NMR IN SUPERCONDUCTORS

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ABSTRACT

Superconductivity is a striking physical phenomenon; it is a manifestation of quantum effects on a macroscopic scale; consequently, the most striking physical phenomena associated with it, are macroscopic ones—the total disappearance of resistivity, exclusion of flux, flux quantization in macroscopic cylinders, interference effects between junctions a macroscopic distance apart. NMR, being a microscopic tool, does not display such striking effects, but is quite suitable to investigate the microscopic nature of the superconducting state. We shall discuss various microscopic features of superconductivity, and nmr experiments relating to them.

Some of the properties of superconductors are:

(1) The pairing of electrons with opposite spins, which is the basic feature of the BCS theory, and which manifests itself in a reduction of the Knight shift.
(2) The creation of a gap, which causes the number of excitations at low temperatures to be proportional to $\exp(-2\Delta/kT)$, and the relaxation rate to be proportional to this quantity.
(3) The coherent nature of the superconducting state, which causes $1/T_1$ just below T_c to exceed $1/T_1$ in the normal state.
(4) The property of gapless superconductivity, observed in some systems (mainly with magnetic impurities, or in a magnetic field), which affects $1/T_1$.
(5) In a magnetic field, some ('type II') superconductors possess an array of magnetic flux lines. Some information about the geometry of this array can be obtained from the nmr linewidth and lineshape.
(6) Inside the flux lines, superconductivity is effectively destroyed and consequently the relaxation rate there, is characteristic of the normal metal.
(7) The magnetic flux lines are not rigid. Therefore, they fluctuate thermally yielding an additional relaxation mechanism.
(8) Very near T_c, the gap parameter Δ is not constant (in time and space), but fluctuates thermally. This yields an additional relaxation mechanism, which should be relatively strong in superconductors with a quasi one-dimensional band structure. This effect has apparently been observed.

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1. INTRODUCTION

The most striking features of superconductivity are, probably (i) the total disappearance of the electrical resistance, (ii) the exclusion of the magnetic flux (Meissner Effect), (iii) the quantization of flux in units of $\phi_0 = hc/2e$ in cylinders, (iv) interference between macroscopically separated tunneling junctions (SQID), and (v) the phenomenon of gapless superconductivity. None of these are nmr effects because the basic property of superconductivity is a quantum effect on a macroscopic scale, while nmr is a microscopic tool. Therefore, the nmr properties of superconductors are not as striking as the above-mentioned effects; however, they can help us to investigate the microscopic aspects of superconductivity.

In this paper, no attempt is made to discuss the theory of superconductivity. Only some features of superconductivity, and the nmr properties related to them, are discussed superficially.

2. THE KNIGHT SHIFT

When the BCS theory was proposed, one of the first critical experiments to check it was the measurement of the Knight shift (KS) in the super-

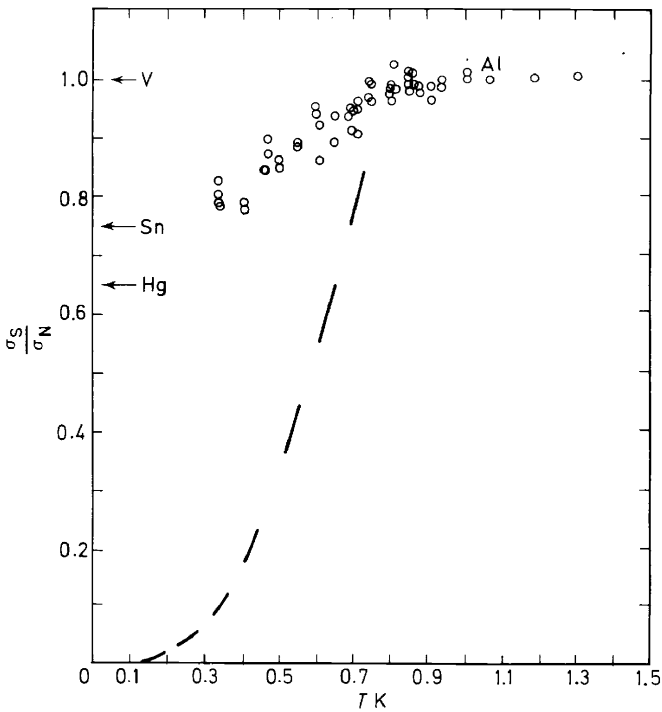

Figure 1. The Knight shift as function of temperature in aluminium, with indications of the KS in mercury, tin and vanadium. (Early data from Hammond and Kelly)

conductive (SC) state[1]. According to the BCS theory, the spins are paired to singlet states, and therefore, it was argued, the KS should disappear. Indeed it was observed that the KS in the SC state is somewhat smaller than in the normal state (by about 30 per cent in Hg, Sn, Al, etc.), but it does not disappear.

