STS in a superconducting junction and the ac-Josephson effect: A new type of spectroscopy

Klaus Baberschke
Institut für Experimentalphysik
Freie Universität Berlin
Arnimallee 14   D-14195 Berlin-Dahlem
Germany

e-mail: bab@physik.fu-berlin.de
http://www.physik.fu-berlin.de/~bab

1. Quasi particle tunneling
2. Josephson effect = pair tunneling, dc, ac
3. Our ac Josephson spectroscopy (~30 years ago)
4. Proposal for a new ac Josephson UHV-LT-STS

Single electron tunneling (quasi particle)

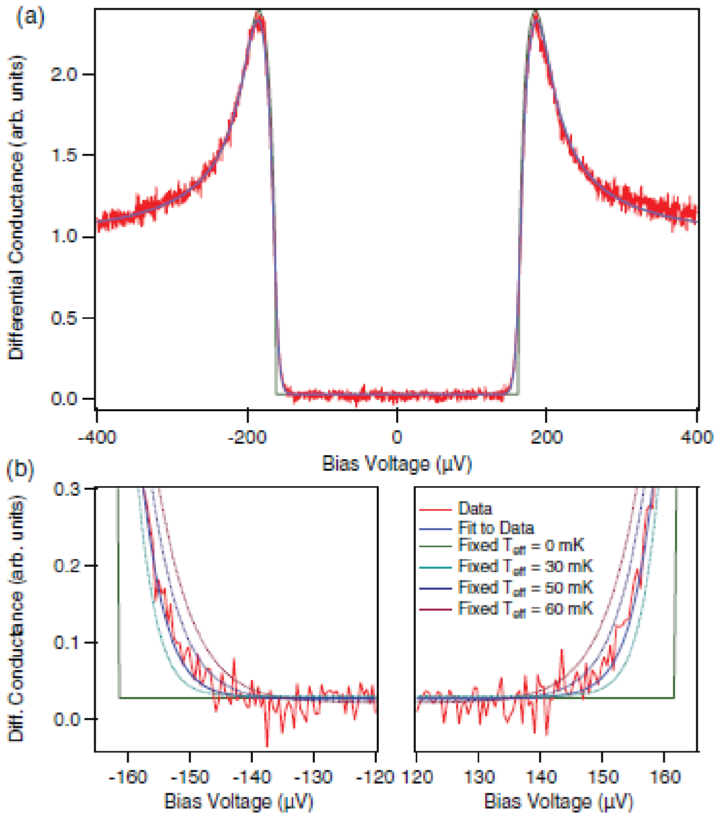
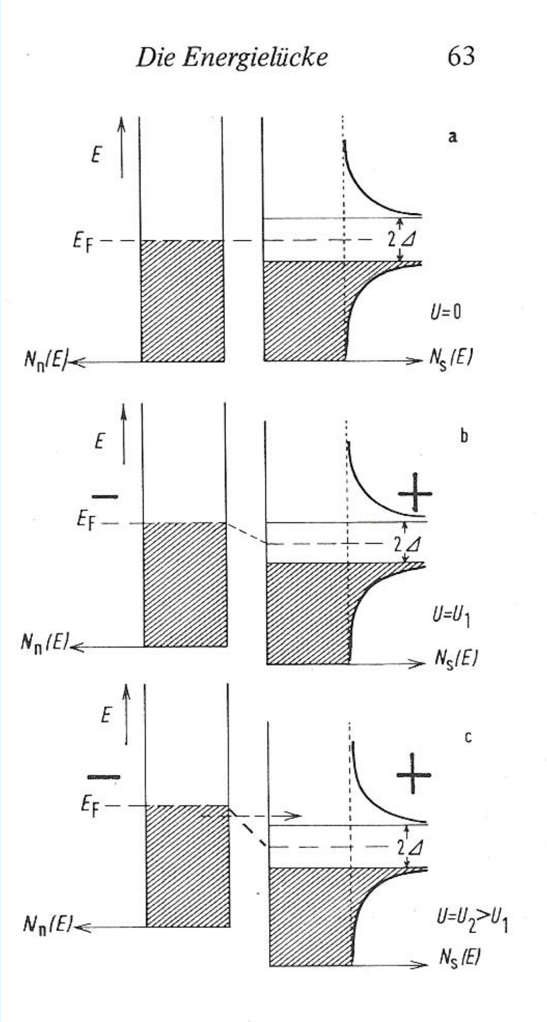


FIG. 16. Measurement of the tunneling conductance between a superconducting Al tip and a Cu(111) surface. (a) The conductance spectrum is shown in red and the fit to the Maki equation is shown in blue. For comparison, a fit at 0 mK is shown in green. (b) Zoom into the corners of the gap. The 0 mK spectrum illustrates that the rounding of the corner is only due to an effective thermal broadening. For comparison, the dotted spectra show a fit to the data for different effective temperatures demonstrating the sensitivity of the fit.

Rev.Sci.Inst.84,22903(2013)



Die Energielücke 63

mal broadening of the measured conductance spectra is accounted for by a convolution of the Maki equation with the derivative of the Fermi-Dirac distribution of the metal sub-

S-S junction

$2\Delta = 3.5\ k_B T_C$; $U \approx$ mV

10 K ↔ 860 μeV

N-N junction

Kondo-resonance on
TTF-TCNQ/Au(111)
PRL **101**, 217203 (2008)

That’s what we do NOT discuss

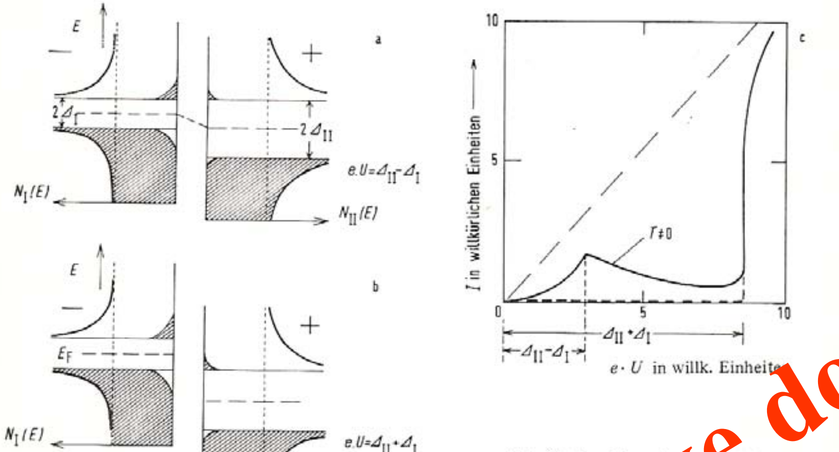


Abb. 31. Zum Tunnelstrom zwischen zwei Supraleitern, $0 < T < T_c$.

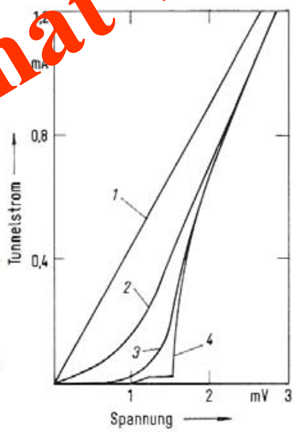
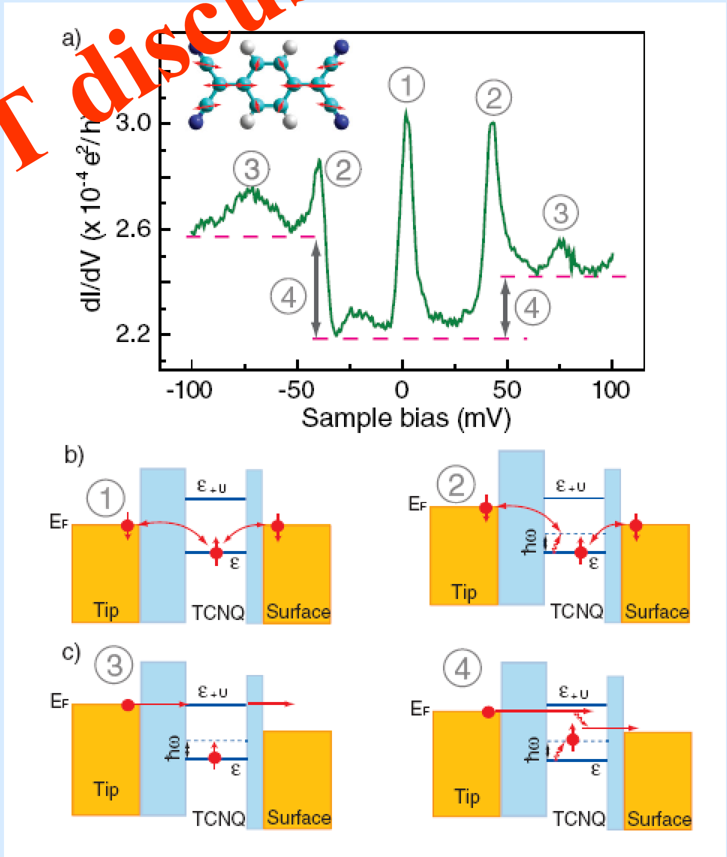


Abb. 33. Strom-Spannungs-Kennlinien eines Tunnelkontaktes Al-Al$_2$O$_3$-Pb, Registrierkurven. 1: $T = 10$ K; 2: $T = 4{,}2$ K; 3: $T = 1{,}64$ K; 4: $T = 1{,}05$ K; bei 1,05 K ist auch das Al supraleitend. Der steile Anstieg bei $eU = \Delta_I + \Delta_{II}$ ist deutlich sichtbar. Übergangstemperaturen: Pb 7,2 K; Al 1,2 (nach [54]).



Coupled superconductors SIS, SNS

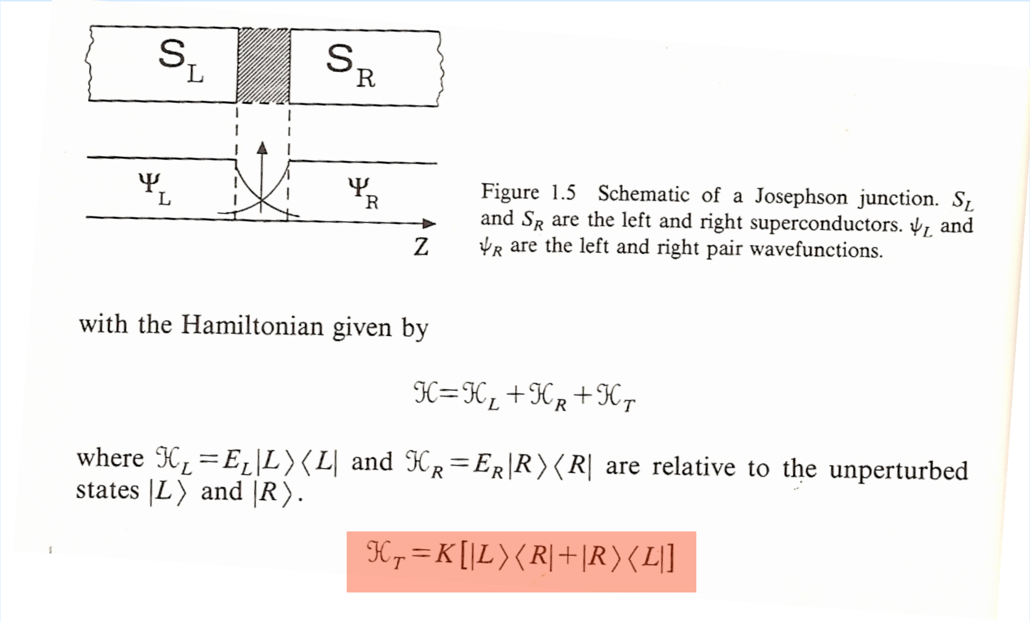


Figure 1.5 Schematic of a Josephson junction. S_L and S_R are the left and right superconductors. ψ_L and ψ_R are the left and right pair wavefunctions.

