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Muons and Muonium in Solids

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A muon is a very special probe of solids, since its spin polarisation can be monitored to define its behaviour in the solid: the site it occupies, the local magnetic field it experiences, and the time-dependence of the local field. The muon is a sensitive, robust and (since resonance is exploited) accurate probe. If its application has left many ambiguities of interpretation, these have usefully eliminated complacency from several areas of solid-state studies. This talk will survey how muons can be exploited both as a probe of the host solid and as a unique analogue of hydrogen in topics as varied as spin glasses, phase transitions and quantum diffusion.

1. Introduction

Almost all new techniques evolve through several stages. First comes the period of euphoria, when a handful of tests hint at a triumphant future. Then comes the time of dismay, when key results misinform, mislead, or simply fail to appear. Finally the age of reason emerges: the anomalies prove to contain their own interesting physics, and understanding takes over in a well-defined range of application. Muon spin rotation has passed from the first to the second stage and is fast moving into the third. I shall concentrate therefore on what this special solid-state probe can measure and how this relates to current directions in solid-state science. General surveys are to be found in references [1-6].

The important feature of muons is that they can be produced by a reaction ($\tau_\pi \sim 2.6.10^{-8}$ sec):

$$\pi^+ \rightarrow \mu^+ + \nu_\mu$$

which leaves the $S = \frac{1}{2}$ muons longitudinally polarised relative to the beam. When the muon itself decays ($\tau_\mu \sim 2.2.10^{-6}$ sec):

$$\mu^+ \rightarrow e^+ + \nu_e + \nu_\mu$$

the positrons are preferentially polarised parallel to the muon spin. There are thus at least two types of experiment. First, one can monitor the way the muon spin direction changes with the time between creation and decay. Secondly, one can ignore the spin and simply monitor the direction distribution of muons channelling after the decay of the pion. I shall only discuss the first method here. The practical aspects are reviewed elsewhere [3, 5, 6] and, for present purposes, I shall merely mention there are two basic types of experiment:

Transverse experiments. Here the magnetic field (either externally or, as in a ferromagnet, internally applied) is normal to the plane containing the positron detectors. Any one detector j records a signal $N_j(t)$:

$$N_j(t)/N_j(0) = \exp(-t/\tau_\mu)\,[1 - G_t P_t(t)\cos(\omega_\mu t - \phi_j)]$$

where G_t contains geometric factors of no interest here, ω_μ is the precession frequency, ϕ_j a phase for detector j, and $P_t(t) \equiv \exp[-\sigma^2 g(t)]$ is the transverse relaxation function.

Longitudinal experiments have a magnetic field along the initial beam direction, and measure the time dependence of the longitudinal polarisation, namely

$$P_\ell(t) = G_\ell\,[N_-(t) - N_+(t)]/(N_- + N_+)$$

with G_ℓ another geometric factor. Zero-field experiments are done with this geometry. Both $P_t(t)$ and $P_\ell(t)$ can be written in terms of correlation functions $< h(t)h(o) >$ which describe the internal fields or other factors which influence the muon behaviour.

Clearly the transverse experiments give the rate and (from the ϕ_j) the sense of precession. This tells one (A) The sign and strength of the local magnetic field; (B) Whether muonium([μ^+ e], analogous to H^o) is formed; (C) The Knight shift, which monitors the magnetic response of conduction electrons; (D) The electric field gradient at neighbours to the muon. Likewise, one can obtain information about muon dynamics from $P_\ell(t)$ or $P_t(t)$, e.g. (a) The mean square random field σ^2 encountered by the muon (and hence, using the anisotropy as the applied field direction is changed, the site occupied by the muon). (b) The correlation time characterising the time dependence of the field the muon encounters. This time may reflect various processes, notably (i) Motion of the muon from site to site, (ii) Spin fluctuations of host atoms, (iii) Trapping processes, e.g. at impurities

with static but randomly-orientated spins. Zero-field experiments [7] readily distinguish (i) and (iii).

It would be wrong to suggest that the analysis of $P_\ell(t)$ or $P_t(t)$ was simple or unambiguous. One is using a short-lived probe, with a time "window" of a few nanoseconds (equipment-limited) to a few microseconds (muon-lifetime limited) in a situation in which many distinct processes can occur. Current muon spin studies are moving slowly from efforts to grasp what is happening to efforts to exploit it to understand dynamic processes.

2. Muons in Semiconductors

The standard view of interstitials in any diamond structure lattice (diamond, Si, Ge) is that they occupy the obvious tetrahedral site except when polarisation energies are large enough to favour the hexagonal site. This naive view is adequate for "hard sphere" interstitials, but scarcely so for those which can form strong chemical bonds.

