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Two-level-system-related zero-bias anomaly in point-contact spectra

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In point-contact spectroscopic measurements on mechanically controllable break (MCB) junctions of several metals, two distinct anomalies are observed near zero bias. The first anomaly is well described by the elastic scattering of electrons from two-level systems with different scattering cross sections for both levels, but may also be explained by another model which involves the interaction between a two-level system and an electronic screening cloud. The experiments suggest that these two-level systems are related to dislocations, due to stretching of the sample at the surface near the contact. The second type of anomaly has an S shape and was observed at higher voltages. This anomaly is found to be remarkably independent of the sample material. The origin of this anomaly is not yet clear.

I. INTRODUCTION

When the size of a contact between two pieces of conducting material is so small that the contact diameter is smaller than the electron mean free path (Sharvin contact or point contact, PC), interactions between electrons and excitations near such a contact have a considerable influence on the PC conductivity. This makes the PC an excellent tool for studying these interactions, of which the direct measurement of the electron-phonon interaction (EPI) is the most highly elaborated and best-known example.[1,2]

Due to the small size of the volume probed (typically 10^3 nm^3 or less), a PC is also a good tool for studying single imperfections which can otherwise be studied only indirectly, e.g., in transport measurements. These imperfections often give rise to anomalies in the PC spectrum (d^2V/dI^2 as a function of the bias voltage V) at low bias voltages. An example of such behavior is the Kondo minimum which has been observed at PC's of diluted magnetic alloys like AuMn and CuFe.[3,4]

Another type of imperfection which is of great interest are those that switch between two metastable states, thus giving rise to the well-known two-level systems (TLS's). The concept of TLS's was originally put forward to describe many of the physical properties of glassy materials (for a review we refer to Black[5]), but has recently found a much wider application. Using metallic nanoconstrictions, Ralls and Buhrman[6] showed that these TLS's are the dominant source of $1/f$ noise in metal films. Such constrictions were also used to study resistance fluctuations due a single TLS.[7,8] These experiments yielded some quite different parameters for the TLS's studied, pointing to TLS's originating from different types of defects.[8] Other studies were concerned with the electromigration of defects through a point contact[9] and the impact of a single defect on the PC conductance.[10] Ralph and Buhrman[11] observed a minimum in the differential conductance of a disordered copper point contact, which they attributed to a nonmagnetic Kondo-like resonance due to a strong coupling between TLS's and conduction electrons, as described by Vladar and Zawadowski.[12] Recently, Akimenko and Gudimenko[13] reported on an anomalous feature in the PC spectrum of a Cu point contact, which they attributed to the elastic scattering of electrons from a point-defect fluctuating between two states, as has been described theoretically by Kozub and Kulik.[14,15]

Because elastic-scattering processes in the quasiballistic and diffusive transport regimes do not depend on electron energy and therefore do not lead to nonlinear contributions to the point-contact conductivity, but only reduce the point-contact spectra intensities,[2] it might be expected that this sort of interaction cannot be observed by PC spectroscopy. In this case, however, the fact that the scattering cross sections of the two states of the defect will in general not be equal, and the fact that the population of the states is bias voltage dependent, lead to the possibility of observing the elastic scattering of electrons from such a two-level system in PC spectra.

Kozub and Kulik[15] have calculated the contribution to the point-contact spectrum due to this elastic scattering of electrons on TLS's, and have expressed it in the form

$$\frac{1}{R}\frac{dR}{dV}=\sum_j \frac{eC_j}{2E_j}(\sigma_j^+-\sigma_j^-)\tanh\left[\frac{1}{2\tau}\right]S(\nu,\tau,q)\ , \quad (1)$$

where ν and τ are the voltage V and temperature T re-

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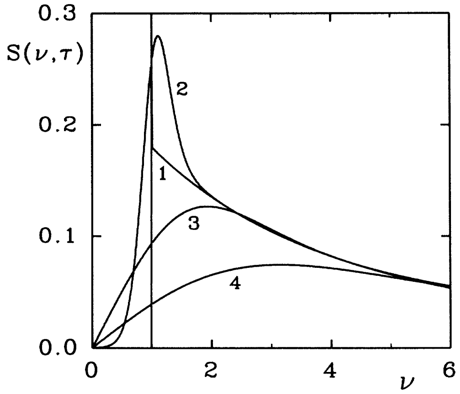

