first appear in fourth order in the tunneling coupling constant. Such fourth-order terms appear to be too small to account for the observed anomalies.

Furthermore, the fact that the anomalies first appear in fourth order implies that the *relative* size of the anomaly compared to that of the background conductance (second order) should change with oxide barrier thickness in the same way as the background conductance does. In fact, what has been experimentally observed[9] is that the relative size of the anomaly compared to background undergoes no appreciable change even though the background conductance varies by two orders of magnitude.

An explanation based on spin-flip scattering from localized impurities has been advanced by Suhl[10] independent of the work of Appelbaum[11] and Anderson.[12] The Hamiltonian assumed by Suhl contains only a term involving the spin-flip transmission of an electron across the junction, and so omits interference terms depending on spin-flip reflection as well. Suhl obtains an anomalous term in the conductance which goes as $(\ln T)^2$ at zero voltage. No detailed calculation of the voltage dependence of the conductance is performed but Suhl estimates that the anomaly should have a voltage-bias width the order of k_BT. These predictions appear to be in disagreement with the temperature- and voltage-dependence studies of Wyatt and Rowell and Shen.

The explanation advanced by the author[11] and the subsequent analysis of the model by Anderson[12] were restricted to those anomalies found in normal-metal junctions of the type first studied by Wyatt. In this paper the same restriction will be assumed to apply, although the relevance of exchange scattering to *p-n*-junction anomalies is discussed briefly.

In Sec. II we will describe the model assumed for the normal-metal tunneling junctions. In Sec. III a model Hamiltonian is derived. The conductance is derived from the model Hamiltonian in Sec. IV. Section V contains a discussion of the results of Sec. IV.

II. A MODEL FOR NORMAL-METAL TUNNEL JUNCTIONS

The tunnel junctions to which we restrict ourselves are A–(oxide A)–B junctions. Metal A is usually a transition metal such as Ta and Nb and metal B is a nontransition metal such as Al, Pb, Ag. However, B–(oxide B)–B junctions, where B is either Pb or Sn, have also shown anomalies in the conductance. The metals are always kept in their normal states. When temperature studies below their superconducting transition temperature were done, magnetic fields large enough to quench the superconductivity were applied.

The nature of the interfaces between A and A oxide and that between A oxide and B is inadequately understood at present. We shall assume that associated with these interfaces are localized paramagnetic states. These localized magnetic states may arise from transition-metal impurities deposited in the oxidation process or, quite possibly, interstitial atoms of the transition metal which lie in the oxide near the metal-oxide interface. We shall assume these localized states have a concentration N_a per unit area[13] on the metal–metal-oxide interface and that the conduction electrons are exchange coupled to these paramagnetic states. Then some of the current across the junction proceeds via exchange scattering off these localized magnetic states. With this model we will be able to reproduce the observed temperature, voltage, and magnetic field dependence of the anomalous conductance, as well as show that the effect can be of the right order of magnitude to agree with the observed size of the anomalies.

At this point the question arises as to the possible applicability of this model to *p-n* junctions. It is well known that paramagnetic impurities (and presumably paramagnetic complexes in the "impurity-band" limit) exist in *p-n* tunnel junctions. These will lead to strongly temperature-dependent terms in the amplitude for the scattering of conduction electrons off these paramagnetic sites.

For a proper treatment of *p-n* junctions within this model it would be necessary to consider the concentration dependence of the paramagnetic centers.[14] In addition, a multiple scattering analysis would be necessary, in which the mean free path for exchange scattering was compared carefully to that of normal scattering. These steps lie beyond the scope of the present paper.

III. MODEL HAMILTONIAN

The purpose of this section will be to derive the tunneling Hamiltonian proposed previously by the author starting from the physical model described in Sec. IV. The results reported here are essentially a simple application of the ideas first used by Cohen, Phillips, and Falicov[15] and then put on firm theoretical ground by Prange.[16] We consider an idealized junction as shown in Fig. 1. What Prange has established theo-

[9] L. Y. L. Shen (private communication).

[10] H. Suhl, Lectures presented at the 1966 International School of Physics "Enrico Fermi," 1966, Varenna, Italy (unpublished).

[11] J. Appelbaum, Phys. Rev. Letters **17**, 91 (1966).

[12] P. W. Anderson, Phys. Rev. Letters **17**, 95 (1966).

[13] We assume throughout that metals A and B are of unit dimensions, so that N_a also equals the total number of impurities, and the current density j is identical to the current.

[14] Some work on the formation of localized moments in degenerate impurity bands of a semiconductor has been done by Y. Toyozawa, J. Phys. Soc. Japan **17**, 986 (1962).

[15] M. H. Cohen, L. M. Falicov, and J. C. Phillips, Phys. Rev. Letters **8**, 316 (1962); in *Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962* (Butterworths Science Publications Ltd., London, 1962), p. 178.

[16] R. E. Prange, Phys. Rev. **131**, 1083 (1963).

retically, and what the success of these methods in the field of superconducting junctions has demonstrated, is that if we wish to calculate the current flowing to lowest order in the electron coupling constant we may construct the second-quantized Hamiltonian for the system by the following procedure. If the Hamiltonian is written as

$$\mathcal{H}=\sum_i \frac{p_i^2}{2m}+\sum_i V(\mathbf{x}_i)+\tfrac{1}{2}\sum_{i\neq j} W(\mathbf{x}_i-\mathbf{x}_j), \tag{1}$$

in second-quantized form it becomes

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_I, \tag{2a}$$

$$\mathcal{H}_0=\int \psi^*(\mathbf{x})\left(\frac{p^2}{2m}+V(\mathbf{x})\right)\psi(\mathbf{x})d^3x, \tag{2b}$$

$$\mathcal{H}_I=\frac{1}{2}\int \psi^*(\mathbf{x})\psi^*(\mathbf{x}')W(\mathbf{x}-\mathbf{x}')\psi(\mathbf{x}')\psi(\mathbf{x})d^3xd^3x', \tag{2c}$$

where

$$\psi(\mathbf{x})=\sum_i a_i\psi_i{}^a(\mathbf{x})+\sum_i b_i\psi_i{}^b(\mathbf{x}), \tag{3a}$$

$$\psi^*(\mathbf{x})=\sum_i a_i{}^*\psi_i{}^{a*}(\mathbf{x})+\sum b_i{}^*\psi_i{}^{b*}(\mathbf{x}). \tag{3b}$$

The $\psi_i{}^a(\mathbf{x})$ are a complete set of states in the region a of Fig. 1, the $\psi_i{}^b(\mathbf{x})$ are a complete set of states for region b, and an asterisk is used for the Hermitian conjugate. We assume that a_i and b_i obey the usual commutation relations among themselves and anticommute with each other. The above prescription would require no special justification except for the difficulties introduced by the nonorthogonality of the states $\{\psi_i{}^a\}$ and $\{\psi_i{}^b\}$ due to their overlap in region $(-x,x)$ (see Fig. 1). This nonorthogonality requires that we treat $W(\mathbf{x}-\mathbf{x}')$ in (2c) as a two-body pseudopotential.[16] The use of (2) to calculate the current beyond second order in the tunneling coupling constant is generally of doubtful validity. The states of interest, $\{\psi_i{}^a(\mathbf{x})\}$ and $\{\psi_i{}^b(\mathbf{x})\}$, are the conduction electron states $\{\varphi_{\mathbf{k}\sigma}{}^a(\mathbf{x})\}$ and $\{\varphi_{\mathbf{k}\sigma}{}^b(\mathbf{x})\}$ on sides a and b, respectively, along with the states $\{\varphi_{d\sigma}{}^a(\mathbf{x}-\mathbf{R}_n)\}$, of the localized electrons. We assume for simplicity that the localized state is spin-degenerate but orbitally nondegenerate. It describes a localized electron centered at coordinates $\mathbf{R}_n$, with the $\mathbf{R}_n$'s confined to a narrow region near the A–(oxide A) interface. In deriving the tunneling Hamiltonian we further assume there is only one localized state. This assumption will be valid if the density N_a of localized states is small—more precisely, if their spacing is large compared to a lattice spacing, and if magnetic interactions between impurities can be neglected.