Experimentally, the dramatic results are these:

(a) Hydrogen in silicon (and probably in diamond) is present in a form which is neither optically nor electrically active. Despite much over-simple theory, there is no experimental reason to accept as an explanation simply that hydrogen at tetrahedral sites acts as a deep donor.

(b) Muons in diamond, silicon and germanium all show two distinct forms (see e.g. [8]): normal muonium, which does indeed resemble a deep donor with tetrahedral symmetry, and anomalous muonium, the rather more common form, which has trigonal symmetry, with considerable anisotropy. It is a distinct possibility that one form is metastable, evolving partly into the other.

(c) Several experiments indicate rapid motion of muonium [9], rather than a localised static state.

(d) In Ge, pion results suggest a tetrahedral site only at higher temperatures, the channelling of emitted muons indicating an off-centre site below about $60^{\circ}K$.

Theoretically, a range of questions and obvious issues for calculations arise. [10] First, do hydrogen, muons and pions behave in the same way? A major question here involves timescale and mode of formation. If atomic

hydrogen can be introduced into a perfect host crystal, it will presumably reach the thermodynamic ground state. If muons or pions are introduced, with their short lifetimes, they may be held up in metastable states and never reach the ideal ground state. There is a further complication too: implanted hydrogen will create damage, notably vacancies, at which hydrogen may bond. Muons cause ionisation and, since this may decay only on a timescale comparable with or longer than the muon lifetime, one is in doubt about whether it is muonium [μ^+e] or some bound exciton complex [μ^+e eh] which is seen. The second main question is the extent to which muonium in diamond, silicon and germanium behaves in the same way. Qualitatively, there are clear analogues. Quantitatively, the hyperfine constants or normal muonium do not vary monotonically with atomic number, suggesting that the simplest models need to include other factors.

Two further questions concern more specific models. Are impurities or defects involved? It seems that donors and acceptors have only a secondary influence. Apart possibly from transient defects created by the muon itself near the end of its path, neither defects nor impurities seem critical in semiconductors. An exception would occur if the muon were tunnelling rapidly around a defect or impurity, as in Haller's model of hydrogen in Ge [10]. Is tunnelling involved, either extrinsically or in a self-trapped state? Evidence from the temperature dependence of hyperfine constants is negative, but only eliminates some of the possibilities.

Two calculations are of importance here. Mainwood and Stoneham [11] have looked at total energy surfaces for μ^+ and [μ^+ e] in large clusters of C and Si using self-consistent semi-empirical methods. They concluded that all minima were shallow, and that the tetrahedral sites were energy maxima. Thus, for muons, either a tunnelling state is involved (presumably impurity-associated) or possibly a bound-exciton complex like [μ^+ e e h] is the source of what is observed. An additional conclusion was that hydrogen in crystalline Si was stable in molecular form ($2H_i \rightarrow H_{2i}$), with motion activation energy close to that observed. Sahoo et al [12] used a self-consistent, non-empirical method unrestricted Hartree-Fock theory) on smaller C clusters, and concluded the tetrahedral site was stable. The resolution is not too clear, for the smaller cluster and more restricted geometries treated may invalidate the apparent advantages of the non-empirical approach.

Whatever the resolution of the states of muonium in diamond, Si, and Ge, the muon studies have forced solid state scientists to recognise the truism that one-electron levels and band structure do not define all that is important in solid state physics. The issues brought to the fore here are

(i) How one calculates total energy surfaces;

(ii) How one treats transient processes and metastable states;

(iii) How one identifies and, where necessary, characterises and calculates, properties of tunnelling states.

3. Oxides

Studies of hydrogen in oxides have been confined mainly to infrared work (for the OH^- species has a well-defined molecular vibration), and to spin resonance in those cases where hydrogen is associated with a suitable defect. Solid-state reactions, like the transformations of hydroxides to oxides, are of interest, but have not yielded atomic-scale information easily. Oxides for fusion reactor systems stimulated work on hydrogen in insulating oxides. The muons brought a specific bonus: the probe could be put into any oxide, without the danger of a separate surface hydroxide phase forming.

The most interesting results so far have been on magnetic oxides (see e.g. [13]). Three main features emerge. First, at temperatures below about $500^{\circ}K$ the muon forms a muoxyl ion ($O\mu^-$), analogous to hydroxyl. This is probably the case in all oxides studied, though there may be rare exceptions. In MgO, for example, $(OH)^-$ is never seen except with defects, and calculations [14] suggest that $(OH)^-$ stability is marginal with respect to interstitial protons, which has interesting consequences. In oxides with cations with low ionisation potential, another possibility is that a host cation may transfer an electron to an interstitial muon, so as to gain Madelung energy. However, muoxyl is the important form for present purposes. Secondly, muons monitor the magnetisation in magnetic oxides. Magnetic phase transitions show clearly in the muon precession frequency. The muon hyperfine interactions have two main components: dipole fields and covalent supertransfer. Thirdly, muons are mobile in oxides. Several distinct forms of motion occur: local tunnelling, small-polaron behaviour, and some unspecified (but not diffusion-controlled) by which thermalised muons can escape from fine-powdered oxides.