In vanadium, it hardly changes at all (*Figure 1*). However, this large discrepancy is not a fault of the BCS theory, but was due to incomplete understanding of the mechanisms contributing to the KS. The KS has an orbital contribution, which is strong in transition metals (like vanadium); this contribution is not affected by anything that happens to the spins, nor by the pairing of $+\boldsymbol{k}$ and $-\boldsymbol{k}$ states, since the orbital angular momentum is anyway quenched by the kinetic energy to an extent of the order of the bandwidth (a few eV) which is very large compared with the SC gap, and therefore is not affected by its existence. This explains why the KS in vanadium hardly changes in the SC state. In mercury, tin etc., spin–orbit interaction, coupled with scattering mechanisms, may be responsible for a large part of the KS (if $\tau_{\text{scat}}(\lambda/\Delta E)^{-2} < h/\Delta$ and SC is not strong enough to affect the spin flipping rate appreciably); while in aluminium, probably impurities in the thin films (or particles) may be responsible, since spin–orbit coupling in aluminium is weak. Also, when the magnetic field is not *exactly* parallel to the film, superconductivity in certain regions is destroyed. More recent measurements by Hammond[2] and Lipsicas[3] on aluminium do yield results that agree with the BCS theory. Anyway, KS measurements in SC teach us more about the quality of the samples than about the validity of the BCS theory, and fail as a critical test of it. However, these measurements are still useful in providing an estimate of how much of the contribution to the KS comes from spins, and how much from orbit, as demonstrated by the work of Clogston, Gossard, Jaccarino and Yafet[4] on V_3Si, V_3Ga.

3. MEASUREMENT OF THE SUPERCONDUCTING GAP Δ

The gap Δ is perhaps the most important parameter characterizing the superconducting state. In order to break a Cooper pair, and create a pair of excitations, an energy of at least 2Δ is required. Δ can be measured conveniently by nmr by measuring the relaxation time T_1, which at low temperatures (say, below $\frac{1}{2}T_c$) is proportional to $\exp(2\Delta/kT)$[5]. Actually, Δ is somewhat temperature dependent, but below $\frac{1}{2}T_c$ this dependence is weak. Determination of Δ by this method is simple, reliable, and accurate. It possesses certain advantages over other methods; namely, if Δ is measured by measuring the specific heat, small amounts of other phases (which perhaps are not superconducting) cause large errors; while in T_1 measurements, they hardly contribute to the relaxation signal at long times. Tunneling yields accurate values of Δ for pure materials with a large coherent length, but for 'dirty' alloys, it yields information about the surface rather than about the bulk[6].

In addition to giving the value of Δ (which agrees with the BCS value of $2\Delta = 3.5\,kT_c$ rather well), nmr measurements also served to prove the existence of a single gap in some multiband alloys[7] (such as V_3Pt, V_3Ga, etc.); where certain theories suggested the possibility of several gaps (say, different gaps for 3d and 4s electrons), or an anisotropic gap. T_1 vs T curves yield a single exponential, which is the same for different nuclei (say, ^{51}V and ^{195}Pt in V_3Pt) for which contributions to T_1 from s electrons and d electrons should be different.

Since T_1 depends on the magnetic field (as will be discussed later), measurements have to be carried out by the pulsed field technique[8] (where the relaxation takes place at $H = 0$, but nuclei are polarized and their magnetization measured in a finite field); or T_1 may be measured as a function of H and extrapolated to $H = 0$ (for type II superconductors, where the magnetic field does not destroy the superconductivity).