We obtain for $\psi(\mathbf{x})$

$$\psi(\mathbf{x})=\sum_{\mathbf{k}1\sigma} a_{\mathbf{k}\sigma}\varphi_{\mathbf{k}\sigma}{}^a(\mathbf{x})+\sum_{\mathbf{k}',\sigma'} b_{\mathbf{k}'\sigma'}\varphi_{\mathbf{k}'\sigma'}{}^b(\mathbf{x})+\sum_\sigma d_\sigma\varphi_{d\sigma}(\mathbf{x}), \tag{4}$$

where $a_{\mathbf{k}\sigma}$ and $b_{\mathbf{k}\sigma}$ are destruction operators for an electron with momentum $\mathbf{k}$ and spin σ on side a and b, respectively, and d_σ is the destruction operator for an electron in a localized state. When $\psi(\mathbf{x})$ and $\psi^*(\mathbf{x})$ are substituted into (2), in which we have taken $W(\mathbf{x}-\mathbf{x}')$ as the appropriate electron-electron interaction, we obtain a Hamiltonian of the following form:

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_3+\mathcal{H}_4+\cdots, \tag{5}$$

where

$$\mathcal{H}_1=\sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}\sigma}{}^a a_{\mathbf{k}\sigma}{}^* a_{\mathbf{k}\sigma}+\sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}\sigma}{}^b b_{\mathbf{k}\sigma}{}^* b_{\mathbf{k}\sigma}. \tag{6}$$

This is just the single-particle conduction-electron energies. The Coulomb interaction among conduction electrons solely on one side or the other is dropped, or better still, taken into the single-particle energies by treating $a_{\mathbf{k}\sigma}$ and $b_{\mathbf{k}\sigma}$ as quasiparticle operators.

$$\mathcal{H}_2=\sum_{\mathbf{k},\mathbf{k}',\sigma}(T_{\mathbf{k}\mathbf{k}'}a_{\mathbf{k}\sigma}{}^* b_{\mathbf{k}'\sigma}+T_{\mathbf{k}'\mathbf{k}}b_{\mathbf{k}'\sigma}{}^* a_{\mathbf{k}\sigma}) \tag{7a}$$

$$+\sum_{\mathbf{k},\sigma} T_{\mathbf{k}d}{}^a(a_{\mathbf{k}\sigma}{}^* d_\sigma+d_\sigma{}^* a_{\mathbf{k}\sigma}) \tag{7b}$$

$$+\sum_{\mathbf{k},\sigma} T_{\mathbf{k}d}{}^b(b_{\mathbf{k}\sigma}{}^* d_\sigma+d_\sigma{}^* b_{\mathbf{k}\sigma}). \tag{7c}$$

The above terms arise from single-particle terms in the Hamiltonian. The first term is due to the direct overlap of the conduction-electron states on sides a and b as they tail into the barrier. This term is what is usually considered responsible for the current in a "normal" tunneling junction. The second and third terms are due to the overlap of the localized d states with the conduction electrons on the a and b sides, respectively.

$$\mathcal{H}_3=\sum_\sigma E_d n_\sigma+U n_\sigma n_{-\sigma}, \tag{8}$$

where U is the direct Coulomb integral between the localized electrons, E_d is the appropriate single-particle energies for the localized electrons and $n_\sigma=d_\sigma{}^* d_\sigma$.

Terms involving the product of four conduction-electron operators not all from the same side of the junction are grouped in $\mathcal{H}_4$. Among these terms are those considered by Kim.[8]

Terms involving the product of four operators for conduction electrons on side a and the localized electrons are contained in $\mathcal{H}_5$. The term of most interest to us is the exchange-scattering term:

$$\sum_{\substack{\mathbf{k},\mathbf{k}'\\ \sigma,\sigma'}} W_{d\mathbf{k};d\mathbf{k}'}d_\sigma{}^* a_{\mathbf{k}\sigma'}{}^* d_{\sigma'}a_{\mathbf{k}'\sigma}. \tag{9}$$

In all the remaining terms we factorize the two-body operators, and retain only terms of the form

$$\sum V_{\mathbf{k}d}{}^a(d_\sigma{}^* a_{\mathbf{k}\sigma}+a_{\mathbf{k}\sigma}{}^* d_\sigma). \tag{10}$$

This is the procedure followed by Anderson when dis-

cussing localized magnetic states in metals [Anderson[17] disregards the exchange interaction (9), retaining only (10)].

In $\mathcal{H}_6$ there are terms involving the product of four operators for conduction electrons on side b and the localized state. Since the coupling between electrons on side b and the localized electron is very small we retain only a term which is first order in this coupling, the product of three electron operators for side b and one localized electron operator. Again we factorize, obtaining

$$\mathcal{H}_6=\sum_{\mathbf{k}\sigma} V_{\mathbf{k}d}'(d_\sigma^* b_{\mathbf{k}\sigma}+b_{\mathbf{k}\sigma}^* d_\sigma). \tag{11}$$

In $\mathcal{H}_7$ there are terms in which conduction-electron operators for sides a and b along with localized electron operators appear. Among these we retain only

$$\mathcal{H}_7=\sum_{\substack{\mathbf{k},\mathbf{k}'\\ \sigma,\sigma'}} W_{\mathbf{k}d;\mathbf{k}'d} a_{\mathbf{k}\sigma}^* d_{\sigma'}^* b_{\mathbf{k}'\sigma'} d_\sigma + \text{Hermitian conjugate} \tag{12}$$

$$+\sum_{\substack{\mathbf{k},\mathbf{k}'\\ \sigma,\sigma'}} W_{\mathbf{k}d;d\mathbf{k}'} a_{\mathbf{k}\sigma}^* d_{\sigma'}^* d_{\sigma'} b_{\mathbf{k}'\sigma} + \text{Hermitian conjugate}. \tag{13}$$

In forming our model Hamiltonian from the above terms we may proceed in two different ways.

Because we are concerned with paramagnetic centers, we may assume that the conditions for the formation of a magnetic moment on the localized state are met.[18] We replace the d operators by spin operators in (9) and (12), obtaining

$$J_a \sum_{\mathbf{k}_1\mathbf{k}'} \{S_z(a_{\mathbf{k}\uparrow}^* a_{\mathbf{k}'\uparrow}-a_{\mathbf{k}\downarrow}^* a_{\mathbf{k}'\downarrow})+S^+ a_{\mathbf{k}\downarrow}^* a_{\mathbf{k}'\uparrow} +S^- a_{\mathbf{k}\uparrow}^* a_{\mathbf{k}'\downarrow}\}+T_{J_a}\sum_{\mathbf{k}_1\mathbf{k}'} S_z\{(a_{\mathbf{k}\uparrow}^* b_{\mathbf{k}'\uparrow}+b_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\uparrow}) -(a_{\mathbf{k}\downarrow}^* b_{\mathbf{k}'\downarrow}+b_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\downarrow})\}+T_{J_a}\sum_{\mathbf{k}_1\mathbf{k}'} +\{S^+(a_{\mathbf{k}\downarrow}^* b_{\mathbf{k}'\uparrow}+b_{\mathbf{k}'\downarrow}^* a_{\mathbf{k}\uparrow}) +S^-(a_{\mathbf{k}\uparrow}^* b_{\mathbf{k}'\downarrow}+b_{\mathbf{k}'\uparrow}^* a_{\mathbf{k}\downarrow})\}, \tag{14}$$

where S_z, S^+, S^- are the standard spin operators of the magnetic state and we have assumed J_a and T_{J_a} are real and constant. In addition we have

$$T\sum_{\mathbf{k},\mathbf{k}',\sigma}(a_{\mathbf{k}\sigma}^* b_{\mathbf{k}'\sigma}+b_{\mathbf{k}'\sigma}^* a_{\mathbf{k}\sigma}) +T_a\sum_{\mathbf{k},\mathbf{k}',\sigma}(a_{\mathbf{k}\sigma}^* b_{\mathbf{k}'\sigma}+b_{\mathbf{k}'\sigma}^* a_{\mathbf{k}\sigma}). \tag{15}$$

The first term of (15) is just (7a). The second term represents all the nonexchange mechanisms for the tunneling of an electron from side a to side b in which the conduction electron interacts with the localized electron. Typical nonexchange mechanisms of this sort are given in (13). They also result from the interference between (7b), (10), (7c), and (11).

Equations (5), (14), and (15) together make up our complete model Hamiltonian.

The second approach, used by Anderson[12] in deriving the model Hamiltonian, retains (5), (6), (8), (10), and (11). One then has a Hamiltonian of the form

$$\mathcal{H}=\sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}\sigma}^a a_{\mathbf{k}\sigma}^* a_{\mathbf{k}\sigma}+\sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}\sigma}^b b_{\mathbf{k}\sigma}^* b_{\mathbf{k}\sigma}+\sum_\sigma E_{d\sigma} d_\sigma^* d_\sigma +Ud_\sigma^* d_\sigma d_{-\sigma}^* d_{-\sigma}+\sum_{\mathbf{k},\sigma} V_{\mathbf{k}d}(a_{\mathbf{k}\sigma}^* d_\sigma+d_\sigma^* a_{\mathbf{k}\sigma}) +\sum_{\mathbf{k},\sigma} T_{\mathbf{k}d}(b_{\mathbf{k}\sigma}^* d_\sigma+d_\sigma^* b_{\mathbf{k}\sigma}). \tag{16}$$

Anderson then uses the results of Schrieffer and Wolff[19] to argue that by eliminating the terms proportional to $V_{\mathbf{k}d}$ and $T_{\mathbf{k}d}$ in (16) to second order by means of a canonical transformation, one obtains our model Hamiltonian. The exchange Hamiltonian which comes from (16) comes from terms whose physical meaning is different from those used to derive (14). Presumably both contribute to the total exchange interaction, and in practice the contributions cannot easily be separated.