The corundum-structured oxides show most of these features. Thus, in Fe_2O_3 and Cr_2O_3 [13] there are some temperature ranges in which the resonance frequency simply follows the macroscopic magnetisation, including the vanishing of the magnetisation at the Neel temperature in Cr_2O_3 and at the Morin temperature in Fe_2O_3. However, Fe_2O_3 also shows a dramatic appearance of splitting below $\sim 120^oK$ as motional averaging over inequivalent sites is frozen out. In Cr_2O_3 below about 200^oK too a sudden splitting occurs, possibly associated with the occupancy of a new site. Theoretical work using model interatomic potentials in conjunction with the shell model [14] appears to correctly reproduce the sites. However, the calculations also show the existence of metastable minima; the existence of such metastable states pervades and influences very many muon experiments. Boekema et al's analysis of the magnetic behaviour suggests dipolar and super-transfer contributions are comparable (whereas dipolar terms dominate in orthoferrites).

4. Metals

In metals many of the issues which arose for oxides and semiconductors emerge once more. The advantages of the technique are evident: muons can be put into metals with low solubility for hydrogen and at temperatures where hydrogen would normally precipitate out; muons can monitor magnetic behaviour through phase transitions and can measure Knight shifts even when host nuclei have inappropriate magnetic moments; muons can monitor time-dependent fields, e.g. as they diffuse through the lattice. The problems are equally evident. When one uses a probe with a finite lifetime, is it the ground state or an excited state which one probes? How does the muon itself perturb the electron density it monitors in the Knight shift?

Muon studies have given caused theorists to make two important revisions of their views. The first came out of Knight shift studies. The simplistic view was that, given the average conduction-electron density, the (structureless) jellium model would give an accurate Knight shift; whilst transition metals might need changes, the simple alkalis should present no problems. The jellium model proved a disaster, both qualitatively and quantitatively [5, 15, 16]. The old truth that solids are made of atoms proves important: inhomogeneity on an atomic scale is important. Models which reflect this atomic nature are indeed more successful, though much remains to be done.

The second stimulus to theory came in relation to diffusion. Light interstitials (notably hydrogen) show quantum diffusion [17] analogous in many respects to small polaron behaviour (for a comparison see the Appendix to [18]). An important component is self-trapping, in which the particle is virtually immobilised by the distortion it causes in the surrounding host lattice. For hydrogen in metals, therefore, one might anticipate two regimes (see [19] for further details): at higher temperatures an incoherent hopping motion, with an activation energy related to the self-trapping energy, and at lower temperatures a coherent motion which became faster as the temperature fell. This coherent regime would be hard to obtain, both because the temperature at which it should take over is low and because the coherent motion can be readily disrupted by the random strains in real crystals. Experimental studies of hydrogen run into problems of precipitation at low temperatures. However, the local motion of hydrogen trapped by O or N in Nb shows excellent accord with the quantum theory of diffusion [20].

Muons introduce new features. First, there is a period after the fast muon enters the sample before the self-trapping distortion is set up. For positrons this lasts until decay or defect trapping. For muons or pions, one would guess self-trapping would occur after a few lattice vibrations (say 10^{-12} sec) once the muon has thermalised; this guess, whilst sometimes correct, can mislead. Secondly, for positrons, muons and hydrogen alike, impurities can be important. In many cases muons may make only a few diffusive jumps (e.g. less than 10^2 jumps) before decay, so very few impurities are encountered on average. Trapping by an isolated impurity, in a case like this, has absolutely nothing to do with the so-called Anderson localisation which leads to a mobility edge.

We may contrast two different pictures of events after a muon enters the metal [21]. In the standard picture, thermalisation and self-trapping are rapid and take place randomly in the metal lattice. Diffusion and trapping then follow, with behaviour like that of other light interstitials. In the alternative picture, thermalisation is rapid. Self-trapping is delayed, however, and is catalysed by impurities: the localisation involved in self-trapping therefore take place preferentially at impurities. Clearly impurities and defects are important; indeed, intrinsic diffusion of self-trapped muons will only be seen after thermal release from traps.