with the Hamiltonian given by

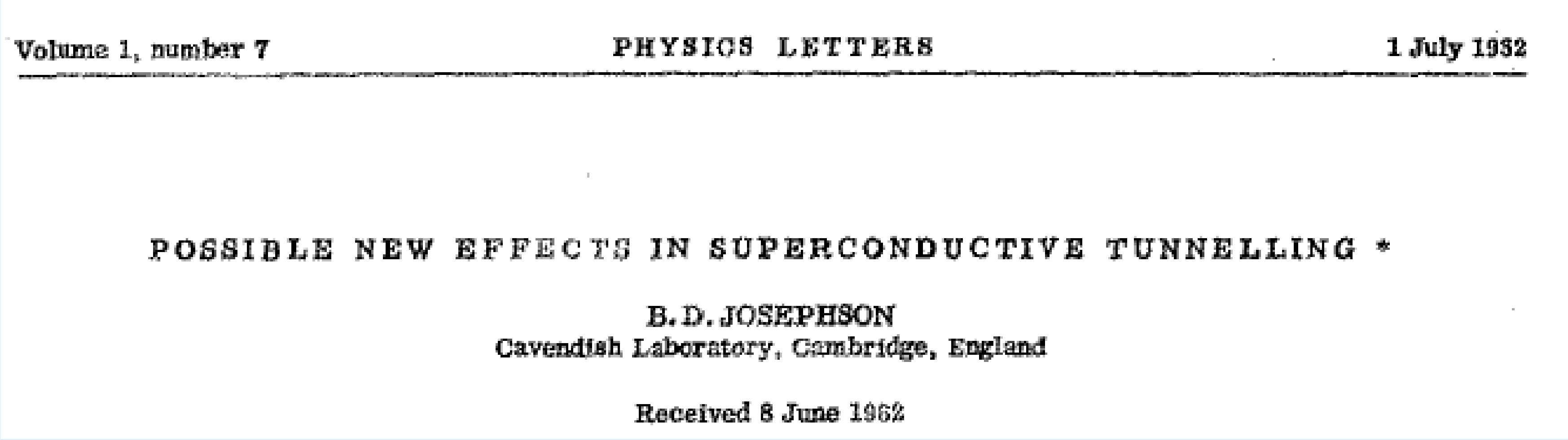
$$\mathcal{H}=\mathcal{H}_L+\mathcal{H}_R+\mathcal{H}_T$$

where $\mathcal{H}_L=E_L|L\rangle\langle L|$ and $\mathcal{H}_R=E_R|R\rangle\langle R|$ are relative to the unperturbed states $|L\rangle$ and $|R\rangle$.

$$\mathcal{H}_T=K[|L\rangle\langle R|+|R\rangle\langle L|]$$

$|\Psi_{L,R}|^2 = \rho$, Cooper pair density
order parameter

We used :   N = Au + rare earth
You may use: I = molecule monolayer



Volume 1, number 7 PHYSICS LETTERS 1 July 1962

POSSIBLE NEW EFFECTS IN SUPERCONDUCTIVE TUNNELLING *

B. D. JOSEPHSON
Cavendish Laboratory, Cambridge, England

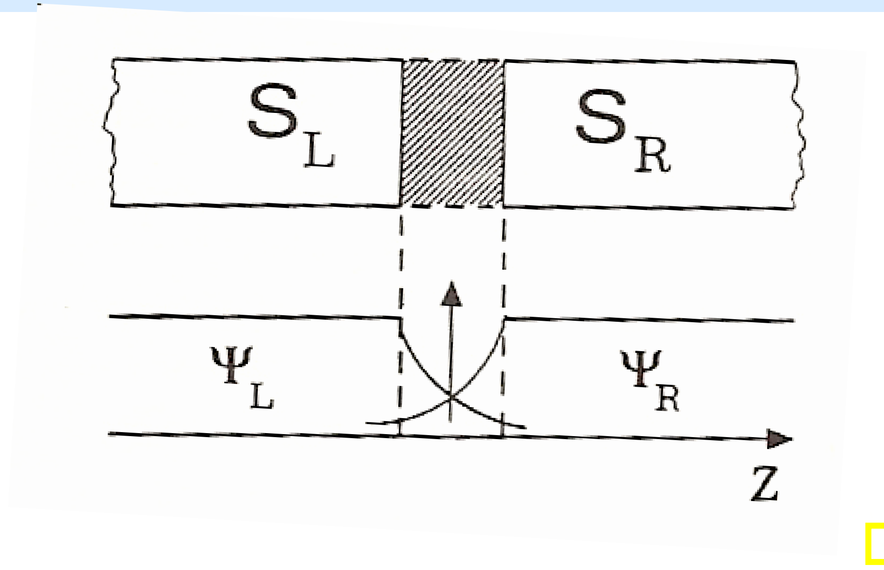
Received 8 June 1962

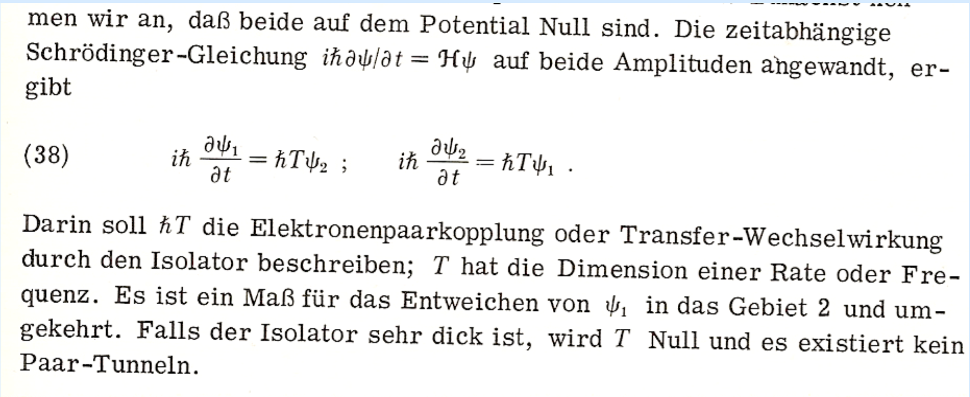
dc -Josephson effect = pair tunneling

Overlap of Ψ_L and Ψ_R. Ψ pair wave fct. leads to a tunnel current of Cooper pairs.

It's a new particle with 2e , 2m and S=0 with Bose statistic.

Ψ is **one macroscopic** wave fct for all Cooper pairs.*



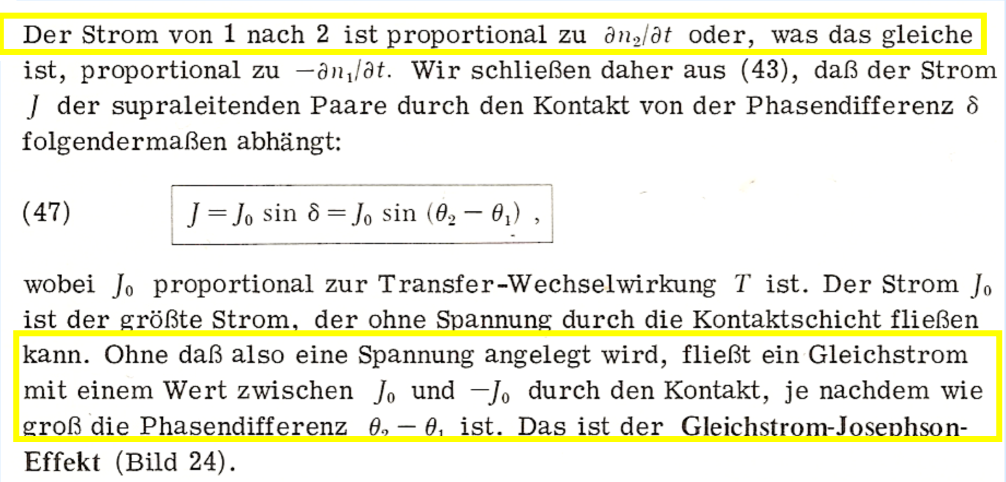


men wir an, daß beide auf dem Potential Null sind. Die zeitabhängige Schrödinger-Gleichung $i\hbar\partial\psi/\partial t = \mathcal{H}\psi$ auf beide Amplituden angewandt, ergibt

(38) $$i\hbar\frac{\partial\psi_1}{\partial t} = \hbar T\psi_2\;;\qquad i\hbar\frac{\partial\psi_2}{\partial t} = \hbar T\psi_1\;.$$

Darin soll $\hbar T$ die Elektronenpaarkopplung oder Transfer-Wechselwirkung durch den Isolator beschreiben; T hat die Dimension einer Rate oder Frequenz. Es ist ein Maß für das Entweichen von ψ_1 in das Gebiet 2 und umgekehrt. Falls der Isolator sehr dick ist, wird T Null und es existiert kein Paar-Tunneln.

$$J_0\hbar = 2T\,(\rho_L\,\rho_R)^{1/2}$$



Der Strom von 1 nach 2 ist proportional zu $\partial n_2/\partial t$ oder, was das gleiche ist, proportional zu $-\partial n_1/\partial t$. Wir schließen daher aus (43), daß der Strom J der supraleitenden Paare durch den Kontakt von der Phasendifferenz δ folgendermaßen abhängt:

(47) $$\boxed{J = J_0\sin\delta = J_0\sin(\theta_2-\theta_1)\;,}$$

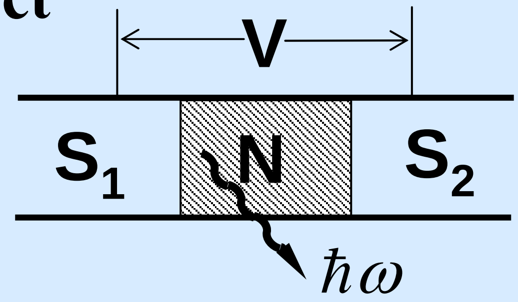
wobei J_0 proportional zur Transfer-Wechselwirkung T ist. Der Strom J_0 ist der größte Strom, der ohne Spannung durch die Kontaktschicht fließen kann. Ohne daß also eine Spannung angelegt wird, fließt ein Gleichstrom mit einem Wert zwischen J_0 und $-J_0$ durch den Kontakt, je nachdem wie groß die Phasendifferenz $\theta_2-\theta_1$ ist. Das ist der **Gleichstrom-Josephson-Effekt** (Bild 24).