While deriving the model Hamiltonian we have assumed that there is a single spin-degenerate localized state which is paramagnetic in nature, located near the junction interface. The model Hamiltonian could be given a much broader interpretation, and its essential form would be maintained for rather complicated localized or quasilocalized magnetic states that may be in the junction region.

IV. CALCULATION OF CURRENT

In a magnetic field $\mathbf{H}$, and with side a at a voltage bias V, the Hamiltonian of our system takes the form:

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}', \tag{17}$$

$$\mathcal{H}_0=\sum_{\mathbf{k}\sigma}\tilde{\epsilon}_{\mathbf{k}\sigma}^a a_{\mathbf{k}\sigma}^* a_{\mathbf{k}\sigma}+\sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}\sigma}^b b_{\mathbf{k}\sigma}^* b_{\mathbf{k}\sigma}+g|\mu_B|\mathbf{S}\cdot\mathbf{H}, \tag{18}$$

$$\mathcal{H}'=\mathcal{H}^T+\mathcal{H}^I, \tag{19}$$

[17] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[18] The conditions necessary for the formation of a localized moment have been discussed by P. W. Anderson, Phys. Rev. **124**, 41 (1961); B. Kjollerström, D. J. Scalapino, and J. R. Schrieffer, Bull. Am. Phys. Soc. **11**, 79 (1966); D. R. Hamann, Phys. Rev. Letters **17**, 145 (1966); and others.

[19] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).

$$\mathcal{H}^T=T_{J_a}\sum_{\mathbf{k},\mathbf{k}'}S_z[(a_{\mathbf{k}\uparrow}{}^*b_{\mathbf{k}'\uparrow}-a_{\mathbf{k}\downarrow}{}^*b_{\mathbf{k}'\downarrow})+(b_{\mathbf{k}'\uparrow}{}^*a_{\mathbf{k}\uparrow}-b_{\mathbf{k}'\downarrow}{}^*a_{\mathbf{k}\downarrow})]+T_{J_a}\sum_{\mathbf{k},\mathbf{k}'}S^+(a_{\mathbf{k}\downarrow}{}^*b_{\mathbf{k}'\uparrow}+b_{\mathbf{k}\downarrow}{}^*a_{\mathbf{k}'\uparrow})$$
$$+T_{J_a}\sum_{\mathbf{k}\mathbf{k}'}S^-(a_{\mathbf{k}\uparrow}{}^*b_{\mathbf{k}'\downarrow}+b_{\mathbf{k}'\uparrow}{}^*a_{\mathbf{k}\downarrow})+T\sum_{\substack{\mathbf{k},\mathbf{k}'\\\sigma}}(a_{\mathbf{k}\sigma}{}^*b_{\mathbf{k}'\sigma}+b_{\mathbf{k}'\sigma}{}^*a_{\mathbf{k}\sigma})+T_a\sum_{\substack{\mathbf{k},\mathbf{k}'\\\sigma}}(a_{\mathbf{k}\sigma}{}^*b_{\mathbf{k}'\sigma}+b_{\mathbf{k}'\sigma}{}^*a_{\mathbf{k}\sigma}),\quad(20)$$

$$\mathcal{H}^I=J_a\sum_{\mathbf{k}\mathbf{k}'}\{S_z(a_{\mathbf{k}\uparrow}{}^*a_{\mathbf{k}'\uparrow}-a_{\mathbf{k}\downarrow}{}^*a_{\mathbf{k}'\downarrow})+S^+a_{\mathbf{k}\downarrow}{}^*a_{\mathbf{k}'\uparrow}+S^-a_{\mathbf{k}\uparrow}{}^*a_{\mathbf{k}'\downarrow}\},\quad(21)$$

where $\epsilon_{\mathbf{k}\sigma}{}^a$ and $\epsilon_{\mathbf{k}\sigma}{}^b$ implicitly include the Zeemann energy and

$$\tilde{\epsilon}_{\mathbf{k}\sigma}{}^a=\epsilon_{\mathbf{k}\sigma}{}^a+eV.\quad(22)$$

If we assume $\mathbf{H}=H\hat{z}$, the last term in (18) takes the form

$$g|\mu_B|\mathbf{S}\cdot\mathbf{H}=\Delta S_z,\quad(23)$$

where $g|\mu_B|H$, the Zeeman splitting of localized spin, is denoted by Δ.

We make the assumption that we may neglect multiple scattering by different localized spins. Then to calculate the total current J_{ab} between sides a and b, we multiply those terms proportional to T_{J_a} or T_a in j_{ab}, the current calculated from H, by N_a, the number of localized spins on side a.

We obtain j_{ab} from

$$j_{ab}=e\sum_M P_M\sum_{\substack{\mathbf{k},\mathbf{k}'\\\sigma,\sigma'}}[W_{\mathbf{k}\sigma M;\mathbf{k}'\sigma'M'}f(\epsilon_{\mathbf{k}\sigma}{}^a)(1-f(\epsilon_{\mathbf{k}'\sigma'}{}^b))]$$
$$-e\sum_{M'}P_{M'}\sum_{\substack{\mathbf{k},\mathbf{k}'\\\sigma,\sigma'}}[W_{\mathbf{k}'\sigma'M';\mathbf{k}\sigma M}f(\epsilon_{\mathbf{k}'\sigma'}{}^b)\times(1-f(\epsilon_{\mathbf{k}\sigma}{}^a))],\quad(24)$$

where e is the charge of the electron, P_M is the statistical probability that $S_z=M$, and $f(\epsilon_{\mathbf{k}})$ is the Fermi-Dirac distribution function; with the Fermi energy appearing in $f(\epsilon_{\mathbf{k}})$ the common Fermi energy ϵ_F of sides a and b when $V=0$. $W_{\mathbf{k}\sigma M;\mathbf{k}'\sigma'M'}$ is the transition probability per unit time that a conduction electron in state $(\mathbf{k},\sigma)$ on side a scatters into state $(\mathbf{k}',\sigma')$ on side b ,with the localized spin undergoing the transition $M\rightarrow M'$. Since spin is conserved

$$\sigma+M=\sigma'+M'.\quad(25)$$

$W_{\mathbf{k}'\sigma'M';\mathbf{k}\sigma M}$ has a similar meaning for transition from side b to side a.

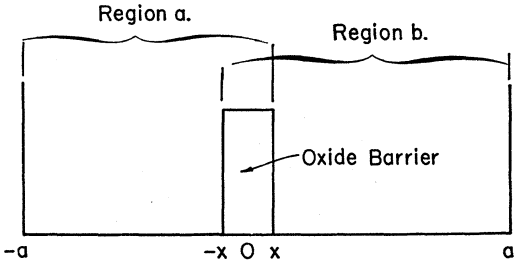

FIG. 1. Shown above is a schematic representation of a tunnel junction.

We treat $\mathcal{H}'$ as a perturbation and following Kondo[20] evaluate $W_{i;j}$ to third order in $\mathcal{H}_{i;j}'$. It is given by

$$W_{i,j}=\frac{2\pi}{\hbar}\left[\sum_{k\neq i}\frac{\mathcal{H}_{ik}'\mathcal{H}_{kj}'\mathcal{H}_{ij}'}{E_i-E_k}+\text{complex conj.}+|\mathcal{H}_{ij}|^2\right]\times\delta(E_i-E_j),\quad(26)$$

where i denotes a conduction electron-localized spin state and E_i its energy. We shall be interested in those terms in $W_{i;j}$ proportional to $(T+T_a)^2$, $T_{J_a}{}^2$, and $(T_a+T)T_{J_a}$.

Let us first consider contributions to $W_{i;j}$ second order in $\mathcal{H}'$.

$$W_{i;j}{}^{(2)}=(2\pi/\hbar)|\mathcal{H}'_{ij}|^2\delta(E_i-E_j).\quad(27)$$

The superscripts (2) and (3) will be used to indicate those quantities which are second and third order in $\mathcal{H}'$, respectively.

