# EFFECT OF ORGANIC IMPURITIES

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## Abstract

## Full Text

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**PHYSICS**

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# EFFECT OF ORGANIC IMPURITIES ON TUNNEL CONDUCTIVITY

Thin-film tunnel junctions Al–$Al_2O_3$ (organic impurity)–Al were investigated. The technology for preparing the samples differed from the generally accepted one by the additional operation of introducing an organic impurity between the aluminum-oxide layer and the upper Al electrode. Naphthalene, benzophenone, and also their alloy were used as impurities. The calculated amount of impurity introduced corresponded to a monomolecular layer adsorbed on the surface of the $Al_2O_3$ film.

**Fig. 1.** Effect of a magnetic field on the anomalous tunnel conductivity of Al –$Al_2O_3$ (naphthalene–benzophenone)–Al

As is known, Appelbaum ([1]) explained the anomalous increase in tunnel conductivity at small voltages by the presence of paramagnetic impurities in the dielectric interlayer.

It is also known ([2]) that such substances as benzophenone and naphthalene, when irradiated with ultraviolet light, can pass into a paramagnetic state. (The ground state of these substances is singlet. Then, alternating, come excited triplet and singlet states, the energy of the triplet state $E_t$ being smaller, although only slightly, than the corresponding energy $E_s$ of the singlet state.) Under irradiation with light with $\hbar\omega = E_s$, the molecules pass into the first excited singlet state, and then into the triplet state, in which, because of the intercombination prohibition, they can remain for a rather long time, up to several seconds.

Therefore, in the present experiment it was proposed to observe a change in the

magnitude of the anomaly as a function of the intensity of illumination. The expected effect was not observed, perhaps because of insufficient illumination of the dielectric interlayer situated between the metallic films, but perhaps also for the fundamental reasons discussed below.

The point is that, even without any illumination, the character of the anomaly changed strikingly upon introduction of organic impurities. Its magnitude increased by a factor of 20 (in comparison with the 20-percent anomaly discussed in Appelbaum' s works), and the shape of the curve became complex. For example, in the case of adding a naphthalene–benzophenone mixture, the anomaly proved to be split in zero field.

The paramagnetic character of the observed anomaly was verified. As the magnetic-field strength is increased, both the magnitude of the anomaly and the magnitude of its splitting decrease. At a magnetic-field strength close to 23 kOe, the splitting practically vanished. At a somewhat higher field strength the anomaly smooths out (Fig. 1). The temperature range of its existence is below 2.1° K. The magnetic measurements were carried out at 1.6° K.

Thus, a connection between the anomaly and organic impurities is evident and, at the same time, the paramagnetic character of the observed anomaly is beyond doubt. It should therefore be assumed either that triplet levels of organic compounds are populated, or that magnetic moments of already existing impurities are polarized by the fields of organic molecules, or, finally, that there is a sharp lowering of the paramagnetic state of the organic molecules.

The first case requires more detailed consideration. Triplet levels correspond to energies of the order of 25 000 $cm^{-1}$. Population of such levels could be appreciable at temperatures of the order of 30 000° K, whereas the experimental temperature is 1.6° K.

Apparently, however, for organic molecules adsorbed on the surface of a metal, such a population mechanism is possible.

Let us write the Hamiltonian of the system in the form

$$H = H_0 + H_I + \hat{a}E_s\left(1 - \frac{\vec{S}^2}{2}\right) + \frac{E_t\vec{S}^2}{2}, \tag{1}$$

where $H_0$ is the Hamiltonian of the conduction electrons; $H_I$ is the Hamiltonian of the exchange interaction of the metal electrons with the electrons participating in the formation of the $E_s$- and $E_t$-states; $\vec{S}$ is the operator of the magnetic moment of the molecule; $\hat{a}$ is an operator with eigenvalues 0 and 1.

It is possible that Hamiltonian (1) does not reflect the real system very well, since high-lying excited electronic states and low-lying collective excitations of the rotational-vibrational type of molecular motion have not been taken into account. In addition, in the interaction Hamiltonian, terms independent of the

magnetic state of the impurity have also been omitted; these would lead to an insignificant renormalization of the levels $E_s$ and $E_t$. Finally, in (1) the collective motion in spin space of all the electrons of the molecule has been replaced by the effective motion of two electrons.

However, despite the simplified nature of the model, it can be used to show the physical reason for the occurrence of an anomalous population of the triplet level.

Using (1), it is not difficult to calculate $E$—the mean value of the energy of a molecule adsorbed on the surface of a metal,

$$E = \operatorname{Sp} e^{-\beta(H-\mu\hat{N})} \left[ \hat{a}E_s \left( 1 - \frac{\vec{S}^2}{2} \right) + \frac{E_t \vec{S}^2}{2} \right] \Big/ \operatorname{Sp} e^{-\beta(H-\mu\hat{N})}; \qquad (2)$$

here $\beta = (kT)^{-1}$; $\mu$ is the chemical potential of the electrons in the metal; $\hat{N}$ is the operator of the number of electrons in the metal.

Carrying out the calculations, we obtain

$$E = \left[ E_s e^{-\beta E_s} + 3E_t e^{-\beta(E_t + \Delta\Omega(\beta))} \right] / \left[ 1 + e^{-\beta E_s} + 3e^{-\beta(E_t + \Delta\Omega(\beta))} \right], \qquad (3)$$

where $\Delta\Omega$ is the increment of the thermodynamic potential per one paramagnetic impurity with $S = 1$, arising as a result of the interaction with this impurity.

In a similar way one can also calculate the mean value of the operator of the square of the spin moment of the molecule:

$$\left\langle \vec{S}^2 \right\rangle = \frac{6e^{-\beta(E_t + \Delta\Omega(\beta))}}{1 + e^{-\beta E_s} + 3e^{-\beta(E_t + \Delta\Omega(\beta))}}. \qquad (4)$$

If in the system (organic compound—metal) the formation of quasi-bound magnetic states is possible, then $\Delta\Omega < 0$, and, as is seen from (3), the population of the triplet level increases owing to the lowering of the energy of the metal.

The formation of quasi-bound magnetic states is possible, according to Nagaoka' s work ([3]), for a negative exchange-interaction constant. In this case it may turn out that $|\Delta\Omega| \gg E_t$, since the region in which the lowering of the energy in the metal occurs is of the order of $10^{-5}$ cm (see, for example, ([3])). In this case the triplet level will be completely populated, and the organic molecule will behave as a paramagnetic impurity with $S = 1$. The form of the anomaly curve is, very probably, connected with the structure of the triplet level.

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*Note: Figure translations are in progress. See original paper for figures.*