FIG. 1. Profile of the point-contact spectral line $S(\nu,\tau,q)$ for $q=0.1$. Curves 1, 2, 3, and 4 correspond to $\tau=0$, 0.1, 0.5, and 1.0, respectively. [According to Kozub and Kulik (Ref. 15).]

duced to the excitation energy E_j of the jth TLS as eV/E_j and k_BT/E_j, respectively. (Typically, $E_j<1$ meV for a TLS). R is the point-contact resistance and $\sigma_j^{\pm}$ stands for the scattering cross sections of the upper and lower levels. The function S as a function of ν is given in Fig. 1 for different values of τ and for a particular value of the parameter q. This parameter represents the electric potential at the location of the TLS normalized to the total potential eV over the contact, where the potential is set to zero at the contact center. The parameter q is equal to 0.5 for a TLS located at the contact center, and drops for TLS's far away from the contact. The line profile is very unusual for traditional spectroscopy. For $T \ll E_j$ it consists of a sharp peak at $eV=E_j$ and a wing, located at energies exceeding E_j. It has been pointed out[15] that this particular line profile can be used to separate this TLS contribution to the PC spectrum from those of inelastic scattering by paramagnetic impurities or by impurities with internal structure.

In the present paper we pay attention to two types of anomalies observed at low bias voltages in a PC spectrum. The first one (called type I) can be attributed to interactions between conduction electrons and two-level systems located near the point contact. The other one (type II) is due to an as yet unknown type of imperfection.

II. EXPERIMENTAL

Recently, Muller, Ruitenbeek, and de Jongh[16] have developed a technique for making highly stable, clean point contacts by breaking and reconnecting small filaments. We have adapted this mechanically controllable break (MCB) junction technique for use with thin films.[17] A metallic film (Au, Cu, Al, Ag, Pb) is vapor-deposited on top of a thin, brittle substrate (e.g., glass, Si wafer). This substrate is then glued on top of a bending beam. The thin-film MCB junction is formed by first breaking film and substrate, and then establishing a contact by bringing the electrodes back together.

For the experiments on the type-I anomaly described in this paper we used 3000-Å-thick Cu films which were evaporated in moderate (10^{-5} Torr) vacuum on heated (60 °C) glass substrates with a high deposition rate. The Cu films all had a residual resistivity ratio ≈5, so the films that were used were of low crystalline quality. The low intensity of the second harmonic V_2 of the modulation voltage signal, as well as the absence of the LA peak in the EPI spectra, implied that the elastic mean free path in the region of the contact was much smaller than the contact diameter d. The type-I anomaly was also observed using bulk MCB junctions of Au, Cu, Ag, and Pt, produced by breaking 50-μm wires as described in Refs. 16 and 18. The type-II anomaly was observed at Au, Cu, Ag, and Al thin-film and bulk MCB junctions.

The spectra for all PC's were obtained using a standard lock-in technique with a modulation frequency of 5 kHz. The samples were immersed in a liquid-He bath which could be varied in temperature between 4.2 and 1.3 K. A magnetic field up to 7 T could be applied.

III. RESULTS AND DISCUSSION

A. The type-I anomaly

The first type of zero-bias anomaly we observed can be described as a strongly asymmetric peak located at biases of 1-4 mV (Fig. 2). These peaks were observed with both negative and positive signs, and did not change when magnetic fields up to 7 T were applied. Recently, this type of spectral feature was reported on by Akimenko and Gudimenko,[13] who found it to be described very well by the above-mentioned theory of Kozub and Kulik.[14,15]

The set of point-contact spectra displayed in Fig. 2(a) was measured using a disordered 3000-Å Cu thin-film