In the transition of a conduction electron with momentum $\mathbf{k}$ on side a to a state with momentum $\mathbf{k}'$ on side b there are four possible spin transitions:

$$\mathbf{k}\uparrow M\rightarrow\mathbf{k}'\uparrow M,\quad\mathbf{k}\downarrow M\rightarrow\mathbf{k}'\downarrow M,$$
$$\mathbf{k}\uparrow M\rightarrow\mathbf{k}'\downarrow M+1,\quad\mathbf{k}\downarrow M\rightarrow\mathbf{k}'\uparrow M-1.\quad(28)$$

The transition rates $W_{i;j}{}^{(2)}$ for the above processes are listed below:

$$W_{\mathbf{k}\uparrow M;\mathbf{k}'\uparrow M}{}^{(2)}=(2\pi/\hbar)([T+T_a]^2+T_{J_a}{}^2M^2+(T_a+T)T_{J_a}M)\delta(\tilde{\epsilon}_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{k}'\uparrow}{}^b),\quad(29)$$

$$W_{\mathbf{k}\downarrow M;\mathbf{k}'\downarrow M}{}^{(2)}=(2\pi/\hbar)([T+T_a]^2+T_{J_a}{}^2M^2-(T_a+T)T_{J_a}M)\delta(\tilde{\epsilon}_{\mathbf{k}\downarrow}{}^a-\epsilon_{\mathbf{k}'\downarrow}{}^b),\quad(30)$$

$$W_{\mathbf{k}\uparrow M;\mathbf{k}'\uparrow M+1}{}^{(2)}=(2\pi/\hbar)T_{J_a}{}^2[S(S+1)-M(M+1)]\times\delta(\tilde{\epsilon}_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{k}'\downarrow}{}^b-\Delta),\quad(31)$$

$$W_{\mathbf{k}\downarrow M;\mathbf{k}'\uparrow M-1}{}^{(2)}=(2\pi/\hbar)T_{J_a}{}^2[S(S+1)-M(M-1)]\times\delta(\tilde{\epsilon}_{\mathbf{k}\downarrow}{}^a-\epsilon_{\mathbf{k}'\uparrow}{}^b+\Delta).\quad(32)$$

Furthermore,

$$W_{\mathbf{k}'\uparrow M;\mathbf{k}\uparrow M}{}^{(2)}=W_{\mathbf{k}\uparrow M;\mathbf{k}'\uparrow M}{}^{(2)},\quad(33)$$

$$W_{\mathbf{k}'\uparrow M;\mathbf{k}\downarrow M}{}^{(2)}=W_{\mathbf{k}\downarrow M;\mathbf{k}'\downarrow M}{}^{(2)},\quad(34)$$

[20] J. Kondo, Progr. Theoret. Phys. (Kyoto) 32, 37 (1964).

$$W_{\mathbf{k}'\downarrow M;\mathbf{k}\uparrow M-1}=(2\pi/\hbar)T_{J_a}{}^2[S(S+1)-M(M-1)]\times\delta(\epsilon_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{k}'\downarrow}{}^b-\Delta), \quad (35)$$

$$W_{\mathbf{k}'\uparrow M;\mathbf{k}\downarrow M+1}=(2\pi/\hbar)T_{J_a}{}^2[S(S+1)-M(M+1)]\times\delta(\epsilon_{\mathbf{k}\downarrow}{}^a-\epsilon_{\mathbf{k}'\uparrow}{}^b+\Delta). \quad (36)$$

It is clear from (29) and (30) that the interference terms between $(T+T_a)$ and T_{J_a} will cancel in the calculation of the current.

We can split the current $j_{ab}{}^{(2)}$ into two terms: $j_{\mathrm{nsf}}{}^{(2)}$, arising from transitions in which there is no spin flip, and $j_{\mathrm{sf}}{}^{(2)}$, arising from spin-flip transitions. The subscript ab on j_{ab} will be dropped henceforth.

$$j^{(2)}=j_{\mathrm{nsf}}{}^{(2)}+j_{\mathrm{sf}}{}^{(2)} \quad (37)$$

$$j_{\mathrm{nsf}}{}^{(2)}=\frac{2\pi e}{\hbar}((T+T_a)^2+T_{J_a}{}^2\langle M^2\rangle_{\mathrm{av}})\sum_{\substack{\mathbf{k},\mathbf{k}'\\ \sigma}}(f(\epsilon_{\mathbf{k}\sigma})-f(\epsilon_{\mathbf{k}'\sigma'}))\delta(\epsilon_{\mathbf{k}\sigma}+eV-\epsilon_{\mathbf{k}'\sigma}), \quad (38)$$

$$j_{\mathrm{sf}}{}^{(2)}=\frac{2\pi e}{\hbar}T_{J_a}{}^2[S(S+1)-\langle M^2\rangle_{\mathrm{av}}]\sum_{\mathbf{k},\mathbf{k}'}[f(\epsilon_{\mathbf{k}\uparrow})-f(\epsilon_{\mathbf{k}'\downarrow})]\delta(\epsilon_{\mathbf{k}\uparrow}+eV-\epsilon_{\mathbf{k}'\downarrow}-\Delta)+\frac{2\pi e}{\hbar}T_{J_a}{}^2[S(S+1)-\langle M^2\rangle_{\mathrm{av}}]$$
$$\times\sum_{\mathbf{k},\mathbf{k}'}[f(\epsilon_{\mathbf{k}\downarrow})-f(\epsilon_{\mathbf{k}'\uparrow})]\delta(\epsilon_{\mathbf{k}\downarrow}+eV-\epsilon_{\mathbf{k}'\uparrow}+\Delta)+\frac{2\pi e}{\hbar}T_{J_a}{}^2\langle M\rangle_{\mathrm{av}}\sum_{\mathbf{k},\mathbf{k}'}[f(\epsilon_{\mathbf{k}\downarrow})(1-f(\epsilon_{\mathbf{k}'\uparrow}))+f(\epsilon_{\mathbf{k}'\uparrow})(1-f(\epsilon_{\mathbf{k}\downarrow}))]$$
$$\times\delta(\epsilon_{\mathbf{k}\downarrow}+eV-\epsilon_{\mathbf{k}'\uparrow}+\Delta)-\frac{2\pi e}{\hbar}T_{J_a}{}^2\langle M\rangle_{\mathrm{av}}\sum_{\mathbf{k},\mathbf{k}'}[f(\epsilon_{\mathbf{k}\uparrow})(1-f(\epsilon_{\mathbf{k}'\downarrow}))+f(\epsilon_{\mathbf{k}'\downarrow})(1-f(\epsilon_{\mathbf{k}\uparrow}))]$$
$$\times\delta(\epsilon_{\mathbf{k}\uparrow}+eV-\epsilon_{\mathbf{k}'\downarrow}-\Delta). \quad (39)$$

In the above

$$\langle M\rangle_{\mathrm{av}}=\sum_{M=-S}^{S}P_M M=\tfrac{1}{2}\coth\frac{\Delta}{2k_BT}-(S+\tfrac{1}{2})\coth(S+\tfrac{1}{2})\frac{\Delta}{k_BT}, \quad (40)$$

$$\langle M^2\rangle_{\mathrm{av}}=\sum_{M=-S}^{S}P_M M^2=\langle M\rangle_{\mathrm{av}}{}^2-(S+\tfrac{1}{2})^2\operatorname{csch}^2(S+\tfrac{1}{2})\frac{\Delta}{k_BT}+\tfrac{1}{4}\operatorname{csch}^2\frac{\Delta}{2k_BT}. \quad (41)$$

$j_{\mathrm{sf}}{}^{(2)}$ assumes the complicated form it does compared to $j_{\mathrm{nsf}}{}^{(2)}$ because of the presence of the term in $j_{\mathrm{sf}}{}^{(2)}$ proportional to $\langle M\rangle_{\mathrm{av}}$.

This term arises because

$$W_{\mathbf{k}\uparrow M;\mathbf{k}'\downarrow M+1} \quad \text{and} \quad W_{\mathbf{k}'\downarrow M;\mathbf{k}\uparrow M-1}$$

differ by a term proportional to M. Instead of the functions $f(\epsilon_i)(1-f(\epsilon_f))$ and $f(\epsilon_f)(1-f(\epsilon_i))$ subtracting to give $f(\epsilon_i)-f(\epsilon_f)$ they add in the term proportional to M.