* This leads to flux quantization and Fresnel interference pattern

– not discussed today.

$$\Phi_0 = hc/2e \cong 2{\bullet}10^{-7}\ \text{G}\ {\bullet}\text{cm}^2$$

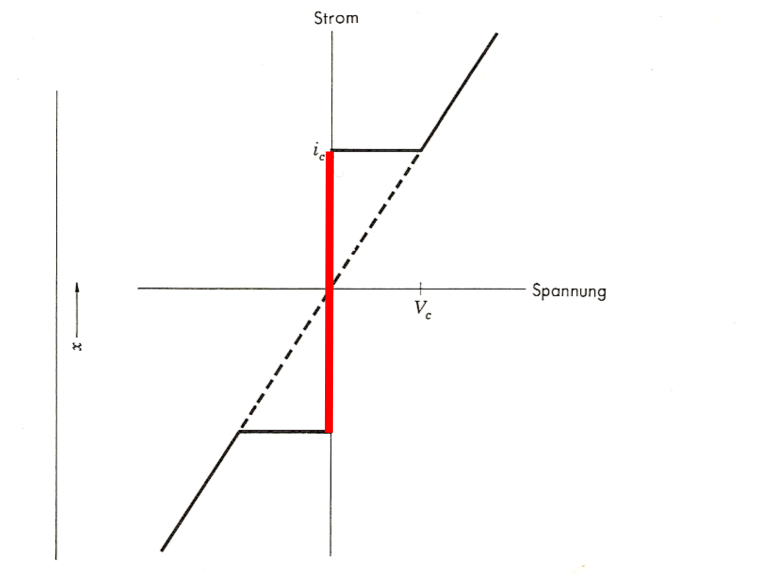
Tunnel junction + voltage = ac Josephson effect



Wechselstrom-Josephson-Effekt. Über den Kontakt sei die Spannung V angelegt. Dies ist möglich, da die Kontaktschicht ja ein Isolator ist. Ein Elektronenpaar, das den Kontakt durchquert, spürt die Potentialdifferenz qV, wobei $q=-2e$. Wir können sagen, daß ein Paar auf der einen Seite die potentielle Energie $-eV$ und ein Paar auf der anderen Seite die potentielle Energie eV hat. Die Bewegungsgleichungen, die wir jetzt anstelle von (38) schreiben müssen, sind

$$i\hbar\,\partial\psi_1/\partial t = \hbar T\psi_2 - eV\psi_1\ ; \qquad i\hbar\,\partial\psi_2/\partial t = \hbar T\psi_1 + eV\psi_2\ . \tag{48}$$

$$\partial(\theta_2-\theta_1)/\partial t = -2eV/\hbar$$



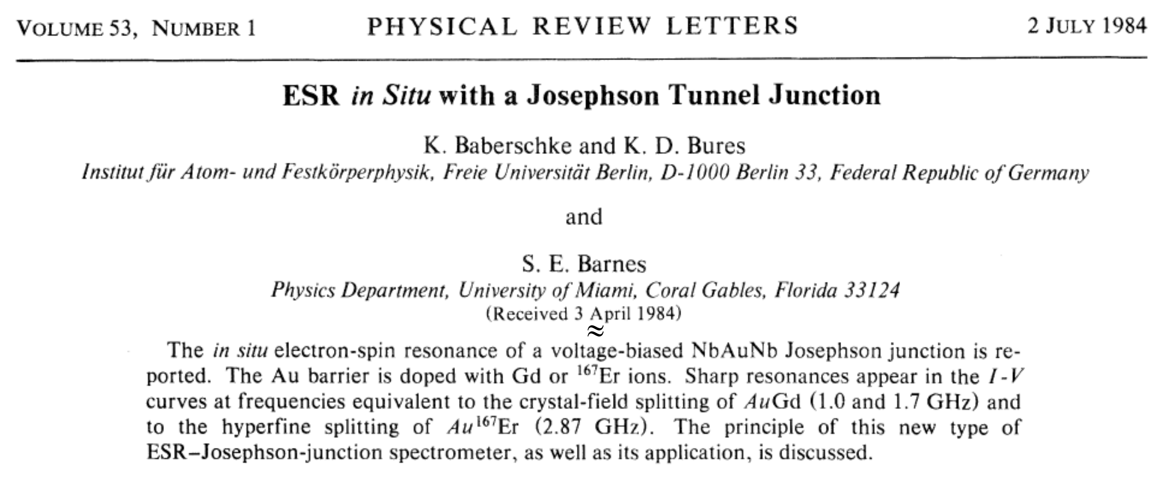
Strom-Spannungscharakteristik einer Josephson-Verbindung. Ohne angelegte Spannung fließen Gleichströme bis zu einem kritischen Strom der Stärke i_c: Das ist der DC-Josephsoneffekt. Bei Spannungen über V_c hat die Verbindung einen bestimmten Widerstand, der Strom hat jedoch einen oszillierenden Anteil mit der Frequenz $\omega = 2eV/\hbar$: Das ist der AC-Josephsoneffekt.

$$J = J_0 \sin(\Delta\Theta - 2eVt/\hbar)$$

$$h\nu = 2eV$$

$$483.6\ \text{MHz} \leftrightarrow 1\,\mu\text{V}$$

Our ac Josephson spectroscopy



VOLUME 53, NUMBER 1 PHYSICAL REVIEW LETTERS 2 JULY 1984

ESR *in Situ* with a Josephson Tunnel Junction

K. Baberschke and K. D. Bures

Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, Federal Republic of Germany

and

S. E. Barnes

Physics Department, University of Miami, Coral Gables, Florida 33124

(Received 3 April 1984)

The *in situ* electron-spin resonance of a voltage-biased NbAuNb Josephson junction is reported. The Au barrier is doped with Gd or ^{167}Er ions. Sharp resonances appear in the I-V curves at frequencies equivalent to the crystal-field splitting of AuGd (1.0 and 1.7 GHz) and to the hyperfine splitting of Au^{167}Er (2.87 GHz). The principle of this new type of ESR–Josephson-junction spectrometer, as well as its application, is discussed.

ac-Josephson effect
as MW-generator
and current as detector

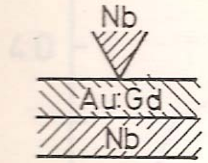


Abb.2.1a

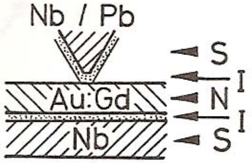
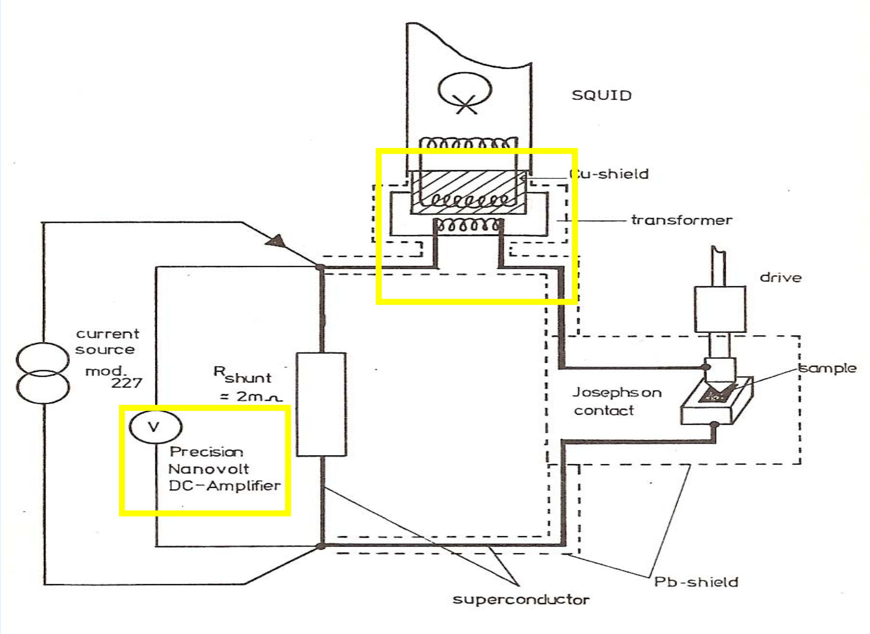
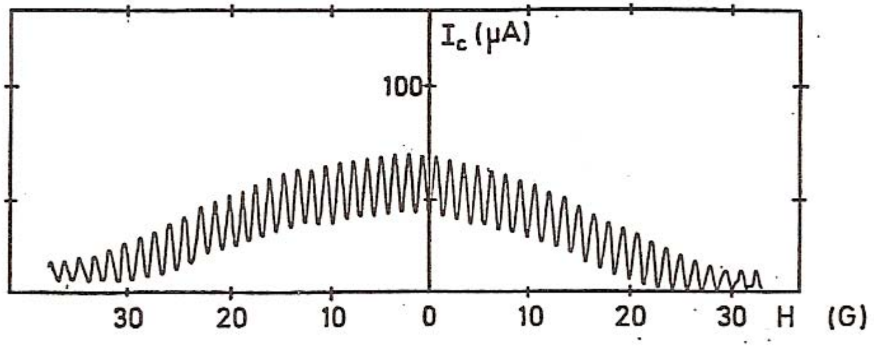


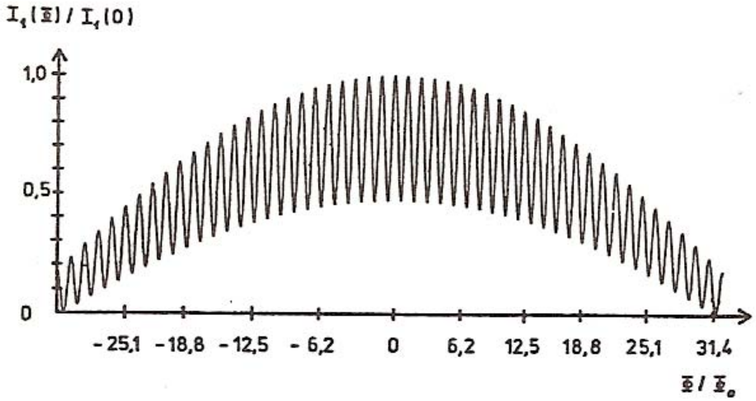
Abb.2.1b

We worked with a tip and film thickness of r and d of few µm, R ≈ 0.5 Ω





I_c(H) der Pr. 2 NbAuGdPb

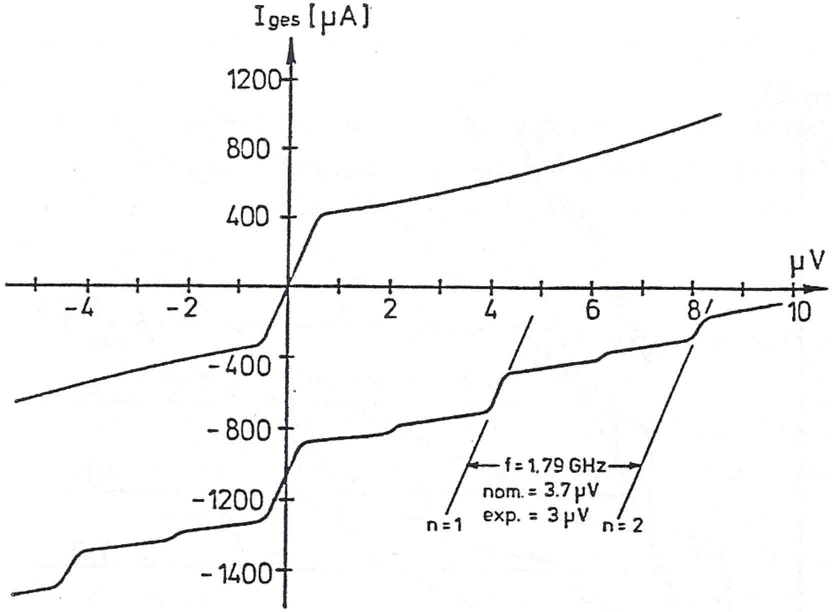


Simulation

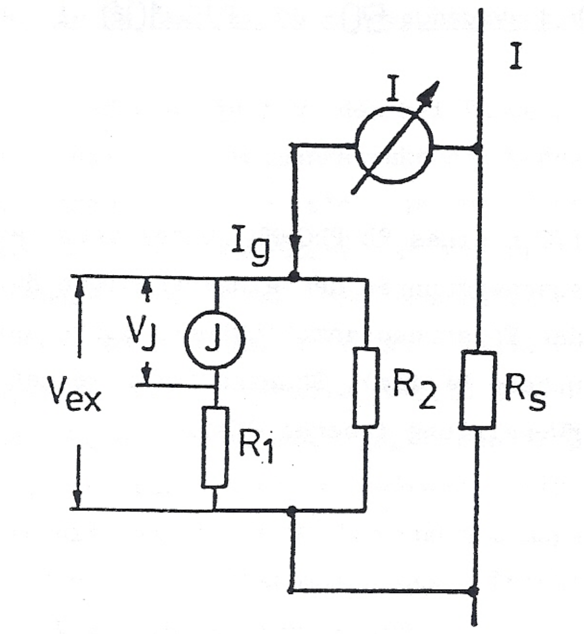
Proof for a good Josephson junction:

Fraundofer diffraction pattern:

$$I \approx \cos(\pi\Phi/\Phi_0)$$



Die gemessenen Stufenbreiten sind kleiner als die nach Gl. 0.3 bestimmten. Das Verhalten dieser resistiven Kontakte kann durch ein Ersatzschaltbild (Abb. 2.22) beschrieben werden. Danach hat die Josephsonverbindung J einen Serienwiderstand R_1 und einen Parallelwiderstand R_2 über J und R_2.



$$i_{tot} = \frac{V}{R} + \frac{i_c^2 R}{2V}$$

Rf-driven Junctions

Shapiro steps

Photon-assisted tunneling

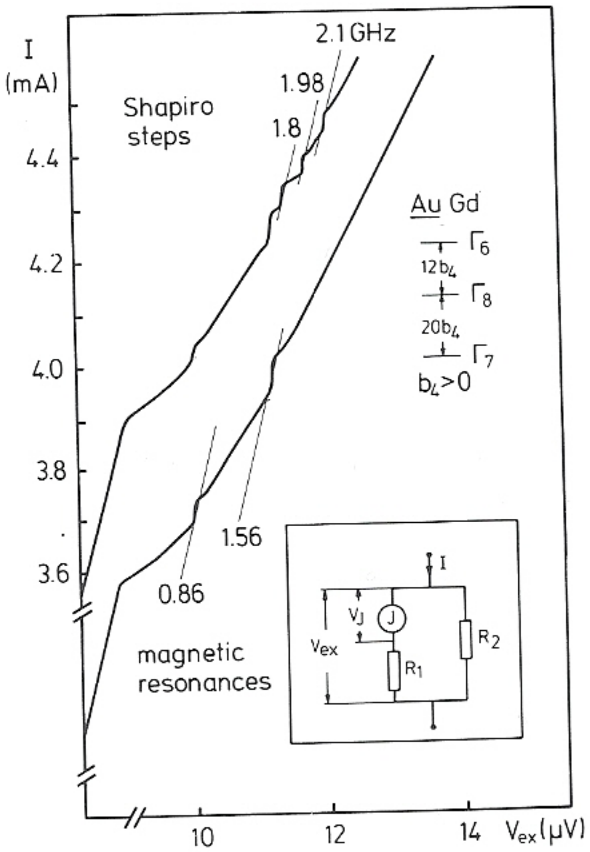


Fig. 1. Two resonances of AuGd (1000 ppm) (lower recorder trace). Resonances and additional Shapiro steps (upper trace). Equivalent circuit of the Josephson junction (lower insert).

For ac Jospheson effects

see standard literature

books by

P. G. de Genne 1964

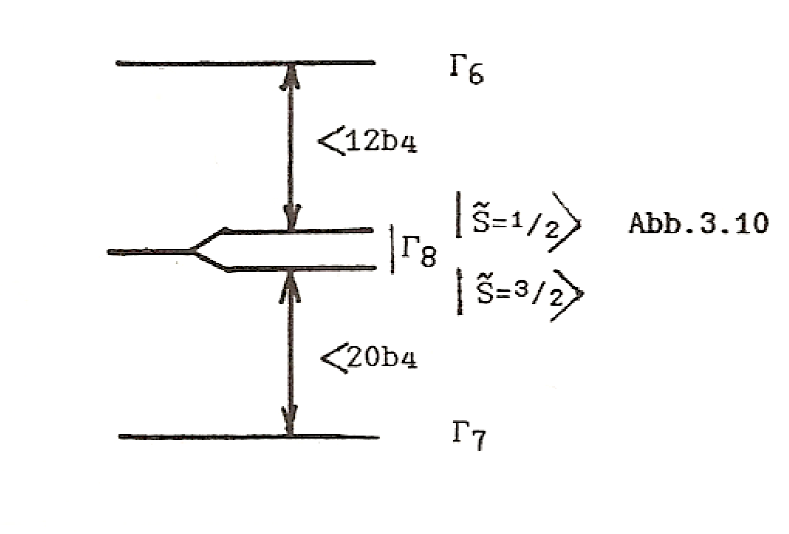
M. Tinkham 1996

A. Barone 1982

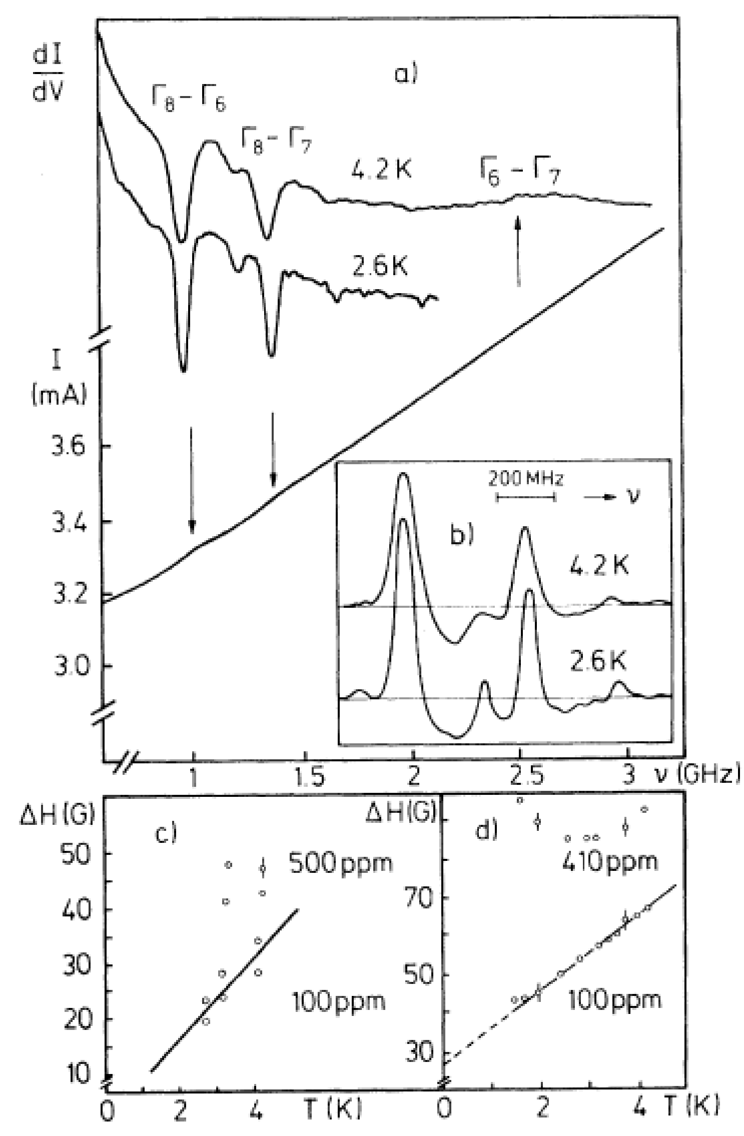
483,6 MHz = 1μV

Gd^{3+} => $^8S_{7/2}$ => 2S+1 = 8

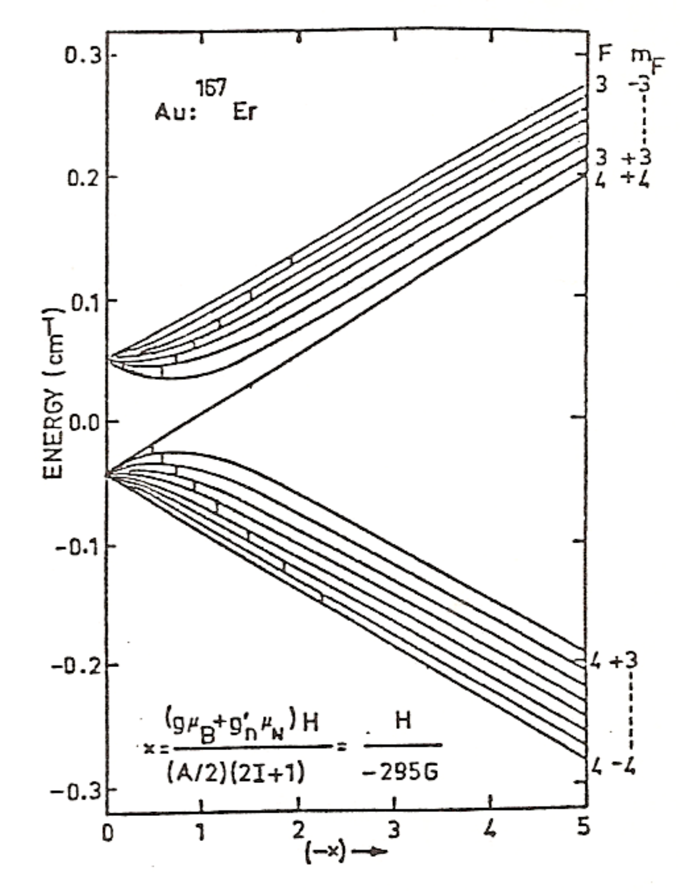
Crystal field splitting

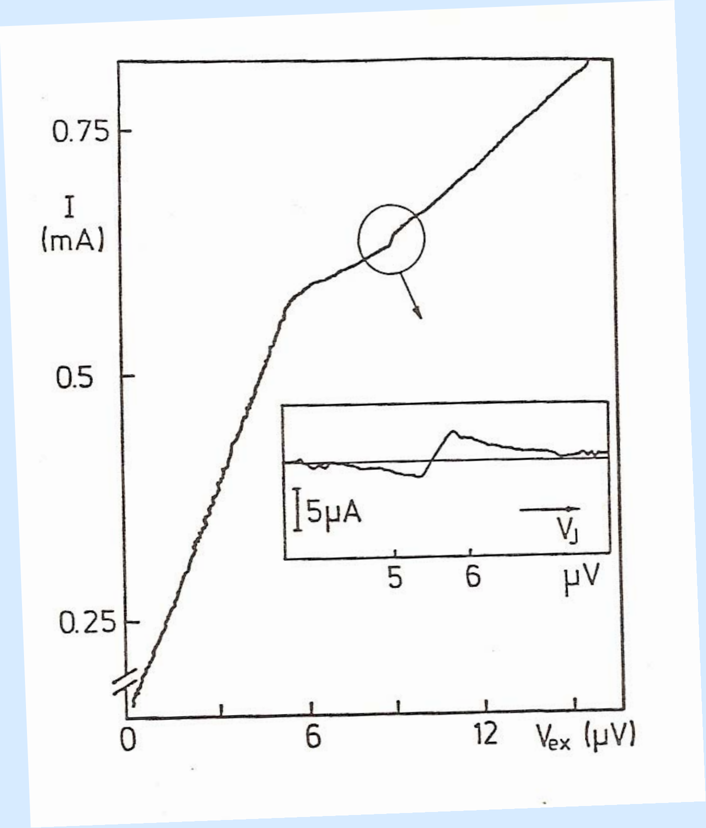


cubic or lower symmetry



Hyperfine splitting of Au ^{167}Er, S + I = F = 3 and 4



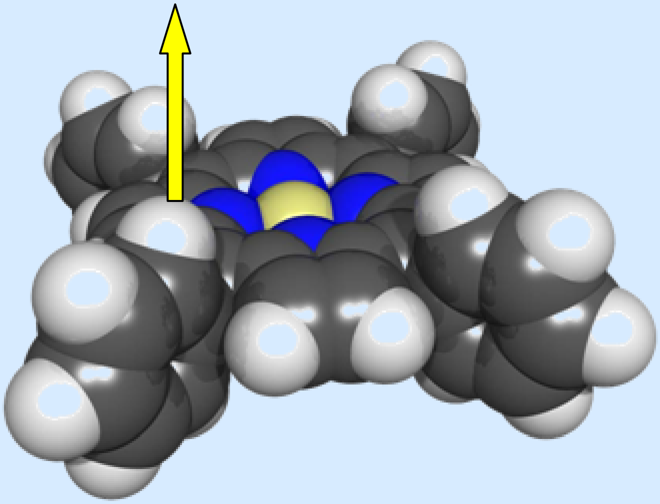


ΔE_{theo} = 2.87 GHz ;