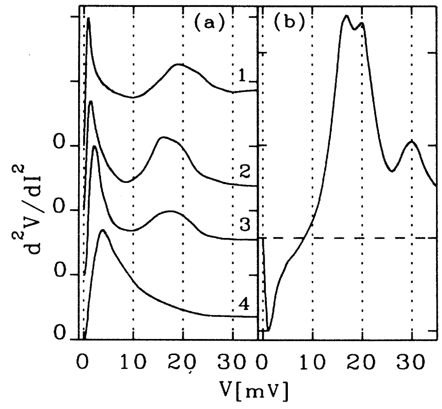

FIG. 2. (a) Point-contact spectra of copper thin-film MCB junctions with resistances 1–1.2 Ω, 2–22 Ω, 3–64 Ω, and 4–400 Ω ($T=1.3$ K). The curves have been shifted for clarity. (b) Point-contact spectrum for a Cu single crystal MCB junction ($R=30$ Ω, $T=2$ K). The peaks at 17–18 mV and 30 mV are due to the electron-phonon interaction; the feature at bias voltages between 0 and 5 mV [positive for (a), negative for (b)] is attributed to interactions between electrons and a TLS.

MCB junction. The most prominent feature of the PC spectra in this figure is the strong "positive" zero-bias anomaly with an intensity comparable to the TA peak for low-ohmic contacts and greatly exceeding the EPI spectrum for high-ohmic junctions.

The relative change in differential resistance $\Delta R/R$ associated with the observed singularities, is usually of the order 0.1–1 % for contacts with resistances from 1 to 100 Ω, but was observed to increase up to 10% for more high-ohmic junctions. This is in good agreement with the estimations[14,15]

$$\Delta R/R \sim |\sigma^{+}-\sigma^{-}|\, l/d^{3} \tag{2}$$

per one two-level system in the diffusive transport regime ($l \ll d$), if we suppose that $|\sigma^{+}-\sigma^{-}| \approx 10^{-14}$–$10^{-15}$ cm^2 (difference between an occupied and an unoccupied lattice site) and assume a TLS density of 10^{-4}–10^{-5} per atom, which is typical for disordered systems.

The peaks near zero bias in Fig. 2(a) are displayed in Fig. 3 on an enlarged scale, together with a theoretical fit. This fit is based on the (reasonable) assumption[13] that only one TLS is present near the contact area. Calculations show that the position $v_{\max}$ at which the theoretical curve has its maximum depends strongly on the reduced temperature τ (see Fig. 1), but varies only slightly as a function of q (for $\tau \geq 0.05$). The effective experimental temperature T_{eff} is composed of the bath temperature T and a contribution due to smearing by the modulation voltage V_1, $T_{\text{eff}}=[T^2+(0.224eV_1/k_B)^2]^{1/2}$. When the modulation contribution to T_{eff} is kept small, the quotient $v_{\max}/\tau$ will be equal to $eV_{\max}/k_B T_{\text{eff}}$, with $V_{\max}$ the voltage at which the peak maximum occurs in the PC spectrum. Thus, it is possible to get a good estimation of the τ value and, using $E_j=k_B T_{\text{eff}}/\tau$, of E_j directly from the experiment. The value of q can then be adapted to optimize the theoretical fit to the data.

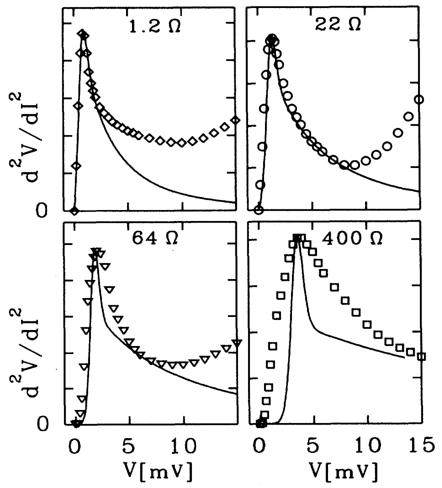

FIG. 3. The zero-bias anomalies from Fig. 2 presented on an enlarged scale (symbols), together with a theoretical fit (lines) described in the text. Starting at voltages between 5 and 10 mV, there is a considerable contribution to the spectrum by the electron-phonon interaction, causing a mismatch between the experimental data and the theoretical curve.