We are in fact interested not in j so much as in g, the conductance, given by

$$g=(\partial/\partial V)j. \quad (42)$$

If the sums over k and k' are replaced by integrals over energy, the derivative with respect to voltage taken, and $-(\partial f/\partial\epsilon)(\epsilon-\omega)$ replaced by $\delta(\epsilon-\omega)$, one obtains for $g_{\mathrm{nsf}}{}^{(2)}$ and $g_{\mathrm{sf}}{}^{(2)}$:

$$g_{\mathrm{nsf}}{}^{(2)}=\frac{\partial}{\partial V}j_{\mathrm{nsf}}{}^{(2)}=\frac{4\pi e^2}{\hbar}\rho^a(\epsilon_F)\rho^b(\epsilon_F)\times[(T+T_a)^2+\langle M^2\rangle_{\mathrm{av}}T_{J_a}{}^2]. \quad (43)$$

$$g_{\mathrm{sf}}{}^{(2)}=\frac{\partial}{\partial V}j_{\mathrm{sf}}{}^{(2)}=\frac{4\pi e^2}{\hbar}T_{J_a}{}^2\rho^a(\epsilon_F)\rho^b(\epsilon_F)\left[S(S+1)-\langle M^2\rangle_{\mathrm{av}}+\frac{\langle M\rangle_{\mathrm{av}}}{2}\left(\tanh\frac{eV+\Delta}{2k_BT}+\tanh\frac{\Delta-eV}{2k_BT}\right)\right]. \quad (44)$$

In the above we have made the assumption that the density of states $\rho(\epsilon)$ is constant, removed it from the integrals within which it appears, and replaced it by its value at $\epsilon=\epsilon_F$, $\rho(\epsilon_F)$. This is justified by the fact that only electrons within a few millivolts of ϵ_F on either side of the junction take part in the tunneling for voltage biases of interest. Notice that for $eV<\Delta$ and $T\to 0$ $g_{\mathrm{sf}}{}^{(2)}\to 0$. This is to be expected on general physical grounds; for with the spins in their ground state $(\Delta/T\to\infty)$ an electron at energy ϵ on side a would have to tunnel into an energy state $\epsilon-\Delta$ on side b if it underwent a spin flip. For $eV<\Delta$, $T\to 0$, this process is forbidden by the exclusion principle. Therefore $j_{\mathrm{sf}}{}^{(2)}=0$ for $V<\Delta$, $T\to 0$, whence $g_{\mathrm{sf}}{}^{(2)}=0$ for $V<\Delta$, $T\to 0$. The above argument is clearly not restricted to second-order processes and is true to all orders in $\mathcal{H}'$.

Combining (43) and (44):

$$g^{(2)}=\frac{4\pi e^2}{\hbar}\rho^a(\epsilon_F)\rho^b(\epsilon_F)\Big\{S(S+1)T_{J_a}{}^2+(T+T_a)^2 +T_{J_a}{}^2\langle M\rangle_{\rm av}\times\tfrac{1}{2}\Big(\tanh\frac{eV+\Delta}{2k_BT}+\tanh\frac{\Delta-eV}{2k_BT}\Big)\Big\}. \quad (45)$$

We proceed now to calculate the third-order transition rate

$$W_{i;j}{}^{(3)}=\frac{4\pi}{\hbar}\sum_{k\neq i}\frac{\mathcal{H}_{ik}'\mathcal{H}_{kj}'\mathcal{H}_{ij}'}{E_i-E_k}\delta(E_i-E_j), \quad (46)$$

where we have used the fact that J_a, T, T_a, and T_{J_a} are assumed real to combine the first and second terms of (26). It is the third-order terms proportional to $T_{J_a}{}^2J_a$ in $W_{i;j}{}^{(3)}$ which are responsible for the anomalous voltage and temperature dependence of the conductance. We shall derive these terms in some detail following rather closely an analysis used by Kondo[20] to explain the low-temperature resistance found in dilute alloys of transition metals dissolved in noble metals.

We first consider transitions in which the initial and final spins of the conduction electron are equal. For $W_{\mathbf{k}\sigma M;\mathbf{k}'\sigma M}{}^{(3)}$ to have the strong temperature dependence characteristic of the experimentally observed conductance the intermediate state must involve a spin-flip process. In Figs. 2, 3, and 4 are shown the processes which are responsible for the anomalous terms in the conductance. Since $W_{i;j}{}^{(3)}$ is an interference term between the first and second Born-approximation scattering amplitudes we have represented it graphically by drawing separately, one above the other, the processes resulting from $\mathcal{H}_{i;k}'\mathcal{H}_{k;j}'$ and $\mathcal{H}_{i;j}'$.

In calculating $W_{i;j}{}^{(3)}$ we stress that the transition from state i to state j by means of an intermediate state k may occur in two different ways. We denote by I the transition in which the electron in state i scatters into state k and then the electron in state k scatters into state j; we denote by II the preemission process in which an electron in the intermediate state k first scatters into the final state j, and then the electron in state i scatters into the hole left by the k electron.

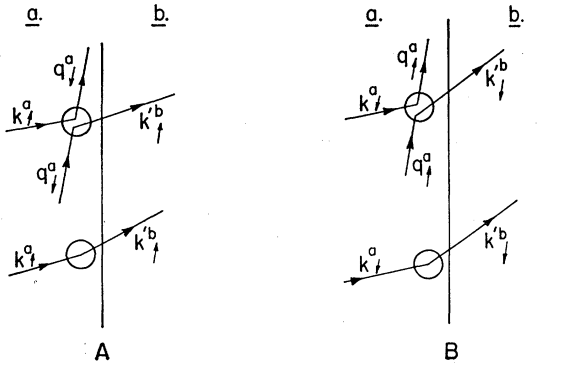

FIG. 2. Diagram A represents the third-order scattering process which contributes to $W_{k\uparrow M;k'\uparrow M}{}^{(3)}$. Diagram B likewise represents the third-order scattering process which contributes to $W_{k\downarrow M;k'\downarrow M}{}^{(3)}$. We have represented $W_{i;j}{}^{(3)}$ graphically by drawing separately, one above the other, the processes resulting from $\mathcal{H}_{i;k}'\mathcal{H}_{k;j}'$, and $\mathcal{H}_{i;j}'$.

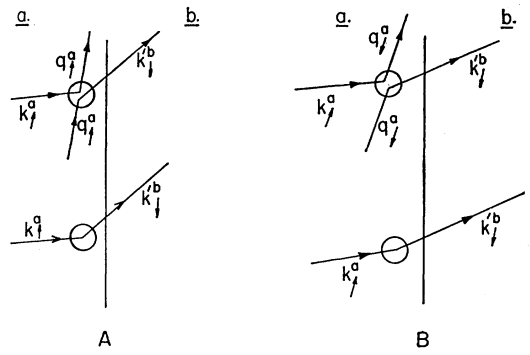

FIG. 3. Diagrams A and B represent third-order scattering processes which contribute to $W_{k\uparrow M;k\downarrow M+1}{}^{(3)}$. We have represented $W_{i;j}{}^{(3)}$ graphically by drawing separately, one above the other, the processes resulting from $\mathcal{H}_{i;k}'\mathcal{H}_{k;j}'$ and $\mathcal{H}_{i;j}'$.

The contribution of processes I and II to $W_{\mathbf{k}M;\mathbf{k}'M}{}^{(3)}$ is:

$$\text{(I)}\quad T_{J_a}{}^2J_aM[S(S+1)-M(M+1)] \times\sum_{\mathbf{q}}\frac{1-f(\epsilon_{\mathbf{q}\downarrow}{}^a)}{\epsilon_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{q}\downarrow}{}^a-\Delta}\delta(\tilde{\epsilon}_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{k}'\uparrow}{}^b) \quad (47)$$

$$\text{(II)}\quad -T_{J_a}{}^2J_aM[S(S+1)-M(M-1)] \times\sum_{\mathbf{q}}\frac{f(\epsilon_{\mathbf{q}\downarrow}{}^a)}{\epsilon_{\mathbf{q}\downarrow}{}^a-\epsilon_{\mathbf{k}\uparrow}{}^a+\Delta}\delta(\tilde{\epsilon}_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{k}'\uparrow}{}^b). \quad (48)$$

If the scattering were not magnetic (I) and (II) would add in such a way that the terms contaning $f(\epsilon_{\mathbf{q}\downarrow}{}^a)$ would cancel. For magnetic scattering involving spin-flip processes that cancellation does not occur. This leads to terms which are strongly temperature-dependent.

