

Nuclear-spin relaxation near the metal-insulator transition

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A novel mechanism of nuclear-spin relaxation in doped semiconductors due to singlet pairs of local moment is introduced. It is argued that this mechanism, together with a Korringa-type relaxation, operates on both sides of the metal-insulator transition. Our picture explains the anomalous temperature and magnetic field dependence observed experimentally.

In a recent Letter¹ the spin-lattice relaxation time of ²⁹Si nuclei in Si:P was measured closer to the metal-insulator transition and down to much lower temperature than in previous work.² The new measurements bring out even more clearly the anomalous magnetic field and temperature dependence of $1/T_1$ and its large deviation from the Korringa behavior even on the metallic side of the metal-insulator transition. In Ref. 1, $1/T_1$ was found to be inversely proportional to the magnetic field B and the temperature dependence was fitted to a power law. A prominent feature of the data is that T_1^{-1} appears to change smoothly through the metal-insulator transition. In this paper, we propose that the relaxation rate actually consists of two contributions: (i) a Korringa-type process due to electrons near the Fermi energy, which operates even when the states are localized, provided the localization length is sufficiently long and (ii) a new relaxation process due to pairs of exchange-coupled localized spins deep below the Fermi energy. These local moments clearly exist in insulators and we argue that they persist smoothly into the metallic side. In process (i), T_1^{-1} is proportional to T but independent of B ; whereas process (ii) is independent of T and proportional to B^{-1} to a good approximation. In Fig. 1 the data from Ref. 1 are replotted to show that the temperature dependence below 100 mK is well accounted for by our model.

We take a highly simplified view of the electronic states near the metal-insulator transition (see Kamimura³ and Takemori and Kamimura⁴). We assume the existence of one-electron states with energy E_α and a mobility edge at E_c . The interaction between the electrons are accounted for

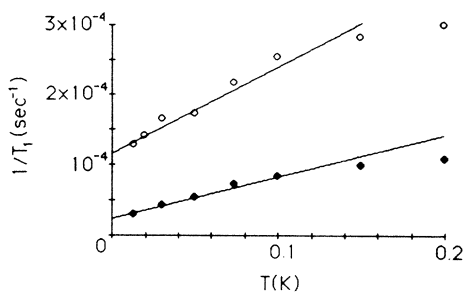


FIG. 1. Nuclear-spin relaxation rate data from Ref. 1 plotted vs temperature. Open and closed diamonds correspond to $n/n_c = 0.9$ and 1.03, respectively. Data were taken in a magnetic field of 0.844 T. Straight lines are guides to the eye. The present theoretical model predicts straight lines with slopes and intercepts which are of the right order of magnitude.

only by an intrastate repulsion U_α so that the energy of a doubly occupied state α is $2E_\alpha + U_\alpha$. We assume that $U_\alpha = 0$ for extended states ($E_\alpha > E_c$) and U_α increases monotonically with decreasing localization length ξ for localized states. In the presence of a magnetic field B , the boundary E_A between singly and doubly occupied states is given by the condition

$$U_A + \mu_e B = E_F - E_A \quad (1)$$

Schematically the solution of Eq. (1) is shown in Fig. 2. The states between the Fermi energy and $E_A(I)$ for insulators and $E_A(M) = \mu_e B$ for metals are singly occupied. Below that, we have a band of doubly occupied states.⁴ At even lower energy, below $E_B(I)$ and $E_B(M)$, the states are singly occupied again. These singly occupied states can be thought of as isolated bound impurity states and carry a local moment. In this picture it is clear that such isolated impurity states would persist into the metallic side.

It is well known that the local moments of these isolated impurity states interact via an antiferromagnetic exchange coupling:⁵⁻⁷

$$H = \sum_{\alpha, \beta} J_{\alpha\beta} \mathbf{S}_\alpha \cdot \mathbf{S}_\beta \quad (2)$$

where $J_{\alpha\beta}$ between the states α and β separated by a distance R is given approximately by⁸

$$J_{\alpha\beta} = 1.636 \frac{e^2}{\epsilon a_B} \left(\frac{R}{a_B} \right)^{5/2} \exp \left(- \frac{2R}{a_B} \right) \quad (3)$$