4. T_1 AT TEMPERATURES CLOSE TO T_C

One of the most striking successes of the BCS theory was the prediction that T_1 just below T_c is *shorter* than in the normal state[8]. By the Korringa relation, $1/T_1 \propto [\rho(E_F)]^2$; and since a gap opens up, and the total number of

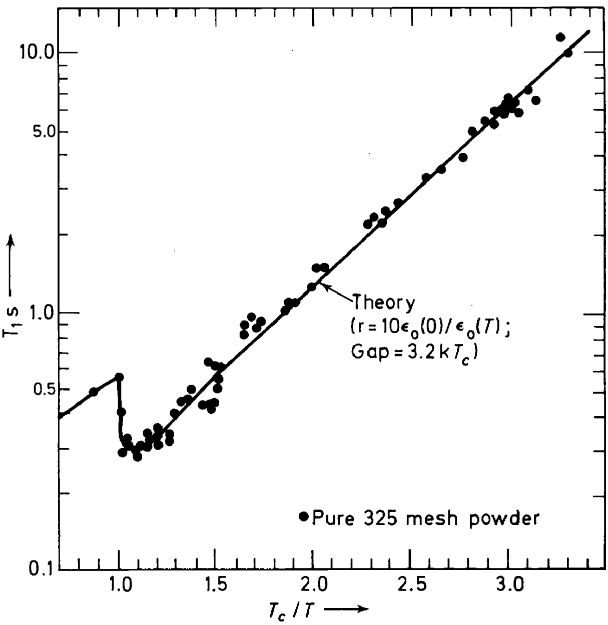

Figure 2. The relaxation time T_1 as function of temperature in aluminium. (From Masuda and Redfield)

states is a constant, it is clear that $\langle \rho(E_F)^2 \rangle$ averaged over an energy interval of about kT (for $T \approx T_c$) is larger in the SC state than in the normal state. Therefore, the shortening of T_1 just below T_c is not surprising; the salient feature of the BCS theory is that for spin-independent phenomena, such as ultrasonic attenuation, this effect does not occur since the matrix element for the transition becomes smaller and cancels the density of states effect, while for relaxation due to the contact interaction the effect is present. Strictly speaking, according to the BCS theory $1/T_1 \to \infty$ at $T = T_c$, since

$\rho(E_F)$ diverges there (so that $\int\rho(E)\mathrm{d}E$ is finite, but $\int[\rho(E)]^2\mathrm{d}E$ diverges); but since the BCS theory is only an approximation, and the excitations in reality have a finite lifetime, $1/T_1$ does not become infinite (see *Figure 2*). Hebel and Slichter[9] incorporated this lifetime effect by an empirical smearing of the density of states function, and Fibich[10] estimated T_1 assuming the lifetime of the quasi-particles is due to electron–phonon interaction. Magnetic impurities, or ordinary impurities coupled with spin–orbit interaction, can have a similar effect.

5. TYPE I AND TYPE II SEMICONDUCTORS

At this stage, we have to mention some properties of superconductors; namely, some are 'type I' and some are 'type II'[11].

There are two lengths that characterize a superconductor: the penetration depth $\lambda, \lambda^2 = mc^2/4\pi ne^2$, which is the depth into which the magnetic field penetrates, and $1/\xi = (1/\xi_0 + 1/l$; $\xi_0 = hv_F/\Delta$ which is the size of a Cooper pair (roughly speaking). The smallest region in which superconductivity can be destroyed (or created) is of size ξ; and into a normal region, magnetic flux can penetrate, and extend a distance λ around it; thus, the magnetic energy gained by creating a normal cylinder (say) is of order $\pi\lambda^2H^2/8\pi$ per unit length, while the energy that must be expended to create a normal region is at least $\pi\xi^2H_c^2/8\pi$ per unit length, since the energy of a superconductor is lower than that of the normal state by $H_c^2/8\pi$ per unit volume. Thus, if $\xi > \lambda$, then whenever $H < H_c$, it is unfavourable to create normal regions, while if $H > H_c$, superconductivity is destroyed completely, If $\xi < \lambda$, for fields $H > H_{c_1} \approx (\xi/\lambda)H_c$ it is favourable to create normal filaments (flux line) in the SC material. The first type are called type I or Pippard SC, while the second kind are called type II or Landau SC. In type I SC, nmr requires thin films (thinner than λ), fine particles, or field pulsing, since the magnetic field does not penetrate into the bulk; while in type II SC, it is possible to perform nmr directly in fields $H > H_{c_1}$.