V_{res}= 5.4(2) µV, ν_{res}=2.6(1) GHz

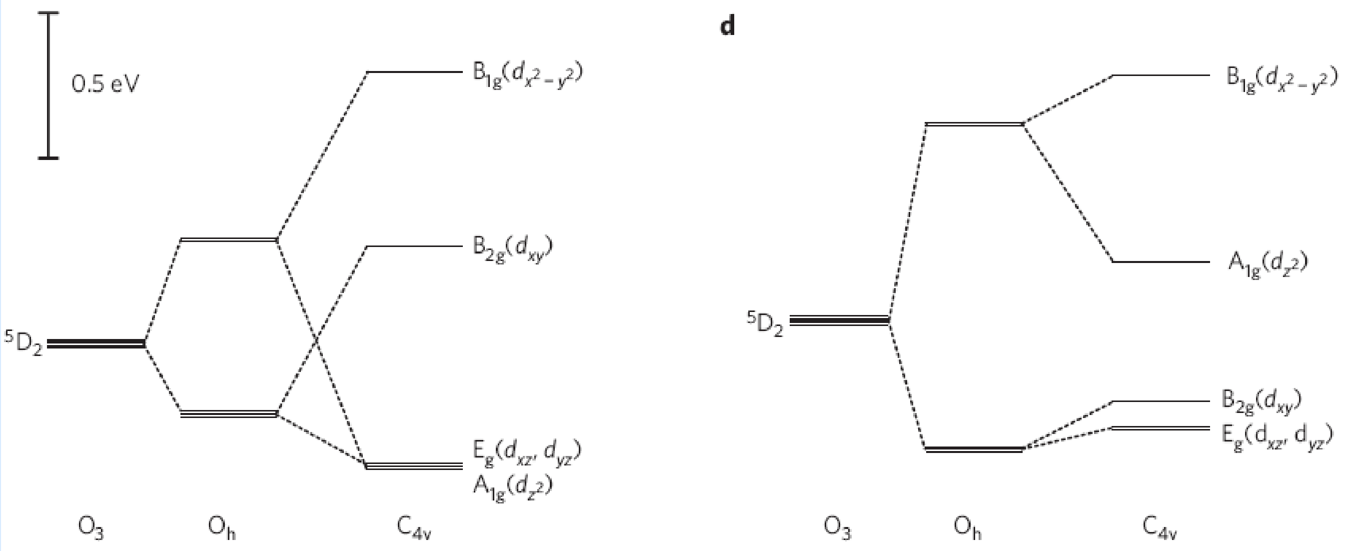
Proposal for new ac Josephson UHV-LT-STS

Fe^{3+} S=5/2



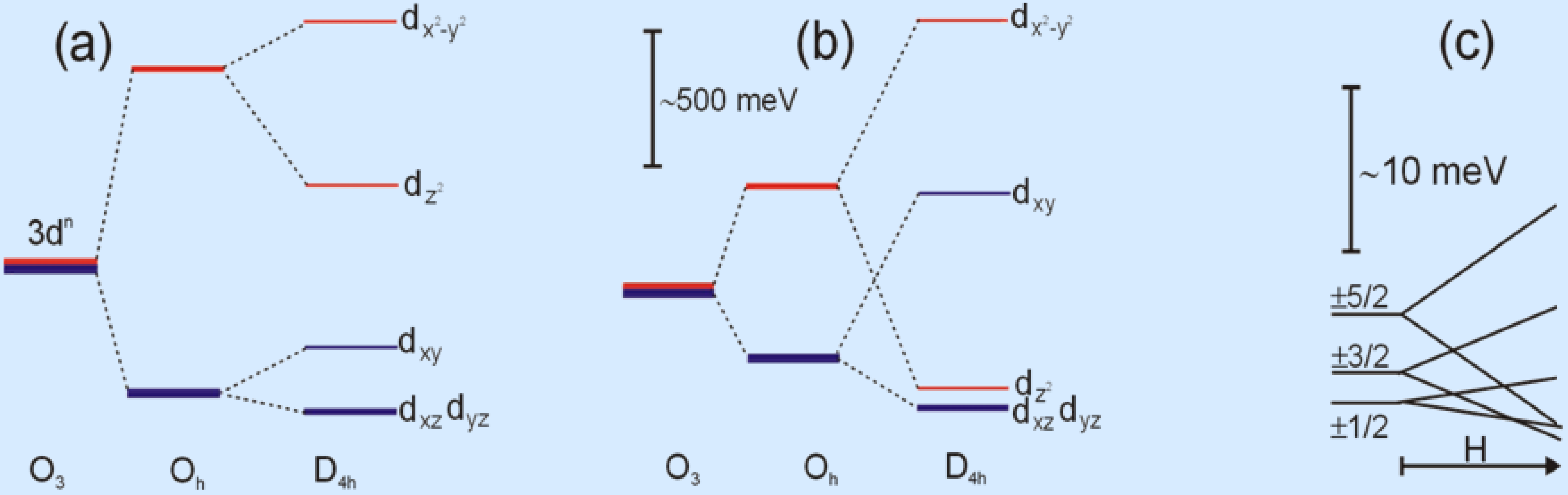
Molecular monolayer
and superconducting
tip and substrate crystal,
e.g. Pb.

Fe^{3+} or Fe^{2+},
HS or LS,
finally there will be
some ZFS within
the (2S+1) manifold



$3d^n$-energy scheme and magnetism of the Fe-ion

Fe $^{3+,2+}$
S= 5/2, 3/2, 1/2
S= 2, 1, 0



Dramatic change of ligand field upon
coadsorption of oxygen.

Gambardella et al. 2009,

Bernien et al. 2009

Unperturbed e_g, t_{2g} eigenstates are no good.

“zero field splitting” ≡ CEF

20110 Ü **Übung zur Festkörperphysik II** **SS 1998**

Baberschke
Farle
Bovensiepen

Ausgabe: 28.0498 Abgabe: 08.05.98

Für einen 3d^1 Zustand mit MX$_6$ Liganden ist die Energieaufspaltung in tetragonaler Symmetrie wie folgt gegeben:

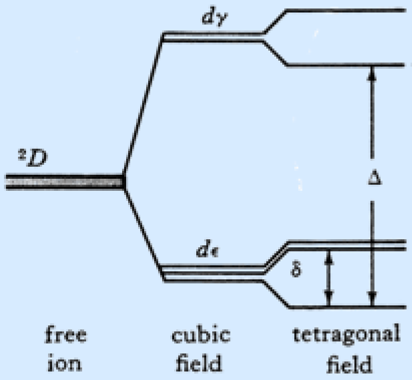


Fig. 3-4 Splitting of the ^2D term by a tetr

3) Berechnen Sie für den Grundzustand

$$\Psi_{2-} = (2)^{-1/2}\{|2> -$$

die Beimischung der angeregten Zustände durc
Spinzustände einzuführen sind (zweckmäßig α|2-> und β|2-> für Spin "up" and "down")

(2 P)

4.) Gerechnen Sie für den in Ü3 gefundenen neuen Grundzustand die anisotropen g-Faktoren g_Z, g_X=g_Y durch "Einschalten" der Zeeman Ww: $\mu_B(L+g_eS)H$ (3 P)

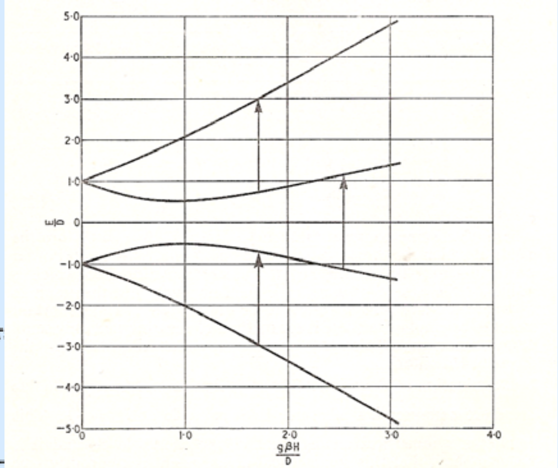
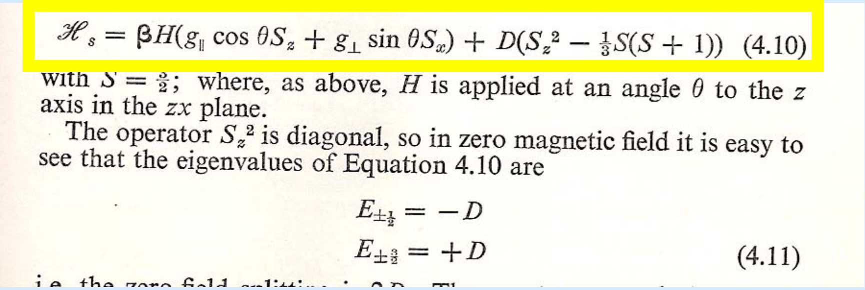


Fig. 4.1. 'Symmetrical' energy levels for the system $S = \frac{3}{2}$ in axial crystal field. The magnetic field H is applied at an angle $\cos^{-1}(1/\sqrt{3})$ (54° 44′) to the crystalline axis

i.e. when the zero field splitting $2D$ is large compared to the micro-



$$\mathscr{H}_s = \beta H(g_\parallel \cos\theta S_z + g_\perp \sin\theta S_x) + D(S_z^2 - \tfrac{1}{3}S(S+1)) \quad (4.10)$$

with $S = \frac{3}{2}$; where, as above, H is applied at an angle θ to the z axis in the zx plane.

The operator S_z^2 is diagonal, so in zero magnetic field it is easy to see that the eigenvalues of Equation 4.10 are

$$E_{\pm\frac{1}{2}} = -D$$
$$E_{\pm\frac{3}{2}} = +D \quad (4.11)$$

i.e. the zero field splitting is 2D.

Zero field splitting:

For Cr^{3+} => S=3/2, in Al$_2$O$_3$

For Fe^{3+} => S=5/2

Splitting in $E_{\pm1/2}$, $E_{\pm3/2}$,$E_{\pm5/2}$

ΔE = 2D, 4D

Range 5 to 40 GHz, Bittl paper

20110 Ü **Übung zur Festkörperphysik II** SS 1998
Baberschke
Farle
Bovensiepen

Ausgabe: 28.0498 Abgabe: 08.05.98

Für einen $3d^1$ Zustand mit MX_6 Liganden ist die Energieaufspaltung in tetragonaler Symmetrie wie folgt gegeben:

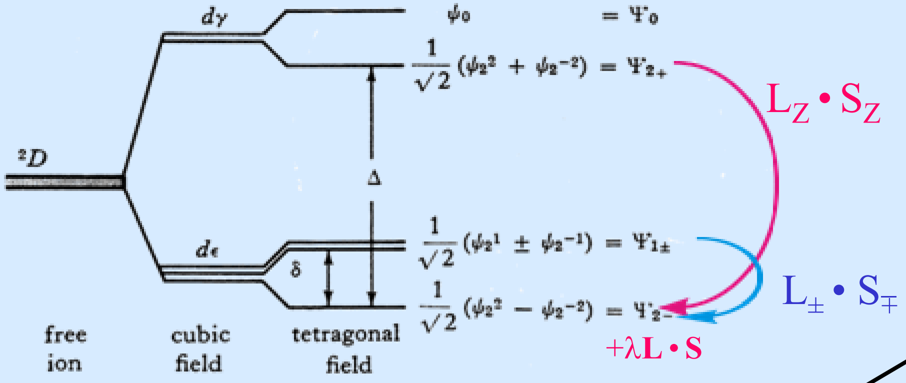


Fig. 3-4 Splitting of the ^2D term by a tetragonally distorted cubic field.