We replace $\sum_{\mathbf{q}}\cdots$ above by

$$P\int_{-E_0}^{E_0}\cdots\rho(\epsilon)d\epsilon,$$

that is, we restrict the principal-valued sum over intermediate states to an energy region of width $2E_0$ centered at the Fermi energy ϵ_F (all energies are measured from ϵ_F), in order to be consistent with our assumptions that $\rho(\epsilon)$, T_{J_a}, and J_a are constant. We can then show that

$$\sum_{\mathbf{q}}\frac{1}{\epsilon_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{q}\downarrow}{}^a-\Delta}$$

is small compared to

$$\sum_{\mathbf{q}}\frac{f(\epsilon_{\mathbf{q}\downarrow}{}^a)}{\epsilon_{\mathbf{k}\uparrow}{}^a-\epsilon_{\mathbf{q}\downarrow}{}^a-\Delta}.$$

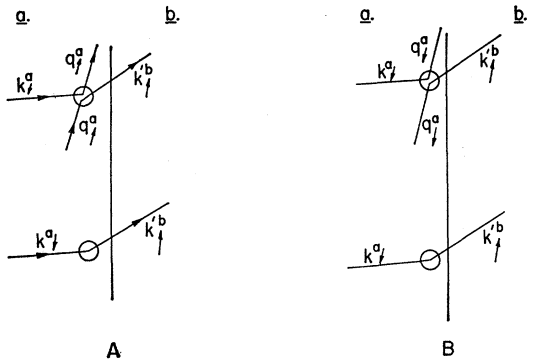

FIG. 4. Diagrams A and B represent third-order scattering processes which contribute to $W_{k\downarrow M;k\uparrow M-1}{}^{(3)}$. We have represented $W_{i;j}{}^{(3)}$ graphically by drawing separately, one above the other, the processes resulting from $\mathcal{H}_{i;j}'$; $\mathcal{H}_{k;j}'$, and $\mathcal{H}_{i;j}'$.

We therefore drop all terms which do not contain $f(\epsilon_q)$.

Combining (47) and (48) we obtain

$$W_{k\uparrow M;k'\uparrow M}{}^{(3)}=-4J_a T_{J_a}{}^2M^2g^a(\epsilon_{k\uparrow}{}^a-\Delta)\times\delta(\tilde{\epsilon}_{k\uparrow}{}^a-\epsilon_{k'\uparrow}{}^b), \quad (49)$$

where

$$g^a(\omega)\equiv\sum_q \frac{f(\epsilon_{q\uparrow}{}^a)}{\epsilon_{q\uparrow}{}^a-\omega}=P\int_{-E_0}^{E_0}\frac{f(\epsilon)\rho^a(\epsilon)d\epsilon}{\epsilon-\omega}. \quad (50)$$

Notice we have dropped the spin index on $\epsilon_{q\uparrow}{}^a$; this is because the Zeeman energy of the electron can be eliminated by a shift of origin in the above integral, and since $\Delta\ll E_0$ the limits of integration need not be changed. We will find throughout that the Zeeman energy of the electrons can be so eliminated. In a similar way we obtain for $W_{k\downarrow M;k'\downarrow M}$:

$$W_{k\downarrow M;k'\downarrow M}{}^{(3)}=-4J_a T_{J_a}{}^2M^2g^a(\epsilon_{k\downarrow}{}^a+\Delta)\times\delta(\tilde{\epsilon}_{k\downarrow}{}^a-\epsilon_{k'\downarrow}{}^b). \quad (51)$$

In Figs. 3 and 4 are shown the graphs which contribute to $W_{k\uparrow M;k'\downarrow M+1}$ and $W_{k\downarrow M;k'\uparrow M+1}{}^{(3)}$. We have:

$$W_{k\uparrow M;k'\downarrow M+1}{}^{(3)}=-2T_{J_a}{}^2J_a[S(S+1)-M(M+1)]\times(g^a(\epsilon_{k\uparrow}{}^a-\Delta)+g^a(\epsilon_{k\uparrow}))\times\delta(\tilde{\epsilon}_{k\uparrow}{}^a-\epsilon_{k'\downarrow}{}^b-\Delta), \quad (52)$$

$$W_{k\downarrow M;k'\uparrow M-1}=-2T_{J_a}{}^2J_a[S(S+1)-M(M-1)]\times(g^a(\epsilon_{k\downarrow}{}^a+\Delta)+g^a(\epsilon_{k\downarrow}{}^a))\delta(\tilde{\epsilon}_{k\downarrow}{}^a-\epsilon_{k'\uparrow}{}^b+\Delta). \quad (53)$$

In evaluating $W_{i;j}{}^{(3)}$ we have considered only those terms proportional to $T_{J_a}{}^2J_a$. These terms represent the interference between reflected and transmitted exchange-scattered currents. We investigate now to see if there are any terms proportional to $(T+T_a)^2J_a$ or $(T+T_a)T_{J_a}J_a$ which exhibit anomalous temperature and voltage dependence. We know from the work of Kondo[20] that only processes like those shown in Figs. 2, 3, and 4 can yield strong temperature-dependent transition probabilities. Terms proportional to $(T+T_a)^2J_a$ clearly cannot yield such graphs, since only one exchange scattering is involved. The terms proportional to $T_{J_a}(T+T_a)J_a$ cannot be dismissed so quickly. It is necessary to investigate whether any temperature-dependent terms survive if for transitions which do not involve spin flip we replace

$$T_{J_a}S_z\sum_{k,k'}\{a_{k\uparrow}{}^*b_{k'\uparrow}+b_{k\uparrow}{}^*a_{k'\uparrow}-a_{k\downarrow}{}^*b_{k'\downarrow}-b_{k'\downarrow}{}^*a_{k\downarrow}\}$$

by

$$(T+T_a)\sum_{k\sigma,k'}(a_{k'\sigma}{}^*b_{k\sigma}+b_{k\sigma}{}^*a_{k'\sigma}).$$

When this is done for the spin-flip transitions in Figs. 3 and 4 no temperature-dependent terms remain. For the transition $\mathbf{k}\uparrow M\rightarrow\mathbf{k}'\uparrow M$ a term

$$-4(T+T_a)T_{J_a}J_aMg^a(\epsilon_{k\uparrow}{}^a-\Delta)\delta(\tilde{\epsilon}_{k\uparrow}{}^a-\epsilon_{k\uparrow}{}^b) \quad (54)$$

appears in $W_{k\uparrow M;k'\uparrow M}{}^{(3)}$.

In the transition $\mathbf{k}\downarrow M\rightarrow\mathbf{k}'\downarrow M$ the term

$$4(T+T_a)T_{J_a}J_aMg^a(\epsilon_{k\downarrow}{}^a+\Delta)\delta(\tilde{\epsilon}_{k\downarrow}{}^a-\epsilon_{k\downarrow}{}^b) \quad (55)$$

appears in $W_{k\uparrow M;k'\downarrow M}{}^{(3)}$. These terms' contribution to the conductance does not vanish for a nonzero magnetic field. The conductance arising from (54) and (55) is odd in V and has the following form:

$$\langle M\rangle_{av}\{F(eV-\Delta)-F(eV+\Delta)\}, \quad (56)$$

where $F(x)$ is an even function of x which changes slowly for a change in $x\sim k_BT$. Although in sufficiently large magnetic fields this term may be observable it is expected to be smaller than the terms proportional to $T_{J_a}{}^2J_a$. We shall neglect this term in deriving the current. This term arises because the impurities are associated specifically with metal A: if our junction were symmetric, that is metal A = metal B, this term would vanish identically.

As we did with $j^{(2)}$, we split $j^{(3)}$ into $j_{nsf}{}^{(3)}$ and $j_{sf}{}^{(3)}$

$$j_{sf}{}^{(3)}=j_{sf\uparrow}{}^{(3)}+j_{sf\downarrow}{}^{(3)}, \quad (57)$$

$$j_{sf\uparrow}{}^{(3)}=\frac{2\pi e}{\hbar}\sum_{k,k'}[\sum_{M=-S}^{S}P_MW_{k\uparrow M;k'\downarrow M+1}f(\epsilon_{k\uparrow})\times(1-f(\epsilon_{k'\downarrow}))-\sum_{M=-S}^{S}P_MW_{k'\downarrow M;k\uparrow M-1}f(\epsilon_{k'\downarrow})\times(1-f(\epsilon_{k\uparrow}))], \quad (58)$$

$$j_{sf\downarrow}{}^{(3)}=\frac{2\pi e}{\hbar}\sum_{k,k'}[\sum_{M=-S}^{S}P_MW_{k\downarrow M;k'\uparrow M-1}f(\epsilon_{k\downarrow})\times(1-f(\epsilon_{k'\uparrow}))-\sum_{M=-S}^{S}P_MW_{k'\uparrow M;k\downarrow M+1}f(\epsilon_{k'\uparrow})\times(1-f(\epsilon_{k\downarrow}))]. \quad (59)$$

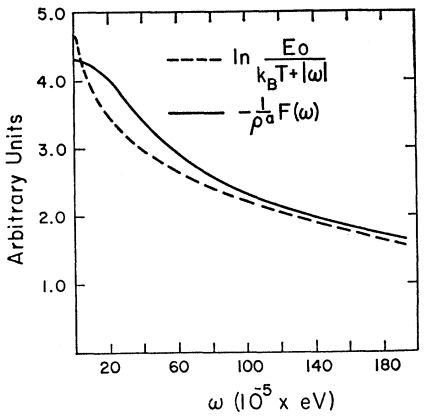

FIG. 5. Drawn above for comparison is $-F(w)$, evaluated numerically, and $\rho^a \ln[E_0/(k_BT+|w|)]$, an interpolative approximation to $-F(w)$, for $E_0=10$ MeV and $k_BT=0.1$ MeV.