The values of τ, E_j, and q for the fits from Fig. 3 are presented in Table I. The value of q is found to decrease with increasing contact resistance. The value of q depends on the distance of the TLS to the contact center normalized to the contact radius. When the contact resistance increases, the contact radius decreases and thus the normalized distance to the contact center increases, leading to a drop in the value of q.

Figure 3 shows that in our experiments the theory fits the experimental data well only for the larger contacts ($T=1.2$ Ω, 22 Ω). For the smaller contact, the theoretical fits are found to be much less broadened than the experimental curves, and there is only a very small onset visible of the theoretically predicted nonlinear behavior close to zero bias. The values of q, τ, and E_j can be adapted in such a way that the theoretical curves also fit the data well for these contacts. However, this would require values of τ and E_j which correspond to an effective temperature of 9 K at the TLS site for the 400-Ω contact. This is an unlikely high value, because the junction was in direct contact with a helium bath at $T=1.3$ K during the experiments, and because there is no known heating mechanism at low voltages that can explain such a large increase of the temperature. It has been found that the temperature of a defect may become higher than the lattice temperature in a PC when voltage is applied,[9] but this increase is very small for voltages below 5 mV. Akimenko and Gudimenko[13] found good agreement between experiment and theory for all contacts they measured on. However, they only measured large contacts with contact resistances smaller than 4 Ω.

Table I shows that the value of the level spacing E_j increases with increasing contact resistance and reaches a value of 3.36 meV for the 400-Ω contact, which is a rather high value of E_j for a TLS. Since the measurements were taken on the same contact with a different contact size, it is assumed that the same TLS was studied in all experiments. Therefore one would expect the value of E_j to be constant, which turns out not to be the case. Again, it is possible to make good fits to the experimental data keeping E_j constant. However, in that case very large τ values are required, corresponding to $T\sim 40$ K for the 400-Ω contact. The shift in E_j may be due to the fact that the TLS's were regarded as point defects in the theoretical description,[14,15] but as soon as at least a few

TABLE I. Values of the parameters τ, E_j, and q for the fitted curves of Fig. 3. T_{eff} is the bath temperature corrected for the applied voltage modulation.

R (Ω)	T_{eff} (K)	τ	E_j (meV)	q
1.2	1.95	0.28	0.60	0.080
22	2.13	0.18	1.02	0.075
64	1.94	0.10	1.67	0.070
400	1.95	0.07	3.36	0.050

neighboring atoms are involved in the TLS formation its "size" may be comparable to the contact diameter for small PC's ($R = 400\ \Omega$ corresponds to $d \approx 20$–25 Å). This may cause some kind of smearing of the peak, thus leading to apparently higher values of E_j or τ.

The temperature dependence of the peak was studied for a 11.3-Ω thin copper film PC. The results of these measurements are shown in Fig. 4, together with a theoretical fit. The theory predicts the observed behavior of the peak height and the position of the peak maximum as a function of temperature rather well, as can be seen from the inset where the observed changes are compared to theory. However, the theoretical fits display values that are much too large in the "wing" at voltages above 2 mV. The fits can be improved strongly in this respect by increasing the value of q to 0.10; however, this leads to less agreement for the overall temperature behavior displayed in the inset.

The predicted temperature smearing of the TLS peak is partly due to the fact that the average occupation times of both TLS states changes with temperature. In order to study whether this would lead to a significant difference from usual temperature smearing in our experiment, we used the approach of Jansen[19] to temperature average a theoretical curve, calculated for $T = 1.5$ K (other parameters were chosen as for Fig. 4), to a temperature of 4.3 K, and compared it to the TLS peak calculated directly for 4.3 K. We must note that the averaging procedure was devised for inelastic-scattering processes like electron-phonon interaction, and may therefore not be entirely correct for the inelastic scattering of electrons from a TLS. However, the order of magnitude of the temperature smearing should be the same ($\sim k_B T$). It turned out that the two curves were quite close together, the averaged curve having a slightly ($\sim 3\%$) higher maximum. Therefore, it is probably not possible to distinguish between usual temperature smearing and the predicted temperature dependence of the TLS peak, unless measurements at very low temperatures ($\ll 1$ K) are performed.