3) Berechnen Sie für den Grundzustand

$$\psi_{2-} \equiv (2)^{-1/2}\{|2> - |-2>\} \equiv |2->$$

die Beimischung der angeregten Zustände durch $\lambda \mathbf{L} \cdot \mathbf{S}$ und beachten Sie dabei, daß auch Spinzustände einzuführen sind (zweckmäßig $\alpha|2->$ und $\beta|2->$ für Spin "up" and "down")

(2 P)

4.) Gerechnen Sie für den in Ü3 gefundenen neuen Grundzustand die anisotropen g-Faktoren g_Z, $g_X = g_Y$ durch "Einschalten" der Zeeman Ww: $\mu_B(\mathbf{L}+g_e\mathbf{S})\mathbf{H}$ (3 P)

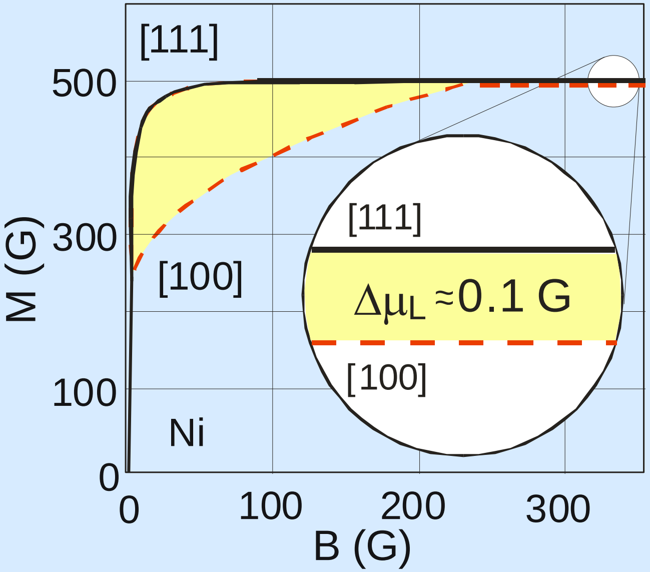
The orbital moment is quenched in cubic symmetry

$$\langle 2- | L_Z | 2- \rangle = 0,$$

but not for tetragonal symmetry

Magnetic Anisotropy Energy (MAE) and anisotropic μ_L

1. Magnetic anisotropy energy = f(T)
2. Anisotropic magnetic moment ≠ f(T)



$$g_{||} - g_{\perp} = g_e\lambda(\Lambda_{\perp} - \Lambda_{||})$$

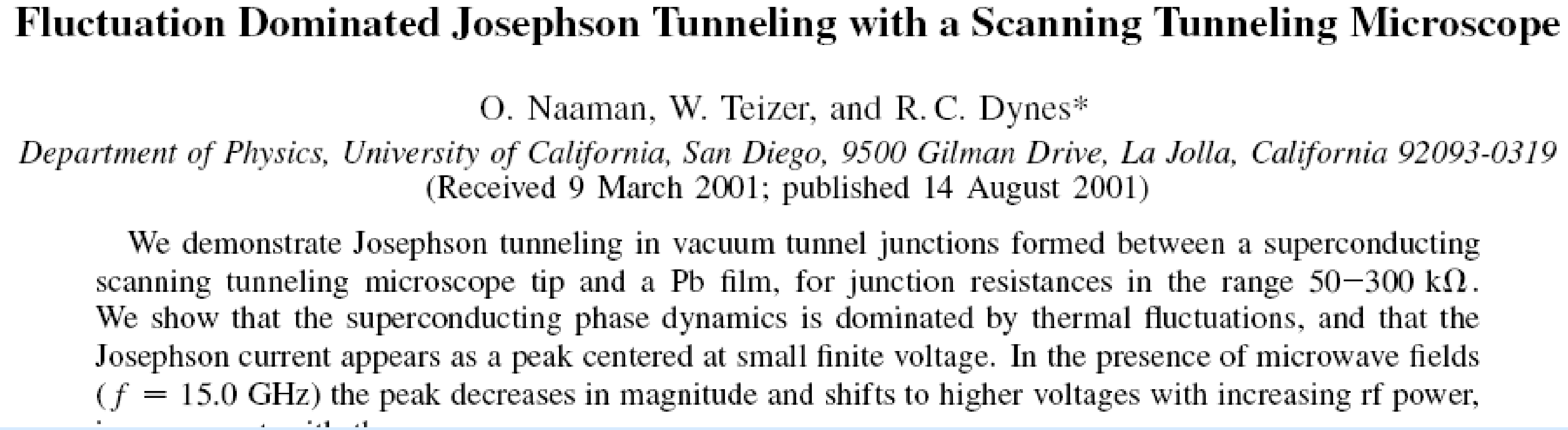
anisotropic μ_L ↔ MAE

$$D = \frac{\lambda}{g_e}\Delta g$$

$$\mathrm{MAE} \propto \frac{\xi_{LS}}{4\mu_B}\Delta\mu_L$$ Bruno (‘89)

Orbital magnetic moments are small, but all important

K. Baberschke, Lecture Notes in Physics, Springer **580**, 27 (2001)

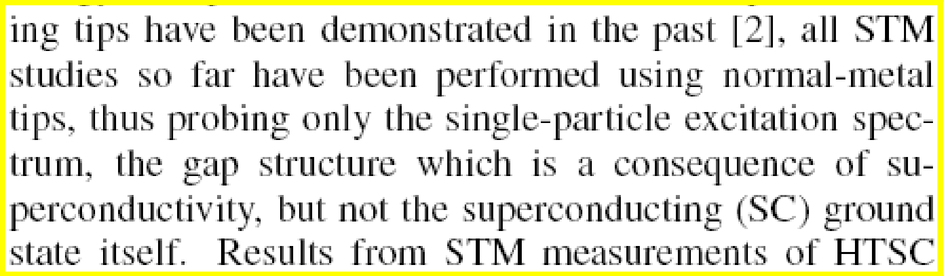


Fluctuation Dominated Josephson Tunneling with a Scanning Tunneling Microscope

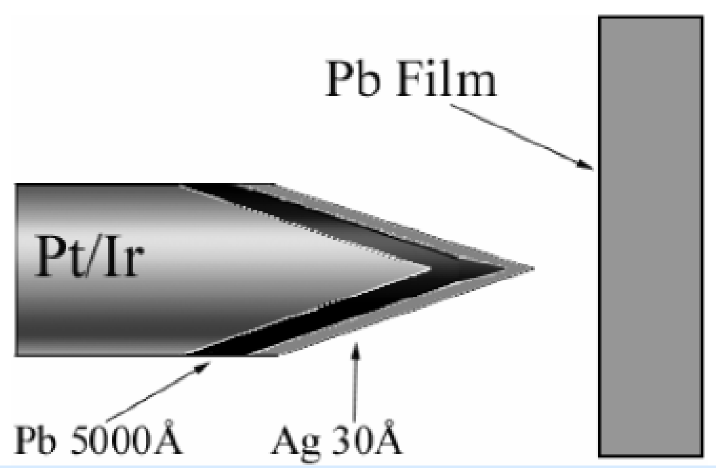
O. Naaman, W. Teizer, and R. C. Dynes*
Department of Physics, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093-0319

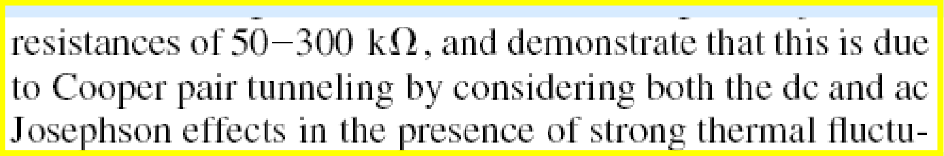
(Received 9 March 2001; published 14 August 2001)

We demonstrate Josephson tunneling in vacuum tunnel junctions formed between a superconducting scanning tunneling microscope tip and a Pb film, for junction resistances in the range 50–300 kΩ. We show that the superconducting phase dynamics is dominated by thermal fluctuations, and that the Josephson current appears as a peak centered at small finite voltage. In the presence of microwave fields ($f = 15.0$ GHz) the peak decreases in magnitude and shifts to higher voltages with increasing rf power,

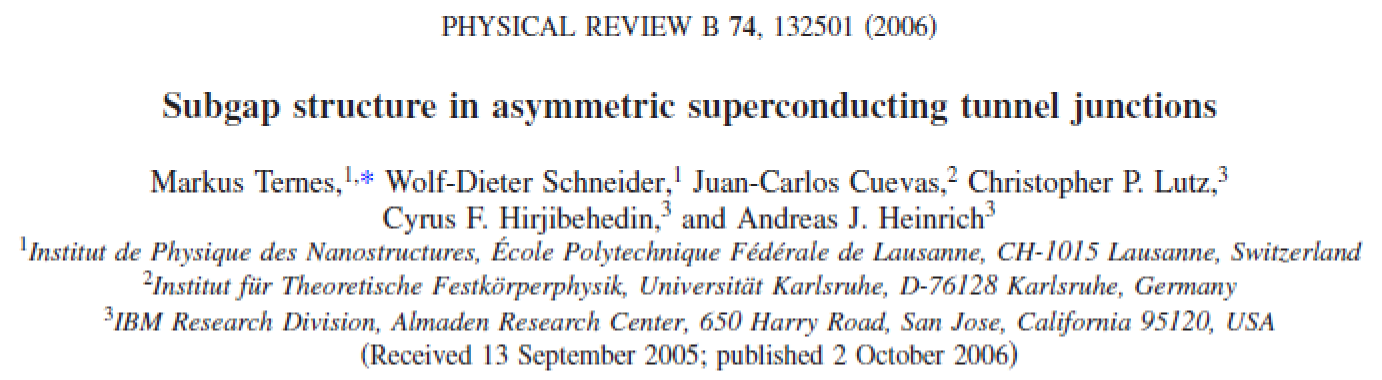


ing tips have been demonstrated in the past [2], all STM studies so far have been performed using normal-metal tips, thus probing only the single-particle excitation spectrum, the gap structure which is a consequence of superconductivity, but not the superconducting (SC) ground state itself. Results from STM measurements of HTSC





resistances of 50–300 kΩ, and demonstrate that this is due to Cooper pair tunneling by considering both the dc and ac Josephson effects in the presence of strong thermal fluctu-



PHYSICAL REVIEW B 74, 132501 (2006)

Subgap structure in asymmetric superconducting tunnel junctions

Markus Ternes,[1,*] Wolf-Dieter Schneider,[1] Juan-Carlos Cuevas,[2] Christopher P. Lutz,[3]
Cyrus F. Hirjibehedin,[3] and Andreas J. Heinrich[3]
[1]*Institut de Physique des Nanostructures, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[2]*Institut für Theoretische Festkörperphysik, Universität Karlsruhe, D-76128 Karlsruhe, Germany*
[3]*IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120, USA*
(Received 13 September 2005; published 2 October 2006)