Substituting (51), (52), and (53) into (58),

$$j_{sf\uparrow}{}^{(3)}=\sum_{k,k'}(-4\pi e/\hbar)T_{J_a}{}^2J_a(S(S+1)-\langle M^2\rangle_{av})$$
$$\times(g^a(\epsilon_{k\uparrow}-\Delta)+g^a(\epsilon_{k\uparrow}))(f(\epsilon_{k\uparrow})-f(\epsilon_{k'\downarrow}))$$
$$\times\delta(\tilde{\epsilon}_{k\uparrow}-\epsilon_{k'\downarrow}-\Delta)+(4\pi e/\hbar)T_{J_a}{}^2J_a\langle M\rangle_{av}$$
$$\times\sum_{k,k'}[g^a(\epsilon_{k\uparrow}-\Delta)+g^a(\epsilon_{k\uparrow})][f(\epsilon_{k\uparrow})(1-f(\epsilon_{k'\downarrow}))$$
$$+f(\epsilon_{k'\downarrow})(1-f(\epsilon_{k\uparrow}))]\delta(\tilde{\epsilon}_{k\uparrow}-\epsilon_{k'\downarrow}-\Delta). \quad (60)$$

If we replace $\sum_{k,k'}\cdots$ by $\int\int d\epsilon d\epsilon'\rho^a(\epsilon)\rho^b(\epsilon')\cdots$, perform the integral over ϵ' and then take the derivative with respect to V of $j_{sf}{}^{(3)}$ we obtain

$$g_{sf\uparrow}{}^{(3)}=-\frac{4\pi e^2}{\hbar}T_{J_a}{}^2J_a[S(S+1)-\langle M^2\rangle_{av}]\rho^a(\epsilon_F)\rho^b(\epsilon_F)$$
$$\times\int d\epsilon[g^a(\epsilon-\Delta)+g^a(\epsilon)]-\frac{\partial}{\partial\epsilon}f(\epsilon-\Delta+eV)\frac{4\pi e^2}{\hbar}$$
$$\times T_{J_a}{}^2J_a\langle M\rangle_{av}\rho^a(\epsilon_F)\rho^b(\epsilon_F)\int d\epsilon[g^a(\epsilon-\Delta)+g^a(\epsilon)]$$
$$\times\tanh\frac{\epsilon}{2k_BT}\frac{\partial}{\partial\epsilon}f(\epsilon-\Delta+eV). \quad (61)$$

Although $-(\partial/\partial\epsilon)f(\epsilon)$ can ordinarily be replaced by $\delta(\epsilon)$ for small k_BT, because of the singular nature of $g(\epsilon)$ this is not done. We may, however, remove $\tanh(\epsilon/2k_BT)$ from the integral, replacing it by $\tanh((-eV+\Delta)/2k_BT)$. We have then,

$$g_{sf\uparrow}{}^{(3)}=-\frac{4\pi e^2}{\hbar}T_{J_a}{}^2J_a\rho^a(\epsilon_F)\rho^b(\epsilon_F)$$
$$\times\left[S(S+1)-\langle M^2\rangle_{av}+\langle M\rangle_{av}\tanh\frac{\Delta-eV}{2k_BT}\right]$$
$$\times(F(eV)+F(eV-\Delta)), \quad (62)$$

where

$$F(\omega)=-\int_{-\infty}^{\infty}g(\epsilon)\frac{\partial f}{\partial\epsilon}(\epsilon-\omega)d\epsilon. \quad (63)$$

A simple interpolative approximation to $F(x)$ used previously by the author is

$$F|x|\cong\rho(\epsilon_F)\ln\frac{|x|+k_BT}{E_0}. \quad (64)$$

A comparison between this approximate form for $F(x)$ and the numerically evaluated $F(x)$ is shown in Fig. 5.

Similarly we obtain for $g_{sf\downarrow}{}^{(3)}$

$$g_{sf\downarrow}{}^{(3)}=-\frac{4\pi e^2}{\hbar}T_{J_a}{}^2J_a\rho^a(\epsilon_F)\rho^b(\epsilon_F)$$
$$\times\left\{S(S+1)-\langle M^2\rangle_{av}+\langle M\rangle_{av}\tanh\frac{\Delta+eV}{2k_BT}\right\}$$
$$\times(F(eV)+F(eV+\Delta)). \quad (65)$$

Likewise, we obtain for $g_{nsf}{}^{(3)}$:

$$g_{nsf}{}^{(3)}=-\frac{8\pi e^2}{\hbar}J_aT_{J_a}{}^2\langle M^2\rangle_{av}\rho^a(\epsilon_F)\rho^b(\epsilon_F)$$
$$\times(F(eV-\Delta)+F(eV+\Delta)). \quad (66)$$

Combining $g^{(2)}$ and $g^{(3)}$, and multiplying the terms proportional to T_{J_a} or T_a by N_a, we obtain for the total conductance G,

$$G=G^{(2)}+G^{(3)}, \quad (67)$$

$$G^{(2)}=\frac{4\pi e^2}{\hbar}\rho^a(\epsilon_F)\rho^b(\epsilon_F)\left\{T^2+N_a\left(2TT_a+T_a{}^2\right.\right.$$
$$+S(S+1)T_{J_a}{}^2+T_{J_a}{}^2\frac{\langle M\rangle_{av}}{2}$$
$$\left.\left.\times\left(\tanh\frac{eV+\Delta}{2k_BT}+\tanh\frac{\Delta-eV}{2k_BT}\right)\right)\right\}, \quad (68)$$

$$G^{(3)}=G_1{}^{(3)}+G_2{}^{(3)}+G_3{}^{(3)}, \quad (69)$$

$$G_1{}^{(2)}=C\left\{1-\frac{\langle M^2\rangle_{av}}{S(S+1)}+\frac{\langle M\rangle_{av}}{2(S+1)S}\right.$$
$$\left.\times\left(\tanh\frac{\Delta-eV}{2k_BT}+\tanh\frac{\Delta+eV}{2k_BT}\right)\right\}\times F(eV), \quad (70)$$

$$G_2{}^{(3)}=\frac{C}{2}\left\{1+\frac{\langle M^2\rangle_{av}}{S(S+1)}+\frac{\langle M\rangle_{av}}{S(S+1)}\tanh\frac{\Delta+eV}{2k_BT}\right\}$$
$$\times F(eV+\Delta), \quad (71)$$

$$G_3^{(3)}=\frac{C}{2}\left\{1+\frac{\langle M^2\rangle_{\rm av}}{S(S+1)}+\frac{\langle M\rangle_{\rm av}}{S(S+1)}\tanh\frac{\Delta-eV}{2k_BT}\right\}\times F(eV-\Delta), \quad (72)$$

where

$$C=-(8\pi e^2/\hbar)S(S+1)\rho^a(\epsilon_F)\rho^b(\epsilon_F)N_aT_{J_a}{}^2J_a. \quad (73)$$

V. DISCUSSION

In zero magnetic field G can be written as

$$G(V,T)=G^{(2)}+G^{(3)}(V,T), \quad (74)$$

$$G^{(2)}=\frac{4\pi e^2}{\hbar}\rho^a(\epsilon_F)\rho^b(\epsilon_F)\times[T^2+N_a(2TT_a+T_a{}^2+S(S+1)T_{J_a}{}^2)], \quad (75)$$

$$G^{(3)}(V,T)=-\frac{\pi e^2 16S(S+1)}{\hbar}\rho^a(\epsilon_F)\rho^b(\epsilon_F)N_aT_{J_a}{}^2J_aF(eV). \quad (76)$$

The temperature and voltage dependence of $G^{(3)}(V,T)$ is the same as that found by Wyatt for the anomalous part of the conductance. In fitting Wyatt's data as well as Rowell and Shen's we must choose for the cutoff parameter $E_0\sim 10$ MeV. This is considerably smaller than the ~ 100 MeV we might have estimated based on the strong variation of the density of states of the transition metals near the Fermi surface. The smaller value of E_0 may be due to renormalization effects similar to those discussed by Abrikosov[21] for the Kondo effect. There remains finally the question of whether $G^{(3)}(V,T)$ can be large enough to account for the observed size of the anomalies. The difficulty involved in answering this question can be best appreciated by recalling that the conductance peaks vary in size by several orders of magnitude, depending on the metals used and impurity contaminants present in fabricating the junctions. All we can hope to do at present is to make some general comments which will at least indicate that the anomalies can be large enough to agree with experiment.