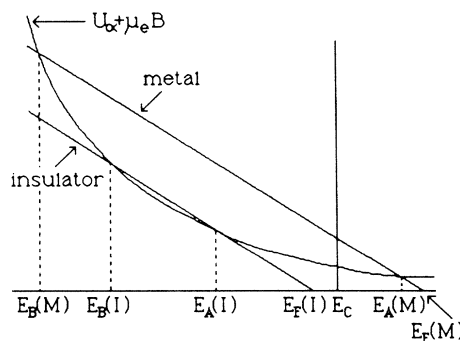


FIG. 2. Schematic solution of Eq. (1). In a metal, states are doubly occupied between $E_A(M)$ and $E_B(M)$ and singly occupied otherwise and similarly in an insulator.

where a_B is the Bohr radius of the impurity state. Bhatt and Lee⁶ have used a scaling procedure to analyze Eq. (2). The essential point is that $J_{\alpha\beta}$ is very broadly distributed as a result of its exponential dependence on R . Thus the spins can be organized naturally into pairs according to the size of J and pairs that are most strongly coupled are frozen into a singlet state. The singlets weakly renormalize the exchange coupling between the remaining spins which in turn form singlet pairs. Thus we can think of the system as consisting of singlet pairs with singlet-triplet splitting given by a distribution $P(J)$. The distribution $P(J)$ should be calculated by a renormalization procedure but we will make a rough estimate a little later.

In the inset in Fig. 3 we show the energy level of a single pair of spins in the presence of a field B . When the splitting between the singlet and the lowest triplet level coincides with $2\mu_n B$, the nuclear-spin splitting, the spin pair will relax the nuclear spin. The relaxation rate is independent of temperature as long as $kT \gg 2\mu_n B$, which is always satisfied in the experiment. Since $\mu_n B \ll \mu_e B$, we have $J \approx 2\mu_e B$ to a very good approximation. The relaxation rate is therefore proportional to the probability of finding $J = 2\mu_e B$, i.e., $P(J = 2\mu_e B)$. Now $P(J) = P_R(R)/|dJ/dR|$, and we expect $P_R(R)$ to be a slowly varying function of R . From Eq. (3) we have $|dJ/dR| \propto J$ as a result of the exponential dependence on R . Thus we conclude that the T_{1p}^{-1} should be roughly proportional to $1/J$, i.e., to $1/B$.

In the following we make a slightly more quantitative estimate of $P_R(R)$. If we ignore the weak renormalization of the remaining exchange coupling by the frozen singlets, $P_R(R)$ is equivalent to the following. Beginning with a random distribution of sites, we first count the shortest bond, then the pair that is bonded is removed, and the next shortest bond is counted, etc. The resulting distribution of

bond length is $P_R(R)$. Let us consider the situation when the bonding processes have reached the length R . Then the number of bonded pairs per unit volume is $\int_0^R P_R(R) dR$. On the other hand, if we surround a spin with a sphere of radius R , the average number of other spins in the sphere is

$$N(R) = \frac{R^3}{R_0^3} \left[1 - \exp\left(-\frac{R^3}{R_0^3}\right) \right],$$

where $R_0^3 = 3/4\pi n_s$ and n_s is the density of spins. These other spins must already be bonded, either to spins inside or outside of the sphere. Thus we set

$$\int_0^R dR P_R(R) = \frac{1}{2} \frac{N(R)}{4\pi R^3/3}.$$

From this we obtain

$$P_R(R) = \frac{9}{8\pi} \frac{1}{R^4} \left[1 - \exp\left(\frac{R^3}{R_0^3}\right) - \frac{R^3}{R_0^3} \exp\left(-\frac{R^3}{R_0^3}\right) \right]. \quad (4)$$

Thus we see indeed that $P_R(R)$ is a slowly varying function of R in the region of interest.

For Si:P, it appears that the spin diffusion among nuclear spins due to dipolar coupling is much faster than T_1^{-1} . In that case T_1^{-1} is just the relaxation rate due to the pairs. This can be calculated with the use of the standard theory if we make the effective-mass approximation for the impurity wave function⁹ and the Heitler-London wave function for the pair. The result is

$$\frac{1}{T_{1p}} = \frac{2\pi}{\hbar} \left\langle \left(\frac{16\pi}{3\sqrt{2}} \mu_e \mu_n |\psi(x_n)|^2 \right)^2 \right\rangle P(J = 2\mu_e B), \quad (5)$$

where $\psi(x_n)$ is the electron wave function at the nuclear site x_n . Taking $a_B = 15 \text{ \AA}$ and $\epsilon = 10$, the results are shown in Fig. 3 for several values of the parameter n_s/n_c . We see that if we take $n_s/n_c \approx \frac{1}{40}$, where n_c is the critical value for the metal-insulator transition given by $n_c^{1/3} a_B = 0.25$ and close to the impurity concentration studied in Ref. 1, we are within the correct order of magnitude of the experimental zero-temperature intercept in Fig. 1. Given the crudeness of the present estimate and the uncertainty of what n_s/n_c should be, this agreement is encouraging.