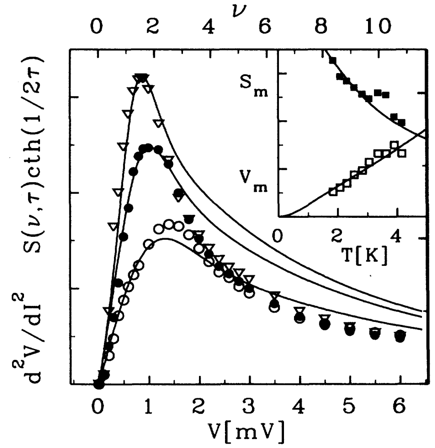

FIG. 4. Experimentally determined temperature dependence of the type-I anomaly for a 11.3-Ω Cu thin-film point contact (symbols) and theoretical fits ($E_j = 0.56$ meV, $q = 0.06$). The effective temperatures are 1.84 K (∇), 2.56 K (●), and 3.90 K (○) and are composed of the real temperatures (1.43, 2.20, and 3.67 K) corrected for smearing by the modulation signal. In the inset the experimentally observed behavior of the peak height (filled squares) and the position of the maximum (open squares) as a function of temperature are compared with their theoretical expressions.

Next, we will discuss some indications on the origin of the TLS's studied. Because there is no need for the scattering by the upper level to be stronger than that by the lower level, situations with $\sigma_j^+ > \sigma_j^-$ as well as $\sigma_j^+ < \sigma_j^-$ can occur. At a copper single-crystal MCB junction we observed a "negative" zero-bias anomaly, which is just the mirror reflection of the above described peak with approximately the same shape and peak position [Fig. 2(b)]. It must be noted, however, that, judging from the well-resolved EPI spectrum with high absolute intensity, which indicates a large elastic relaxation length, the TLS's in this contact cannot be related to some inherent disordered crystal structure, but are more likely connected with linear defects like dislocations, which may arise in the breaking process. However, we have strong indications that the TLS's causing the peaks that were observed at the Cu thin-film MCB junctions were also created while breaking the samples, rather than being a result of the low crystalline quality of the film. We have studied a considerable number of Cu thin-film samples which were all prepared by evaporating Cu under the same conditions on glass slides. These slides were cut into small rectangular pieces which were then glued on top of phosphorbronze bending beams. At about half of all samples a scratch, intended as a break starter, was made on the down side of the slide with a diamond pen before gluing. The breaking of the two types of samples was closely studied by breaking some of them in air under visual observation. It turned out that the scratched samples broke quickly at the scratch, and that the copper film broke at the same time. However, the other samples had to be bent much further (stretching the film in the process) and it happened several times that the glass slide broke without the film breaking; the film only broke after a further increase of the bending angle. At such samples a TLS peak was observed in all cases, while the scratched samples never displayed a strong peak at low energies. The same correlation between sample preparing and the probability of finding this low-energy peak was also found for samples which were broken in a He atmosphere at several temperatures (300, 77, 4.2 K). Therefore, the appearance of a TLS peak in our spectra seems to be related to the amount of bending and stretching of the film (which is known to cause dislocations) in the breaking process. Similarly, Akimenko and Gudimenko[13] found that the probability of observing a low-energy peak in their experiments was larger when they used crystalline samples they had strained by a slight bending.

It is possible to remove the low-energy peak from the spectra by annealing the samples for a few days at room temperature. On the other hand, the low-energy peak has been observed using samples that had been kept for several days at room temperature before breaking them.

This also indicates that the TLS's studied are related to some nonequilibrium defect created in the breaking process rather than being related to some defect inherent to the low crystalline quality of the as-evaporated Cu films. Until now, only "positive" peaks were observed for the Cu film junctions, while for single-crystal junctions of Cu, Ag, and Pt we only observed "negative" peaks. Whether this relation between the amount of structural order of the MCB junction and the sign of the observed TLS peak is real or just coincidental, is not yet clear.