The two cases which have led to greatest discussion have been copper and aluminium. These two relatively simple, cubic, metals behaved in ways which are quite different.

Muons in Copper. Early studies suggested this was a classic example of "standard" behaviour. The site, the diffusion rate down to hydrogen temperatures, the dipolar linewidth and a rather detailed theory all fitted to at least the accuracy one could reasonably expect. Only when work down to $0.5^{o}K$ and below became available did problems arise. In essence, the zero-field data show that the dipolar width stays constant close to the value expected for the octahedral site. The transverse data show a change about $0.5^{o}K$, which the zero-field hopping analysis indicates is due to a hopping rate which changes its temperature dependence at that temperature. A further analysis will be given elsewhere. However, it is very likely that muon motion is involved, even below $0.5^{o}K$. It is equally probable that there are two distinguishable muon states separated by an energy of order $k.0.5^{o}K \simeq 10^{-4}$ eV. Whether the observed features reflect different occupancies of these states, or merely different transition rates into or between them, is not clear. Nor is the nature of the states obvious; early suggestions of the effects of isotopic differences (^{63}Cu versus ^{65}Cu neighbours) remain possible but still leave problems.

Muons in aluminium. Early studies showed this to be an anomalous case: motional narrowing was apparently complete, with no depolarisation of muons discerned. Impurity effects have been systematically studied [22], with the depolarisation rate Γ depending on concentration (f in atomic parts per million) and temperature (θ in millikelvin). For low temperatures, below 1K say,

$$\Gamma_{exp} \sim (2.3.10^{5}\ sec^{-1})\ f^{+0.69}\ \theta^{-0.57}$$

Two quite distinct explanations have been proposed. Both agree that Γ_{exp} is not simply determined by diffusive jumps, which would give $\Gamma' \sim d^{2}/D$ with d the jump distance. Kehr et al favour the sequence (i) rapid self-trapping (ii) coherent diffusion of the thermalised, self-trapped muon at a rate determined by conduction-electron scatter, giving (iii) diffusion-limited trapping giving depolarisation. Browne and Stoneham [23] favour (i) thermalisation without self-trapping, following by (ii) capture-limited trapping giving

depolarisation. Qualitatively, both have parallel features: the thermalised propagation, irrespective of whether self-trapping has occurred or not, gives a slow temperature dependence; the role of trapping in depolarisation gives the concentration dependence. The relative merits will be discussed more elsewhere. Broadly, the main problems with the extended "standard" picture of Kehr et al are how one can reconcile coherent motion with known random strains, and a large inconsistency between theory and experiment for the electron-scatter diffusion constant. Moreover, this model does not suggest why Cu and Aℓ should prove such different hosts. The main problem with the "alternative" model is explaining the delay in self-trapping. However, the model suggested [23] based on metastable states at other interstitial sites, does suggest why Cu and Aℓ should differ, and why there should be an apparent change in site observed in Aℓ at low temperatures. No detailed calculation of the capture cross-section has been attempted though, to agree with experiment, a sensible value of the order of an atomic area is needed, with an acceptable temperature dependence. Both models have parallels with other systems.

5. Prospects

We can take a broader look at some of the patterns and trends in solid state science to see where muons can contribute. Clearly there are some topics for which muons are inappropriate: they have only limited value where space resolution is needed, and none at all for long-term phenomena with timescales much greater than microseconds. Nevertheless, one might give as examples:

(1) Studies of dynamic behaviour, e.g. defect processes, chemical reactions in the solid state, or phase transitions. For phase transitions the muon can be a non-interfering probe, as for magnetic transitions in Ni and Fe_2O_3 of Fe_3O_4; it may, however, play a more useful and active role. In Pd:H, or ice, or other hydrides, the muon probes just as the next hydrogen would, and can monitor both microscopic and macroscopic ordering.

(2) Evolution of microstructure. Just as positrons have been used to probe how vacancies aggregate and how larger voids emerge, so muons have been used in studies of dilute alloys [24]. Here, if the potential of the technique is to be realised, it will be essential to back up μSR with detailed conventional techniques like metallography.

(3) Disordered systems. The μSR technique has already been applied extensively and successfully to the study of spin glasses [25]. Conventional glasses offer opportunities, especially in conjunction with hydration and dissolution behaviour. Amorphous silicon (a-Si:H) is a case where the muon could both probe and act as the "next" hydrogen. As a final possibility I should like to see higher-temperature studies. Whilst present detectors melt at uncomfortably low temperatures, liquid Fe would be especially interesting. The observed H diffusion rate is much larger than the usual upper bound of (largest phonon frequency) x (separation of interstitial sites)^2, and it would be interesting to test proposals [26] of why this might be so.

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