We next discuss process (i), the relaxation due to the electrons near the Fermi surface. On the metallic side this is the familiar Korringa process. The linear- T coefficient in Fig. 1 for the metallic sample is about three times the free-electron estimates.¹ This kind of enhancement can be due to correlation in the Fermi-liquid picture and is certainly reasonable. The deviation from linearity above 100 mK may be indicative of the small energy scale for a system near the metal-insulator transition. Transport measurements⁹ also showed that the true low-temperature behavior is apparent only below 100 mK.

On the insulator side, the nuclear spin can relax by the spin-flip scattering of weakly localized electrons near E_F . These processes include the following: (a) A spin-down electron in a doubly occupied state near $E_A(I)$ scatters into an empty state near E_F and inverts. (b) A spin-down electron in a singly occupied state scatters into an empty state and inverts. (c) A spin-down electron in a singly occupied state inverts and scatters into a singly occupied state with a spin-down electron. At very low temperature, process (a) is

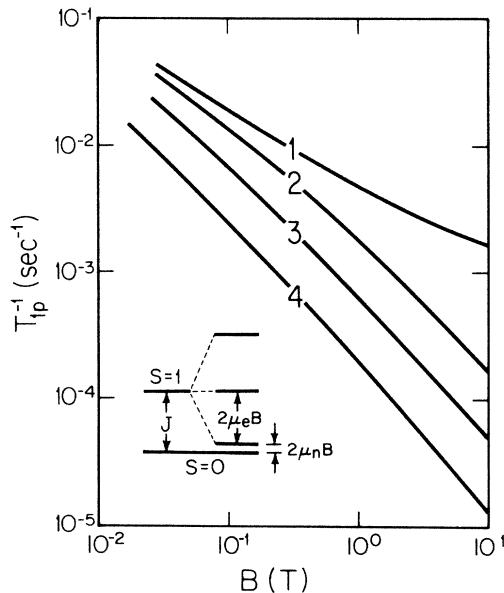


FIG. 3. The field dependence of T_{1p}^{-1} evaluated according to Eq. (5) for four spin densities n_s with parameters given in the text following Eq. (5). (1) $n_s = n_c$, (2) $n_s = 0.1n_c$, (3) $n_s = 0.05n_c$, and (4) $n_s = 0.025n_c$. Note the approximate B^{-1} behavior. The inset shows the energy levels for a pair of exchange-coupled local moments which relaxes the nuclear spin.

dominant. The condition of conservation of energy is

$$\epsilon_i + 2\mu_e B + U_i = \epsilon_j + 2\mu_n B . \quad (6)$$

Subscripts i and j correspond to the initial and final states. From Eq. (6), the relaxation rate of these processes can be calculated as follows:

$$\frac{1}{T_{1k}} = \frac{2\pi}{\hbar} \sum_{i,j} \left[1 + \exp\left(-\frac{\mu_n B}{k_B T}\right) \right] |M_{ij}|^2 f_s(E_i) f_s(E_j) \times \delta(E_F + 2\mu_n B - E_i - U_i - 2\mu_n B) , \quad (7)$$

where $f_s(E)$ is the Fermi function of the singly occupied state E and M_{ij} is the transition matrix element which involves the overlap between the initial and final single-particle wave functions. We introduce $P^{(2)}(E_1, \mathbf{R}_1, E_2, \mathbf{R}_2)$ as the probability of finding states with energies E_1 and E_2 localized at \mathbf{R}_1 and \mathbf{R}_2 . It can be written as

$$P^{(2)}(E_1, \mathbf{R}_1, E_2, \mathbf{R}_2) = G(E_1, \mathbf{R}_1, E_2, \mathbf{R}_2) P_0(E_1) P_0(E_2) ,$$

where $P_0(E)$ is the density of localized state per unit volume. It is easy to show that the average T_{1k}^{-1} due to this process is reduced from the Korringa relaxation T_{1k}^{-1} by the following factor:

$$\mu = \frac{1}{\pi^2 \xi_A^3 \xi_F^3} \int d\mathbf{R}_1 d\mathbf{R}_2 \exp\left[-\frac{2|\mathbf{R}_1 - \mathbf{R}_n|}{\xi_A} - \frac{2|\mathbf{R}_2 - \mathbf{R}_n|}{\xi_F}\right] \times G(E_A, \mathbf{R}_1, E_F, \mathbf{R}_2) , \quad (8)$$