Generally, pure materials are type I, while dirty materials (small mean free path) are type II; however, niobium is type II even when clean. When $H_{c_1} < H < H_{c_2}$, the state is called a mixed state. In some materials, like Nb_3Sn, $H_{c_1} \approx 400$oer and $H_{c_2} \approx 300000$ oer. Thus the mixed state extends over a very wide region.

6. GAPLESS SUPERCONDUCTIVITY

Reif[12] discovered that in some superconductors, namely, ones with magnetic impurities, there is no energy gap. Since magnetic impurities reduce the lifetime of quasi-particles, and since a short lifetime means smearing in energy, it is clear that the gap is smeared out; what is perhaps surprising is that the resistivity stays zero even when there is no gap (as observed by tunneling, for example). (Strictly speaking, all superconductivity is gapless, since the BCS theory is only an idealization and in reality all excitations have a finite lifetime and therefore a finite density of states at zero energy. However, usually $n(0)$ is orders of magnitude smaller than in the normal state, while in 'gapless' superconductors it is of the same order).

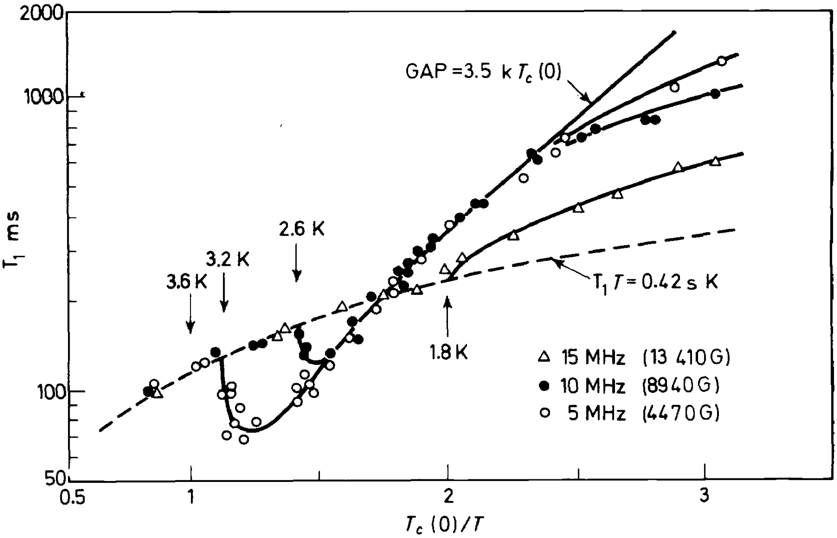

Figure 3. T_1 as function of T in V_3Sn in different fields. (From Okubo and Masuda)

Type II SC, near the critical field H_{c_2}, are an example of a 'clean' gapless SC. They have been investigated by nmr by Okubo and Masuda, McLaughlin and Rossier[13], and others. In the gapless state, T_1 changes, and $d(T_{1n}/T_{1s})/dT \propto dH_{c_2}/dT$[14] (for $l \ll \xi_0$; the 'dirty limit'). In V_3Sn, the measurements indeed are in agreement with theory; the effect is very striking, namely, at low fields (and relatively high temperatures) T_1 gets shorter just below T_c, while at high fields (and low temperatures) it always gets longer (*Figures 3* and *4*). In pure niobium, the effect is qualitatively similar, but quantitatively not yet understood (*Figure 5*).

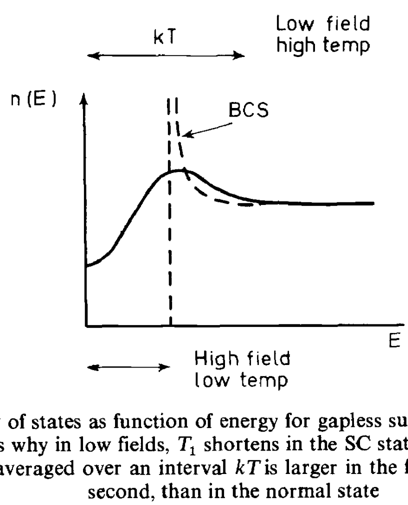

Figure 4. The density of states as function of energy for gapless superconductivity (schematic). This *Figure* illustrates why in low fields, T_1 shortens in the SC state, while in high fields it gets larger, since $[\rho(E)]^2$ averaged over an interval kT is larger in the first case, and smaller in the second, than in the normal state