The question may arise if it is possible to state something about the location of the studied TLS's. Because the film will be deformed most strongly at the point where it breaks, the surfaces that are brought into contact to form the MCB junction are expected to contain a lot of defects. Therefore, the TLS's studied are likely to be located somewhere in or close to the contact plane. Furthermore, one may assume that a defect switching between two states is more likely to appear near the edge of the contact plane, because defects at such a location may be less bound to surrounding atoms than a defect in the contact center. The TLS being located near the edge of the contact plane may explain the strong influence it has on the PC spectrum of the Cu film MCB junction [Fig. 2(a)], since the current density through a point contact in the diffusive limit is much larger near the edges than in the contact center.[2] Furthermore, it may give an explanation for the fact that in all our experiments, the fitted value of q was found to be between 0.05 and 0.10. As was mentioned above, the parameter q depends on the electrical potential at the TLS site, and thus gives an indication of the location of the TLS with respect to the contact center. For a TLS on the axis through the contact center, perpendicular to the contact area, $q=0.05$–0.10 corresponds to a distance to the contact center of 2–3 times the contact radius. Yet, the probed volume in usual point-contact spectroscopy is assumed to be a sphere with the same radius as the contact area. This would require the studied TLS to be at a distance to the contact center which should not be much larger than the contact radius. Calculations show that for a TLS located close to the contact plane, near the edge of the contact, small values of q may well be possible. The TLS originating from some defect near or at one of the surfaces brought into contact might also explain the fact that the level spacing E_j increases with the contact resistance, considering that the defect may be going from some location in the bulk to a surface location as the contact size decreases.

In the above it has been shown that the behavior of the asymmetric peak observed in PC spectra is described quite well by the Kozub and Kulik model of elastic electron scattering from TLS's with different scattering cross sections for the two states. However, an asymmetric peak with approximately the same shape is predicted by the already mentioned nonmagnetic Kondo interaction model, which was developed by Vladar and Zawadowski[12] to describe the low-temperature behavior of metallic glasses. In this theory the defect motion which represents the TLS causes a change in the localized potential acting on the electron gas, which is followed by the buildup of an electronic screening. At low temperatures the movement of this charge screening cloud is highly correlated with the TLS motion, and below a certain temperature a bound state is formed. The theoretical model is formally the same as that describing the antiferromagnetic Kondo problem, where below a certain crossover temperature a bound state is formed in which the impurity spin is completely screened by the spin polarization of the conduction electrons.

A comparison of the two TLS models shows that they both predict the same temperature dependence for both the spectrum and the resistivity, namely proportional to $\ln(T)$. Yet, there is a difference in the voltage dependence of the "tail" of the spectral peak at voltages much higher than the voltage at which the peak maximum is located. Vladar and Zawadowski predict a logarithmic behavior of the resistivity, so the spectral peak is expected to be proportional to $1/V$. Kozub and Kulik, on the other hand, predict a behavior proportional to $1/(V+\alpha)^3$, where α is a constant. We have compared these predictions with our experimental data. It turned out that both descriptions were equally good for all cases. Ralph and Buhrman[11] demonstrated a voltage dependence of the resistivity of a Cu nanoconstriction proportional to $\ln(V)$, corresponding to the Vladar and Zawadowski theory. However, fitting the Kozub and Kulik theory to data taken from their publication shows an equally good agreement. The fact that these two descriptions, which are quite different, give equally good results might seem quite remarkable. However, the voltage range over which these predictions can be tested is very limited (less than one decade) due to a background in the measurements originating from the electron-phonon interaction. On such a limited interval it is quite possible that different descriptions give equally good fits.

From the measurements presented here it is not possible to tell which of the theoretical descriptions mentioned is more accurate. The model of Vladar and Zawadowski, which is formally the same as that describing the antiferromagnetic Kondo problem, only predicts minima in the resistivity corresponding to a positive peak in the spectrum. However, negative peaks were observed also. Since this theory has not been devised explicitly for point contacts, it is not clear in what way the point-contact geometry may influence the obtained results.