where ξ_A and ξ_F are the localization length at E_A and E_F . If the sites of localized state are distributed completely at random in space, $G \approx 1$ and we have $\mu \approx 1$. Thus any deviation from $\mu \approx 1$ must come from the fact that states are correlated in the sense that states that are nearby in energy are far apart in space. The physical origin of this correlation must come from level repulsion. Let us introduce a length L_c ,

$$L_c = \left(\frac{3}{4\pi P_0(E_F)} \right)^{1/3} (E_A - E_F)^{-1/3} , \quad (9)$$

which is the average separation of localized states with an energy difference $E_F - E_A$. If ξ_F (and/or ξ_A) is greater than L_c , it is clear from Eq. (8) that $\mu \approx 1$. The opposite situation is more complicated. While the states are on the average L_c apart and the relaxation rate due to these states is small [$\sim \exp(-L_c/\xi)$], it is possible to find states that are much closer than average, and these states will dominate the relaxation rate. It is only level repulsion that prevents states from being too close together. As originally discussed by Mott and Davis¹⁰ and Mott,¹¹ states with strong overlap will have a certain minimal splitting in their energies. This splitting is difficult to estimate except in the limit when the states are basically localized impurity-bound states. While it is difficult to make quantitative predictions, these considerations suggest to us that the Korringa-type linear- T -dependent contribution to T_1^{-1} probably persists deep into the insulator side of the metal-insulator transition.

In summary, our model of two types of contribution to T_1^{-1} appears to account for existing data.¹² Our model is obviously highly idealized. Some problems require further

discussion.

(1) We have treated the local moments and the states near the Fermi level as two separate entities. The question arises whether the exchange interaction between the local moment will be affected by the rest of the electrons, e.g., via some kind of indirect exchange interaction. The indirect exchange interaction can be estimated in analogy with the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in metals. We must remember that the RKKY interaction in a dirty metal decays exponentially as $\sim 1/R^3 \exp(-R/\lambda)$,¹³ where λ is the mean free path of electrons. Near the metal-insulator transition, $\lambda \approx k_F^{-1}$ is of the order of a_B , whereas the direct exchange would decay much more slowly on a length scale given by the localization length. Besides this, the preexponential factor J_0^2/E_F of the RKKY interaction is also smaller than the preexponential factor of the direct exchange interaction. We therefore conclude that the indirect exchange interaction is weaker than the direct interaction, and does not change the characteristic of the exchange interaction between the local moments. Thus, an exchange interaction given by Eq. (3) with a_B replaced by a different parameter is a valid starting point (see below).

(2) In Si:P the multivalley degeneracy enhances the binding energy of clusters.¹⁴ The isolated impurities are actually at the top of the Hubbard band and near the Fermi level. Thus, the most likely candidates for the local moment are the clusters with an odd number of electrons. The exchange interaction between these clusters is obviously more complicated than Eq. (3), but the qualitative feature of our model is unchanged. Our estimate of the absolute value of T_1 is clearly only qualitative, but the temperature and field dependence should be correct.

(3) A proper calculation of the renormalized $P(J)$ should be possible along the lines of Ref. 6. In particular, according to Ref. 6, $P(J)$ may be approximated by the form $J^{-\alpha}$, where α decreases gradually from unity as the cutoff is reduced. However, we must emphasize that in Ref. 1 the experiments were performed in the limit $\mu_e B \gg kT$ so that the magnetic field energy rather than kT is the cutoff. Since $\mu_e B$ is fairly large, the renormalization is probably not too strong so that α may be close to 1. In particular, the behavior of the spin susceptibility $\chi \sim T^{-0.7}$ quoted in Ref. 1 is valid only in the limit of zero field and the exponent 0.7 may be considered an empirical lower bound on α . Thus we expect T_1^{-1} to vary as $B^{-\alpha}$, where α is between 0.7 and 1. It will be interesting to use the magnetic field dependence to separate out the local moment and the Korringa-type contribution to T_1 and study more carefully the field dependence of the local moments part.

Finally, we point out that our model should be applicable to any metal-insulator transition system. In particular, the data in the mixed bronze¹⁵ may be interpreted by similar ideas except that the nuclear-spin diffusion is very slow in that case and one should observe a broad distribution of T_1^{-1} in the insulator phase due to paired local moment relaxation. We believe the existing data strongly support the existence of paired local moment on both sides of the metal-insulator transition, and this picture should have implications for a scaling description of the transition.

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