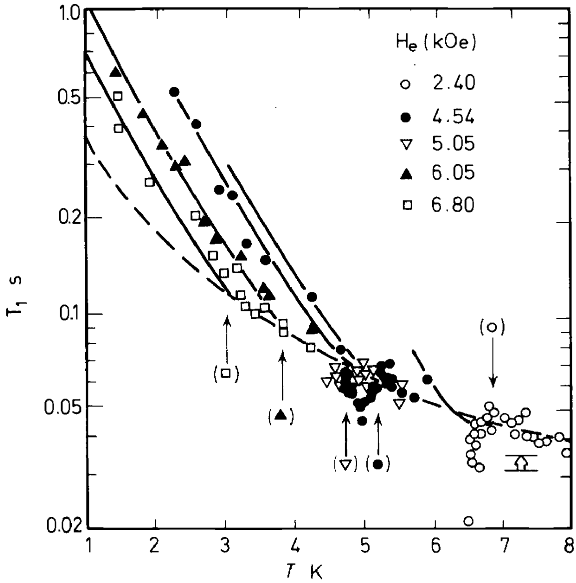

Figure 5. T_1 as function of T in Nb in different fields. (From Rossier and MacLaughlin)

7. FLUXOID LATTICE

The magnetic flux lines in a type II SC form a lattice, usually triangular. In the early days, people wanted to find out whether the lattice is indeed triangular or square. In principle, nmr can distinguish between the two cases, since the field distribution is different; at point '□' H is minimum, while 'x' is a saddle point, with a relatively large volume seeing a field H_S (*Figure 6*). It is clear that in the triangular lattice $H_{\square}$ is closer to H_x than in the square lattice, and the field distributions are as in *Figure 7*. The field distribution is reflected in the lineshape, which, experimentally, indeed confirms the triangular distribution[15].

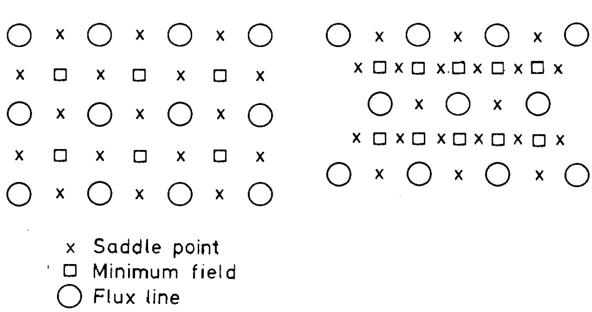

Figure 6. Field distribution for square and triangular flux distributions (schematic)

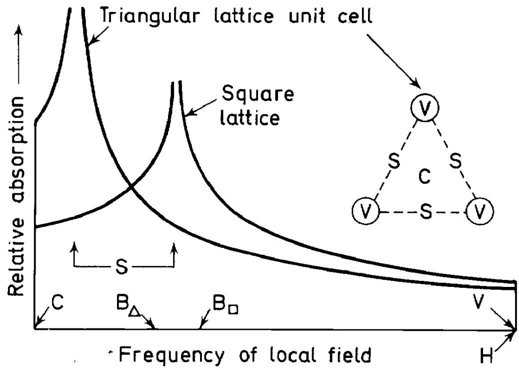

Figure 7. Expected lineshapes for square and triangular flux distributions. S is the saddle point (× in *Figure 6*); C the minimum (□ in *Figure 6*), and V, H are the maximum (O in *Figure 6*). $B_\triangle$ and $B_\square$ correspond to the resonance conditions in the normal state. (From Fite and Redfield)

However, other methods, such as the microscopy method of Trauble and Essman[16], shows the flux distribution much more clearly and in much more detail, including the defects, and thus nmr is not the best method to investigate this phenomenon (*Figure 8*).