B. The type-II anomaly

Now let use turn to a second type of low bias anomaly that we have observed for several materials (Cu, Ag, Au, Al) at both crystalline wire and thin-film MCB junctions. The anomaly has been observed at about 10% of all samples and is represented by an elongated S-shaped singularity in the second harmonic signal (minimum in the differential resistance) in a wide energy range, starting from 4–5 meV and up to the Debye energy. On rare occasions a few (mainly an even number) of such singularities can be observed in this range, often corresponding pairwise to minima and maxima in R_{diff}. Some typical examples of these singularities are shown in Fig. 5. The relative change of differential resistance is much smaller

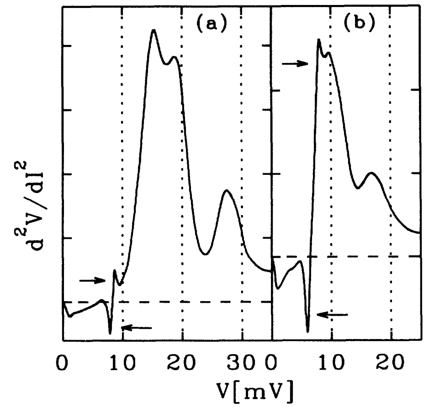

FIG. 5. S-shape anomalies observed in the point-contact spectra of MCB junctions. (a) Cu wire, $R=8\ \Omega$, $T=1.3$ K. (b) Au wire, $R=64\ \Omega$, $T=1.3$ K. The arrows indicate the minima and maxima of the anomalies.

than in the previous case (0.02–0.2 % only), but the shape of the EPI spectrum may be heavily distorted if the singularity is located at an energy that is close to the peaks in the phonon density of states [Fig. 5(b)]. This sort of anomaly has never been observed with usual pressure-type point contacts, and "annealing" of the MCB junction at room temperature results in a complete disappearance or an appreciable reduction of its amplitude. Therefore, there is little doubt that nonequilibrium defects, created while breaking the sample, are responsible for the observed singularity.

The most striking feature of these anomalies is that their position in the spectra depends very strongly on contact resistance. Figure 6 demonstrates such a dependence for an Al MCB junction. The position of the anomaly versus the square root of the contact resistance, plotted in Fig. 7 for different metals, may be represented by a straight line and is nearly the same for all metals investigated. This means that the energy at which the singularities are observed is inversely proportional to the contact diameter (in the quasiballistic regime) and does not depend significantly on the specific material. This may suggest some nonequilibrium state in the contact geometry, for instance along the contact edge, depending strongly on the contact size but almost independent of the contact material. On the other hand, since it also means that the anomaly appears at a constant level of power dissipation in the contact region ($P=V/R^2$), it may well be that we are observing some phase transition in the nonequilibrium defect system. However, it remains quite peculiar that this anomaly exhibits the same behavior for different materials. It must be noted that on rare occasions the anomaly is observed at bias voltages which are low compared to the data of Fig. 7 [e.g., the S-shape anomaly of Fig. 5(b)]. The position of the anomaly is still found to be proportional to $\sqrt{R}$ for these cases.

Note also that the amplitude of the effect remains practically unchanged (all curves in Fig. 6 were taken at the same modulation voltage $V_1 \approx 0.5$ mV), while the relative intensity of the EPI spectra drops for increasing PC resistance. This indicates that the observed singularities are a result of elastic (or resonant) rather than inelastic scattering. On a Cu thin-film MCB junction at $T=4.2$ K, we observed an S-shape anomaly which decreased strongly in amplitude with increasing contact resistance, disappearing at $R>9\ \Omega$. When resistance was lowered again, the anomaly reappeared. However, the position of the anomaly was still proportional to $\sqrt{R}$ and the anomaly was located at almost the same energies. Apparently, the intensity of the anomaly strongly depends on the location of the defect with respect to the center of the contact, while

