PHYSICA B

Biased diffusion and pairing of impurities in quantum crystals

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We calculated the time of pairing of *ortho*-H_2 impurities in solid *para*-H_2. The quantum diffusion has a strong directional bias which at moderate temperatures is against a mutual approach of particles and creates a "kinetic barrier." At lower temperatures, this barrier freezes out causing a rapid increase in pairing rates. This explains a well-developed maximum in the pairing time as a function of temperature.

The main feature of quantum diffusion is a very small tunneling frequency ω_0 for impurity particles. This makes the diffusion sensitive to any inhomogeneities of the potential relief. If the inhomogeneities are random, the global diffusion is isotropic. Sometimes diffusion exhibits a strong directional bias which may be caused by an external field or, in case of pairing of impurities, by a non-random distortion of a potential relief by the interaction U(r) of the pairing particles. When $\hbar\omega_0$ is comparable with U(r), the diffusion is anisotropic with a bias induced by U(r). The time of mutual approach of impurities (the pairing time), which is important for clustering of impurities in helium or hydrogen crystals, recombination or fusion of atomic hydrogen in a solid matrix, *etc.* may be affected by this directional bias.

We have analyzed pairing of o-H_2 impurities in solid p-H_2. An additional motivation was a pronounced peak in the temperature dependence [1] of the pairing time, Figs. 1,2. This peak was surprising since all reasonable diffusion mechanisms have diffusion rates which decrease with decreasing temperature or saturate. Attempts to explain this peak by some new diffusion mechanism have been unsuccessful. A different idea [2] was that a directional bias may lead to a non-monotonic temperature dependence of the pairing time even for monotonic individual hopping rates.

The quadrupole interaction of o-H_2 impurities $U(r) = U_0(n)(a/r)^5$ causes the energy mismatches $\varepsilon_{ij} = U(r_i) - U(r_j)$ which hinder the tunneling from the site i to j (a is the lattice size, $U_0 \sim 0.8$ K depends on the orientation of the pair of molecules). The impurity can tunnel if the energy ε_{ij} is taken care of by spontaneous emission of phonons with $\omega = \varepsilon_{ij} > 0$ or by inelastic scattering of thermal phonons [3,4]. The probability of the spontaneous emission increases with frequency as ω^3, while the probability of the inelastic scattering drops as $1/\omega^2$. The inverse time of the phonon-assisted tunneling from i to j is

$$\frac{1}{\tau_{ij}} = \frac{\omega_0^2}{\Theta}\left[\frac{\Theta^2}{\varepsilon_{ij}^2}\left(\frac{\xi T}{\Theta}\right)^9 + \left(\frac{\xi_1\varepsilon_{ij}}{\Theta}\right)^3\theta_{ij}\right] \quad (1)$$

where $\theta_{ij} = 1$ if $\varepsilon_{ij} > 0$ and is 0 if $\varepsilon_{ij} < 0$, Θ is the Debye temperature, ξ, ξ_1 are fitting parameters. If $\varepsilon_{ij} < \omega_0$, then the tunneling time $1/\tau_{ij} = \omega_0$ is by several orders of magnitude shorter than (1).

We calculated the time dynamics of the number of nearest-neighbor pairs. For two impurities all that matters is a change in a relative positions of impurities. We considered one impurity as mobile, while others were static. The mobile impurity diffuses among the static ones, and can pair with any of them. The potential for the mobile impurity includes its interaction with all impurities and is determined self-consistently using the current distribution of impurities. The immobility of other impurities is the main approximation.

The time dependence of the number of pairs looks like a staircase rather than an exponential curve, and pairing is characterized by a set of times. A similar difficulty was encountered in experiments [5]. To avoid ambiguity, we use as a pairing time the time for the pairing of about 10% of impurities. The characteristic time in
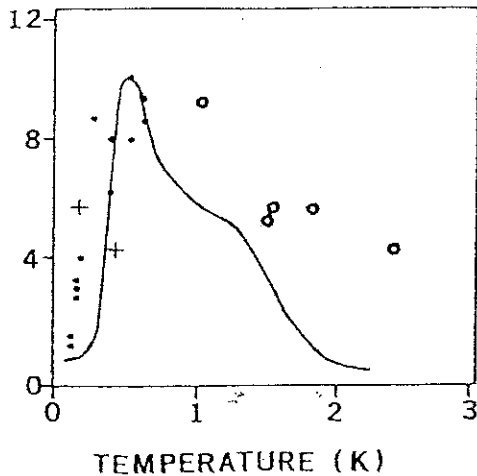
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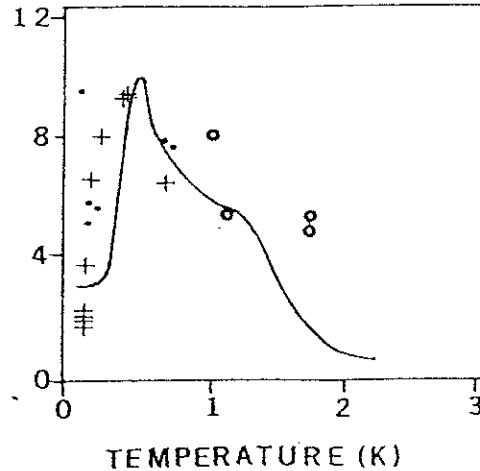Figure 1. Pairing time (in hours) for x = 1%. Experimental data are taken from Ref.1.

Figure 2. Pairing time (in hours) for x = 0.19%. Experimental data are taken from Ref. 1.

initial and intermediate stages *always* exhibits a sharp temperature maximum. The pairing time in the final stages is much longer and does not have a maximum because some impurities are trapped in certain crystallographic positions.

Figs. 1 and 2 show our numerical results. The experimental error bars (not shown) are larger than the distance between the curves and experimental points. The existence of the peak and its shape are not sensitive to the values of the fitting parameters. Independent parameters in (1) are the tunneling frequency ω_0 and the ratio ξ_1/ξ^3 (ξ is of the order of the coordination number [6,7]). The third parameter remains free. The ratio ξ_1/ξ^3 fixes the position of the peak. The data [1] are consistent with its position anywhere between 0.4 K and 0.7 K. This may change ξ_1/ξ^3 by an order of magnitude (in the figures ξ_1/ξ^3 = 31). The estimates [1,8] give $\omega_0 \sim 10^3$ s^{-1}. This leads to $\xi \sim 50$. A more realistic value, $\xi \sim 12$, leads to $\omega_0 \sim 10^5$s^{-1}. These estimates give upper and lower bounds for ω_0. For comparison, ω_0 for ^{3}He impurities in ^{4}He is 10^7 s^{-1}.

In summary, our results confirm that the low-temperature peak in the pairing time is caused by a directional bias in diffusion imposed by the interaction of the pairing particles. One of the diffusion mechanisms - the tunneling with inelastic phonon scattering - is biased against the mutual approach of particles and is, in some sense, is counterproductive with

respect to pairing. When this mechanism dominates, a decrease in temperature results in a slow-down of all motion, including the pairing. At low temperatures, a temperature-independent motion with emission of phonons is more important. Then the freezing of the former mechanism, biased against pairing, increases the pairing rates. In contrast to a more detailed version [9], we performed separate fits to experimental data at different concentrations.

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