8. STRUCTURE OF FLUX LINES

We mentioned that inside flux lines the material is effectively normal (Caroli and Matricon[17]). Therefore, it should relax nuclei like a normal material and the Korringa relationship should hold. Thus, there should be a contribution to $1/T_1$ of $(1/T_1)_{\text{Korringa}}\, n\pi\xi^2$, where n is the density of flux lines per unit area, $n = B/\phi_0$, $\phi_0 = hc/2e$. This contribution to the relaxation is indeed observed[18], and yields reasonable values for ξ (when $T \approx \frac{1}{4}T_c$).

The problem with this kind of experiment is that there exists no *quantitative* theory. The simple order of magnitude estimate assumes a square-well gap parameter and a 'local' situation. In reality, Δ varies continuously as function of distance and the relaxation at point r depends not only on $\Delta(r)$ but also on $\Delta(r')$ where r' is near r. In the region where the effect is strong ($\Delta \approx \Delta_0$), the Landau–Ginzburg equations do not apply, and whatever equations do, are nonlinear. Therefore the theory of this effect has not yet been worked out (*Figure 9*).

For $H \ll H_{c_2}$, the contribution to $1/T_1$ is linear in H to a good approximation. Thus the relaxation per fluxoid is (at least experimentally) a well defined property (*Figure 10*).

Another interesting feature predicted by Caroli and Matricon[19] is a gap of order Δ^2/E_F at the centre of the flux line. In V_3X compounds, the effective E_F is very small (of order 200K) and 2Δ may be about 60K; thus, Δ^2/E_F may be of order of a degree. T_1 was measured in V_3Si down to about 1/3K by Clark[20], but no evidence for a gap was found. This may be because V_3Si is

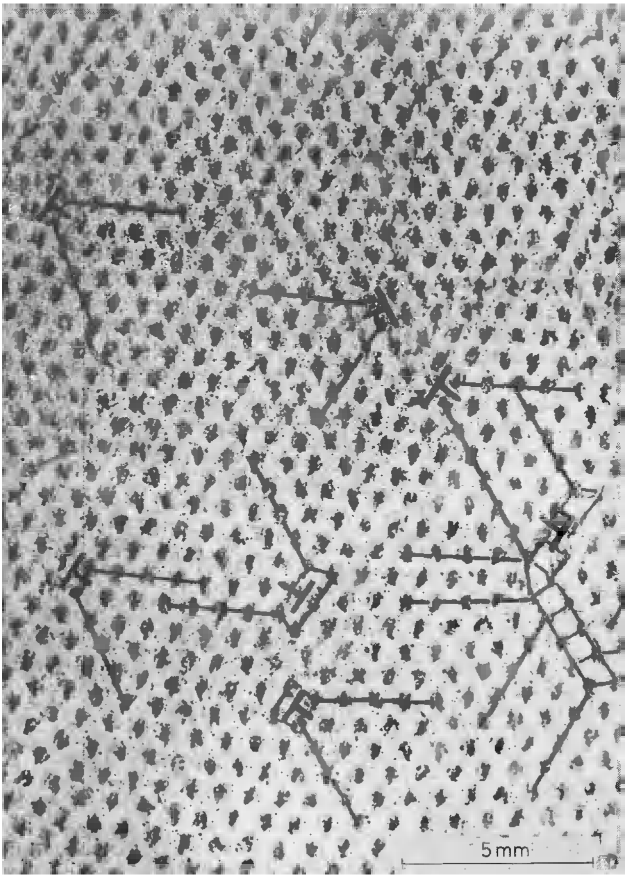

Figure 8. Distribution of flux lines. (From Trauble and Essman)

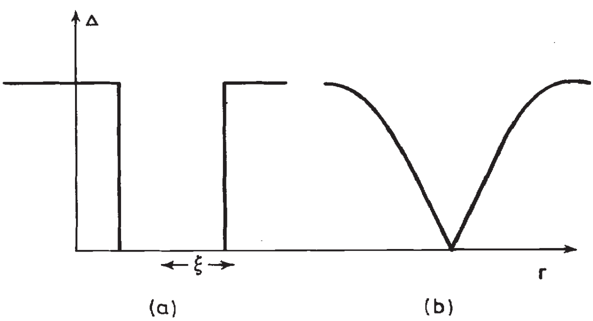

Figure 9. The gap parameter Δ as function of distance for an idealised situation (square well) and a more realistic situation (schematic)