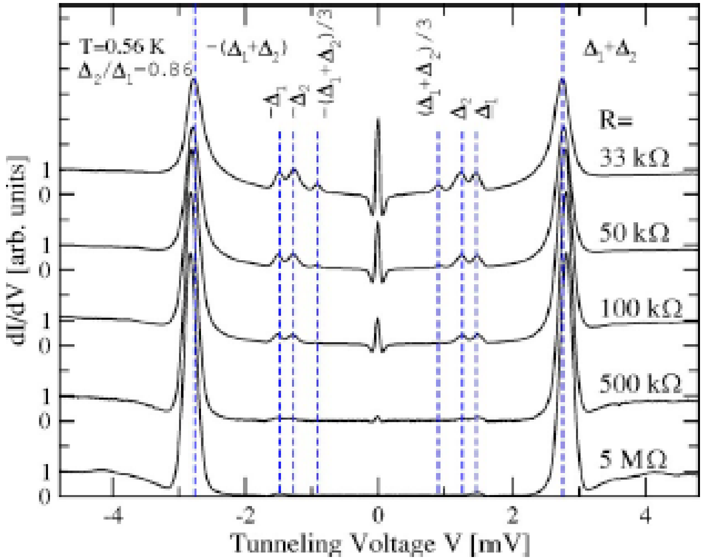
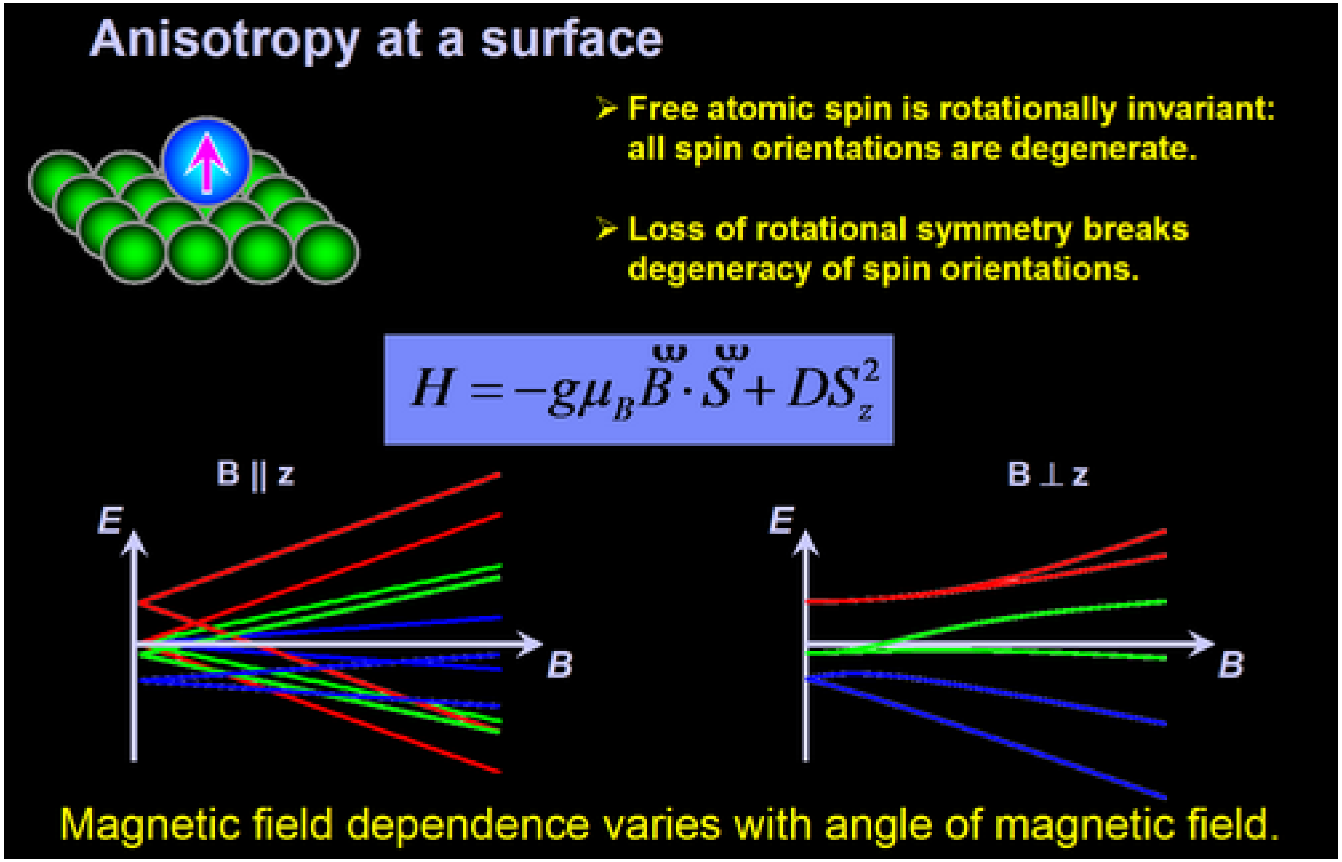


FIG. 1. (Color online) *dI*/*dV* spectra observed at 0.56 K between a superconducting sample and tip with nearly equal gaps ($\Delta_1 = 1.47$ meV, $\Delta_2 = 1.27$ meV) showing Andreev reflections for different junction resistances. All spectra are normalized by *R*. The peak evolving at $V=0$ is due to the Josephson supercurrent. The dotted lines are a guide for the eye marking characteristic features in the spectra. The spectra are shifted vertically with respect to each other for better visibility.

100μV ≈ 48 GHz

Magnetic Anisotropy



Anisotropy at a surface

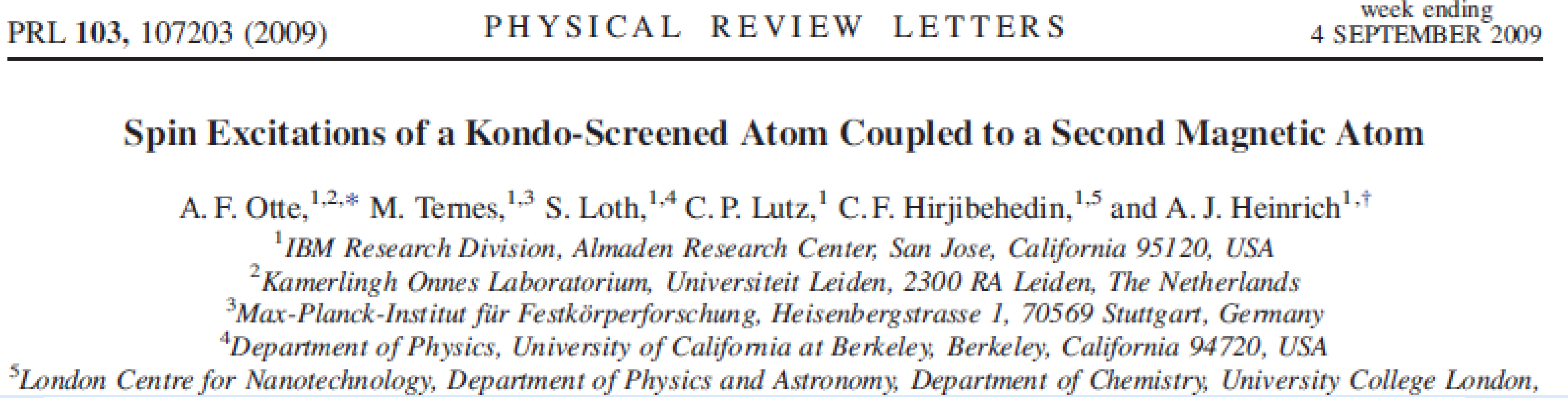
- Free atomic spin is rotationally invariant: all spin orientations are degenerate.
- Loss of rotational symmetry breaks degeneracy of spin orientations.

$$H = -g\mu_B \vec{B}\cdot\vec{S} + DS_z^2$$

Magnetic field dependence varies with angle of magnetic field.

Cyrus F. Hirjibehedin, Chiung-Yuan Lin, Alexander F. Otte, Markus Ternes, Christopher P. Lutz, Barbara A. Jones, and Andreas J. Heinrich, "Large Magnetic Anisotropy of a Single Atomic Spin Embedded in a Surface Molecular Network," *Science* **317**, 1199 (2007).

variable frequencies 0.5 – 50 GHz are needed to measure CFS with and without magnetic fields

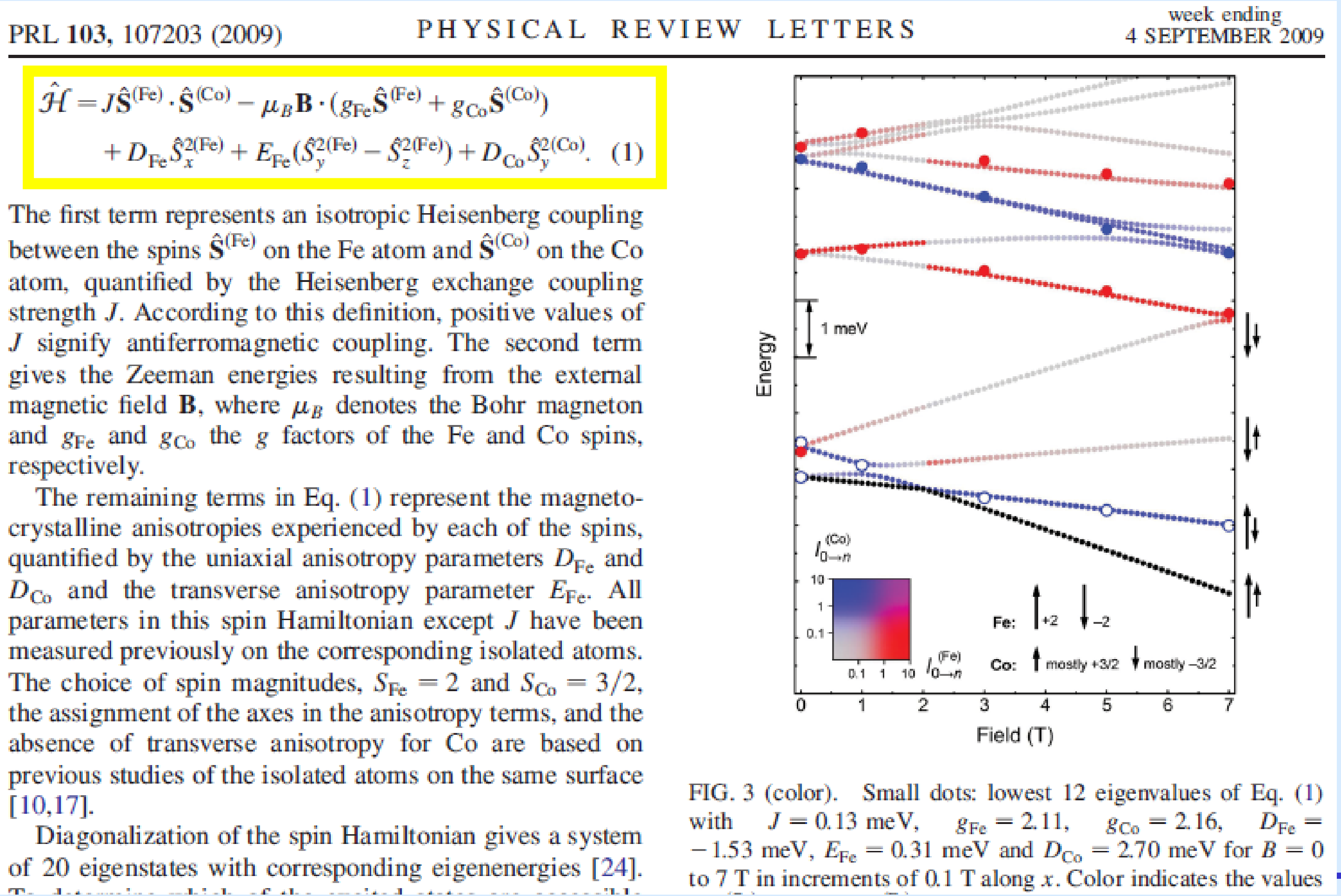


PRL **103,** 107203 (2009) PHYSICAL REVIEW LETTERS week ending 4 SEPTEMBER 2009

Spin Excitations of a Kondo-Screened Atom Coupled to a Second Magnetic Atom

A. F. Otte,[1,2,*] M. Ternes,[1,3] S. Loth,[1,4] C. P. Lutz,[1] C. F. Hirjibehedin,[1,5] and A. J. Heinrich[1,†]

[1]*IBM Research Division, Almaden Research Center, San Jose, California 95120, USA*
[2]*Kamerlingh Onnes Laboratorium, Universiteit Leiden, 2300 RA Leiden, The Netherlands*
[3]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany*
[4]*Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA*
[5]*London Centre for Nanotechnology, Department of Physics and Astronomy, Department of Chemistry, University College London,*