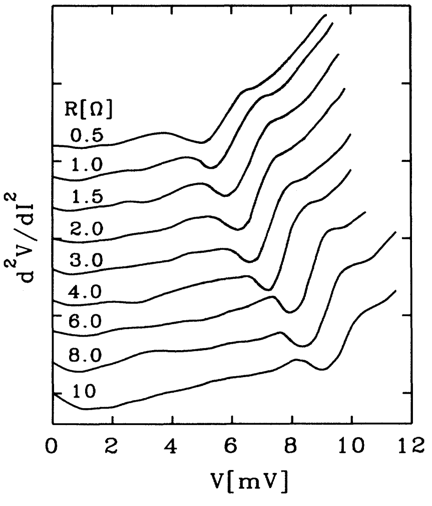

FIG. 6. Point-contact spectra of Al wire MCB junctions displaying an S-shape anomaly for contacts with different resistances. The modulating signal level of 0.5 mV is the same for all PC's ($T=1.3$ K). The curves have been shifted vertically for clarity.

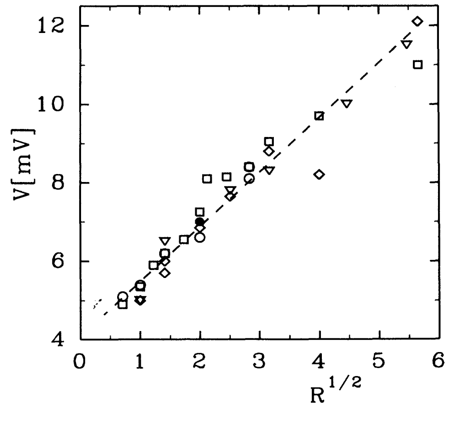

FIG. 7. Dependence of the S-shape anomaly position on the MCB-junction contact resistance for different metals: □ Al wire, ◇ Ag wire, ▽ Au wire, ○ Cu wire, and ● Cu thin film ($T=1.3$ K).

the position of the anomaly hardly does. We have no clear indication that this type of anomaly is related to the TLS's which cause the first type of anomaly, because they were often observed for contacts with almost no zero-bias anomaly in the PC spectra. Yet the amplitude of the singularities was observed to increase appreciably for contacts with deep "negative" type-I anomalies, and their positions were shifted to lower energies compared to the data from Fig. 7. Like the type-I anomaly, the S-shape type was found not to change when magnetic fields up to 7 T were applied.

IV. CONCLUSION

As described above, the position of the type-II anomaly was observed to be proportional to $\sqrt{R}$. When the position of the maxima of the zero-bias anomaly of the first type, observed for Cu thin films, is plotted against $\sqrt{R}$, one finds a rather large scatter in the data. This may be caused by the dependence of the energy of the maxima at nonzero temperature on the exact position of the TLS's near the contact, and by a probable dispersion in E_j for different junctions. However, it is still possible to approximate it by a straight line. Extrapolating to very large contact diameters, where the contact size is certainly much larger than the TLS size, and the TLS is very close to the contact center, a value of $E_j \approx 0.5$–0.6 meV is obtained. This value can be adopted as a bulk value for the type of TLS we are observing.

Because the energies at which the TLS peak and the S-shape anomaly are located are both proportional to $\sqrt{R}$, and because the S-shape anomaly is more pronounced when it appears together with the TLS peak, one can speculate about the S-shape anomaly being the result of switching from both the first and second level to a third one at a somewhat higher energy than the lower two. Intuitively, one would then expect the separation between the minimum and maximum in the S shape to be of the same magnitude as the splitting of the lower two levels, which is indeed the case. The appearance of S-shape anomalies without a TLS peak being present can be explained by taking the scattering cross sections of the two lower levels to be equal. However, it cannot explain why no difference is observed for different materials. Analogous to the presence of positive and negative type-I anomalies, one would also expect to observe sometimes a single anomaly with first a maximum and then a minimum (N shape), but so far this has not been the case.

In summary, in point-contact spectra we observed an asymmetric peak at low (~ 1 mV) voltages which can be explained from interactions between TLS's and conduction electrons. Two models are available that are capable of describing the features of the peak in a reasonable way. The observed zero-bias anomalies are possibly related to defects caused by film stretching. Additionally, S-shape anomalies of which the origin is still unknown were observed in the second harmonic signal.

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