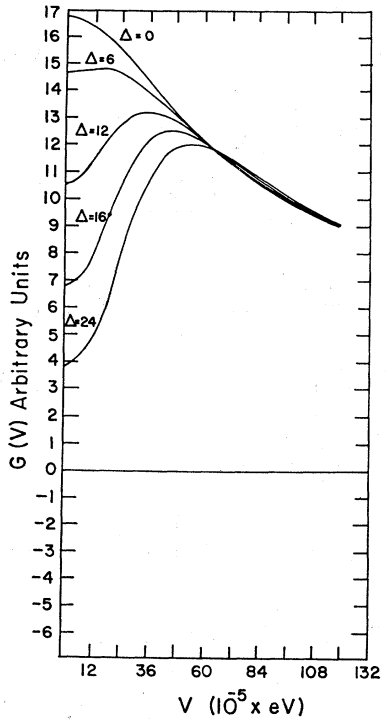

FIG. 6. The voltage-dependent part of G is plotted for different Zeeman energies Δ, and for $S=\frac{5}{2}$, $k_BT=0.12$ MeV (1.4°K), and $E_0=10$ MeV. Δ is measured in units of 0.01 MeV.

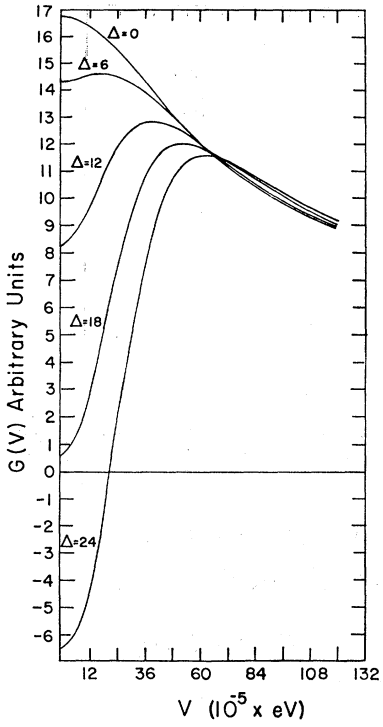

FIG. 7. The voltage-dependent part of G is plotted for different Zeeman energies Δ, and for $S=\frac{5}{2}$, $k_BT=0.12$ MeV (1.4°K), and $E_0=10$ MeV. Δ is measured in units of 0.01 MeV.

We consider the most unfavorable case, Ta-(Ta Oxide)-Al, where the anomaly is largest ($\sim 10\%$). $G^{(3)}(V,T)$ must be smaller than the term in $G^{(2)}$ proportional to $T_{J_a}{}^2$ if our perturbation approach is to be valid. We assume[22] that $G^{(3)}(0,T)$ is 40% of $G^{(2)}$ for $T=1.4$°K. This implies that $J_a\rho^a\sim 0.01$, a not unreasonable value. Notice that $J_a>0$, implying antiferromagnetic coupling between the conduction-electron spin and the localized spin.

Our contention that $G^{(3)}(V,T)$ can be large enough will be established if the term in $G^{(2)}$ proportional

[21] A. A. Abrikosov, Physics **2**, 5 (1965); **2**, 61 (1965).

[22] For sufficiently small temperature $G^{(3)}$ will become larger than the $T_{J_a}{}^2$ terms in $G^{(2)}$, indicating a breakdown in our perturbation expansion. This has been discussed extensively for the Kondo effect by Abrikosov (Ref. 21), Nagaoka [Y. Nagaoka, Phys. Rev. **138**, A1112 (1965)], and Suhl [H. Suhl, Phys. Rev. **138**, A515 (1965)], among others. For our assumption that $G^{(3)}$ is 40% of $G^{(2)}$ at $T=1.4$°K, this breakdown will not occur at readily obtainable temperatures.

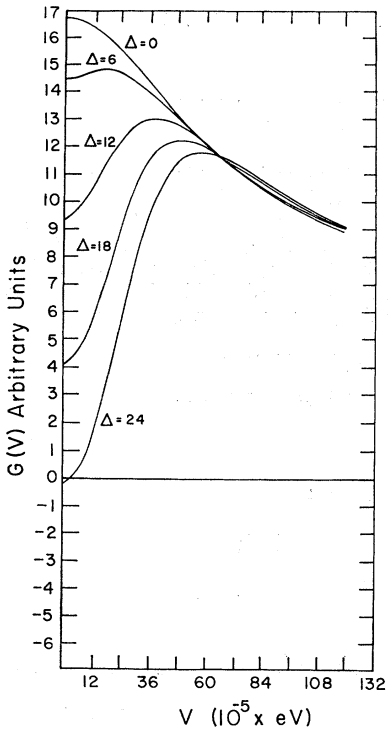

FIG. 8. The voltage-dependent part of G is plotted for different Zeeman energies Δ, and for $S=\frac{1}{2}$, $k_BT=0.12$ MeV (1.4°K), and $E_0=10$ MeV. Δ is measured in units of 0.01 MeV.

to $T_{J_a}^2$ can be shown to be a substantial fraction of $G^{(2)}$ (20%). We begin by remarking that

$$(T_a^2+S(S+1)T_{J_a}^2)N_a$$

may predominate over T^2 even for spin concentrations of a few percent. This is because (as noted by Anderson[12]) the localized states act as a bridge between the exponentially tailing wave functions of the conduction electrons on opposite sides of the junction, effectively decreasing the size of the barrier for those electrons which tunnel across the junction by means of the localized states. Because the coupling constants vary exponentially with junction thickness, a decrease in the effective thickness of the junction by a few angstroms could make $T_a^2+S(S+1)T_{J_a}^2$ sufficiently greater than T^2 to compensate the factor N_a.

In a magnetic field we must use for G the rather complicated expressions given in (67)–(73). The effect of the magnetic field on $G^{(3)}$ is to split the peak into three peaks, one centered on zero-voltage bias (70) and the other two displaced symmetrically to either side of zero bias by Δ. The coefficient of $F(eV)$ in (70) is the same as those of $F(eV-\Delta)$ and $F(eV+\Delta)$ as $\Delta\to 0$. As Δ becomes large the coefficient of $F(eV)$ tends to zero while those of $F(eV-\Delta)$ and $F(eV+\Delta)$ do not change greatly, which has the effect that one never sees the center peak, but only the two displaced peaks.

The magnetic field also affects $G^{(2)}$ through the last term in (68). The effect of this term is to decrease $G^{(2)}$ near zero voltage. The smaller the spin of the localized state, the greater the change. The combined effect of the destruction of the central peak in $G^{(3)}$ and this decrease in $G^{(2)}$ can, somewhat surprisingly, cause G to dip below background near zero voltage for large enough fields (see Fig. 8). This is because the background current contains contributions from $T_{J_a}^2$ as well as T^2.

The effect of the magnetic field on G is clearly revealed in Figs. 6, 7, and 8. We have plotted the conductance versus voltage at fixed temperature for various values[23] of Δ and for different choices of the spin. We have assumed as above that $G^{(3)}(0,T)$ is 40% of $G^{(2)}$ for $T=1.4$°K ($\Delta=0$) and that $E_0=10$ MeV.

Some preliminary data taken by Rowell and Shen on the magnetic field dependence of G exhibits the same functional dependence of G on magnetic field as shown in Figs. 6, 7, and 8. Because of the complex character of the paramagnetic centers, the effective g and S values which may be needed to fit experiment vary depending on the particular A-O-B junction studied,[24] but in all cases where the anomaly is small the theoretical functional dependence is in good agreement with the observed field effects.

ACKNOWLEDGMENTS

The author has benefited from discussions with K. Bennemann, M. H. Cohen, H. Fritzsche, and J. C. Phillips. He would like to thank L. Y. L. Shen and J. Rowell for making available to him some preliminary data on the magnetic field dependence of the anomalous conductance in Sr–SnO_z–Sn and Ta–TaO_2–Al tunnel junctions. Finally, the author wishes to express his appreciation to J. C. Phillips for suggesting this problem and for his encouragement and guidance during its execution.

[23] Δ has been used as a parameter instead of H because of the difficulty of estimating the g value of the localized states.

[24] In the Ta–Ta oxide–Al junction, for example, an interstial Ta atom could have a g value between 0.4, its free atom L-S coupling value, and 2, which would correspond to complete crystal-field quenching of the orbital angular momentum.