$$\hat{\mathcal{H}} = J\hat{\mathbf{S}}^{(\mathrm{Fe})}\cdot\hat{\mathbf{S}}^{(\mathrm{Co})} - \mu_B \mathbf{B}\cdot(g_{\mathrm{Fe}}\hat{\mathbf{S}}^{(\mathrm{Fe})} + g_{\mathrm{Co}}\hat{\mathbf{S}}^{(\mathrm{Co})}) + D_{\mathrm{Fe}}\hat{S}_x^{2(\mathrm{Fe})} + E_{\mathrm{Fe}}(\hat{S}_y^{2(\mathrm{Fe})} - \hat{S}_z^{2(\mathrm{Fe})}) + D_{\mathrm{Co}}\hat{S}_y^{2(\mathrm{Co})}. \quad (1)$$

The first term represents an isotropic Heisenberg coupling between the spins $\hat{\mathbf{S}}^{(\mathrm{Fe})}$ on the Fe atom and $\hat{\mathbf{S}}^{(\mathrm{Co})}$ on the Co atom, quantified by the Heisenberg exchange coupling strength J. According to this definition, positive values of J signify antiferromagnetic coupling. The second term gives the Zeeman energies resulting from the external magnetic field $\mathbf{B}$, where μ_B denotes the Bohr magneton and g_{Fe} and g_{Co} the g factors of the Fe and Co spins, respectively.

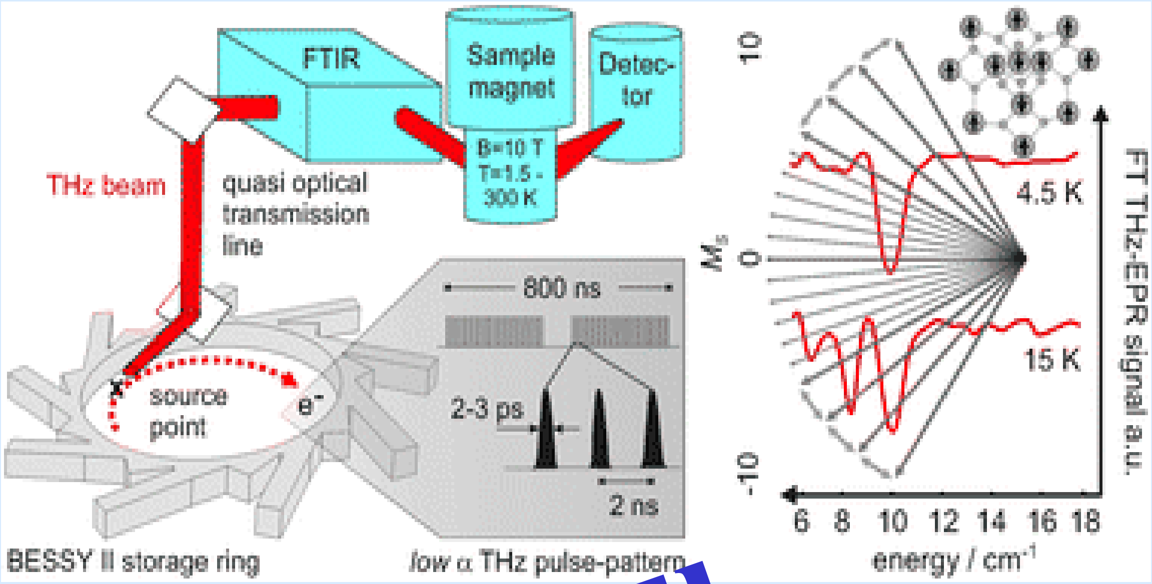
The remaining terms in Eq. (1) represent the magnetocrystalline anisotropies experienced by each of the spins, quantified by the uniaxial anisotropy parameters D_{Fe} and D_{Co} and the transverse anisotropy parameter E_{Fe}. All parameters in this spin Hamiltonian except J have been measured previously on the corresponding isolated atoms. The choice of spin magnitudes, $S_{\mathrm{Fe}} = 2$ and $S_{\mathrm{Co}} = 3/2$, the assignment of the axes in the anisotropy terms, and the absence of transverse anisotropy for Co are based on previous studies of the isolated atoms on the same surface [10,17].

Diagonalization of the spin Hamiltonian gives a system of 20 eigenstates with corresponding eigenenergies [24].

FIG. 3 (color). Small dots: lowest 12 eigenvalues of Eq. (1) with $J = 0.13$ meV, $g_{\mathrm{Fe}} = 2.11$, $g_{\mathrm{Co}} = 2.16$, $D_{\mathrm{Fe}} = -1.53$ meV, $E_{\mathrm{Fe}} = 0.31$ meV and $D_{\mathrm{Co}} = 2.70$ meV for $B = 0$ to 7 T in increments of 0.1 T along x. Color indicates the values

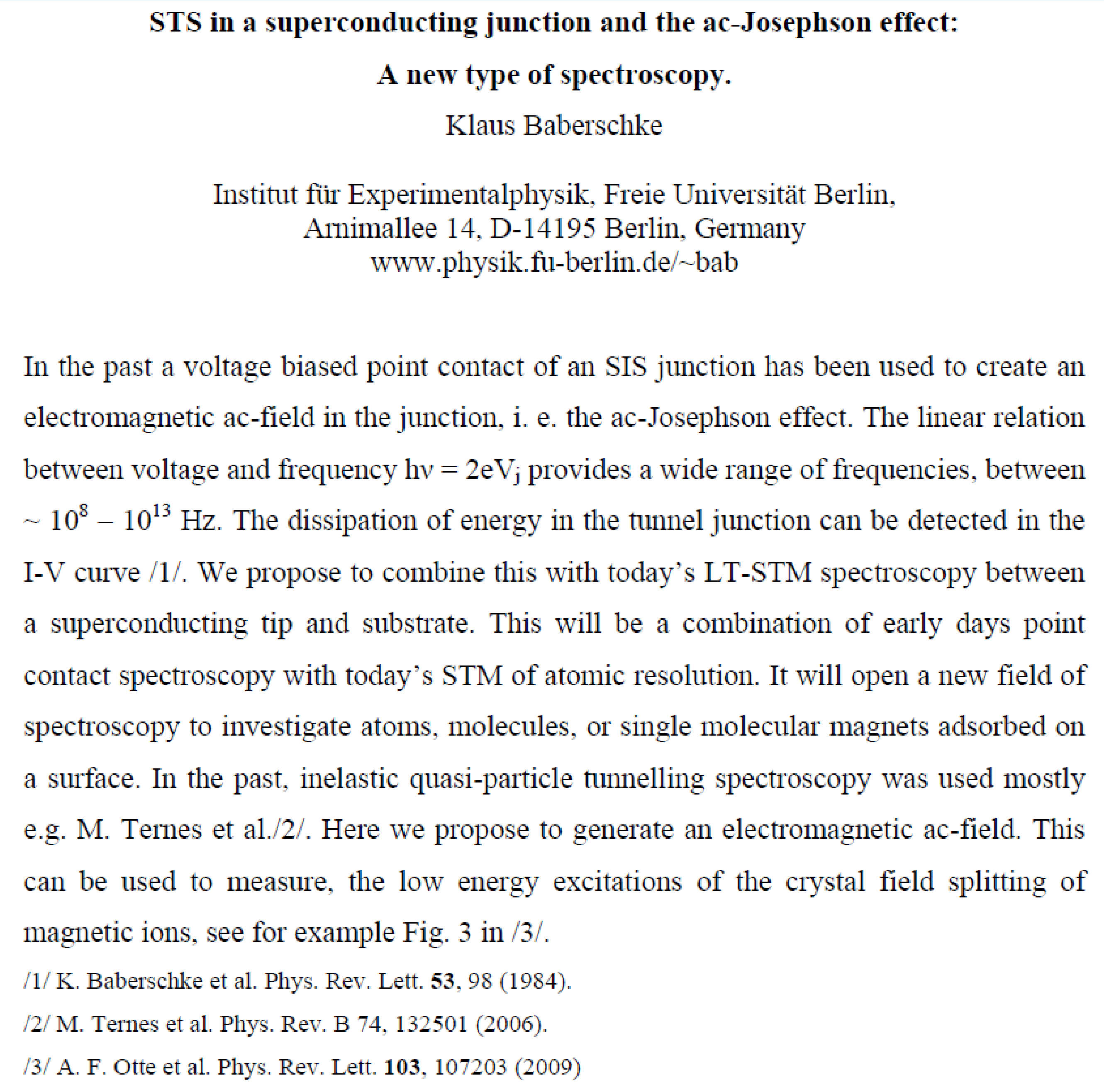
Alexander Schnegg et al. ***Phys. Chem. Chem. Phys.*****, 11,** 6820 (2009)

Frequency domain Fourier transform THz-EPR on single molecule magnets using coherent synchrotron radiation



Frequency domain Fourier transform THz electron paramagnetic resonance (FD-FT THz-EPR) based on coherent synchrotron radiation (CSR) is presented as a novel tool …. at the BESSY II storage ring … in a frequency range from 5 cm^{-1} up to 40 cm^{-1} … together with first measurements on the **SMM Mn$_{12}$Ac** where **$\Delta M_S = \pm 1$ spin transition** was studied ….

Thank you



STS in a superconducting junction and the ac-Josephson effect:

A new type of spectroscopy.

Klaus Baberschke

Institut für Experimentalphysik, Freie Universität Berlin,
Arnimallee 14, D-14195 Berlin, Germany
www.physik.fu-berlin.de/~bab

In the past a voltage biased point contact of an SIS junction has been used to create an electromagnetic ac-field in the junction, i. e. the ac-Josephson effect. The linear relation between voltage and frequency $h\nu = 2eV_j$ provides a wide range of frequencies, between ~ $10^8 - 10^{13}$ Hz. The dissipation of energy in the tunnel junction can be detected in the I-V curve /1/. We propose to combine this with today's LT-STM spectroscopy between a superconducting tip and substrate. This will be a combination of early days point contact spectroscopy with today's STM of atomic resolution. It will open a new field of spectroscopy to investigate atoms, molecules, or single molecular magnets adsorbed on a surface. In the past, inelastic quasi-particle tunnelling spectroscopy was used mostly e.g. M. Ternes et al./2/. Here we propose to generate an electromagnetic ac-field. This can be used to measure, the low energy excitations of the crystal field splitting of magnetic ions, see for example Fig. 3 in /3/.

/1/ K. Baberschke et al. Phys. Rev. Lett. **53**, 98 (1984).

/2/ M. Ternes et al. Phys. Rev. B 74, 132501 (2006).

/3/ A. F. Otte et al. Phys. Rev. Lett. **103**, 107203 (2009)