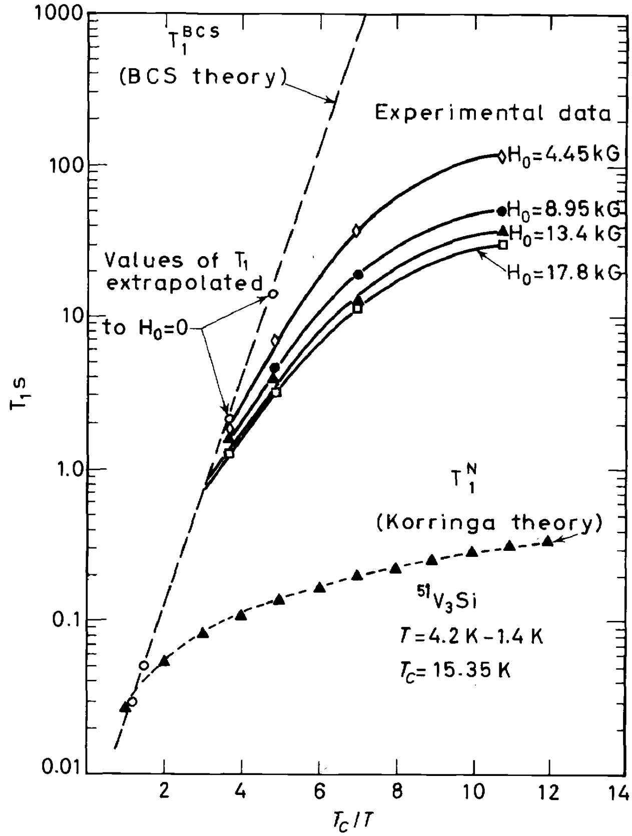

Figure 10. T_1 as function of T in V_3Si in different fields. (From Silbernagel, Weger and Wernick)

dirty (very small l), and the theory was proposed for clean materials; or perhaps because thermal fluctuations of fluxoids become important (relatively speaking) at very low temperatures.

It appears that the relaxation inside fluxoids at very low temperatures ($T < \frac{1}{10} T_c$) is still a mystery, both theoretically and experimentally.

9. THERMAL VIBRATIONS OF FLUXOIDS

Flux lines are somewhat like strings, and have normal modes of vibrations. The frequency of these modes is determined by the energy of a flux line per unit length (tending to make it as short as possible); the Lorentz force acting on a moving flux line perpendicular to its motion; and the distance between pinning centres and the interaction between flux lines. The normal modes have been investigated by de Gennes *et al.*, and by Fetter[21], and they were observed experimentally in pure niobium by Maxfield and Johnson, and Renard and Rocher[22] at very low frequencies. For typical 'dirty' superconductors, with

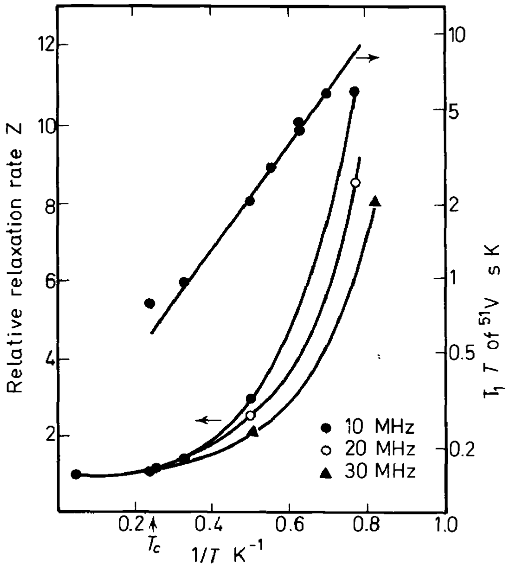

Figure 11. T_1 as function of T in Ti-V-H, for ^{51}V and H. (From Ehrenfreund, Goldberg and Weger)

many pinning centres, the modes may be expected to be in the MHz region and highly damped. Thermal fluctuations of the flux lines may be expected to contribute to the nmr relaxation rate. This process competes with the regular relaxation processes. Since the interaction between flux lines and nuclei is 'purely' magnetic, while most other relaxation processes proceed via the hyperfine interaction, the process may be observable for nuclei with a very low hyperfine field; protons appear suitable for this. The relaxation rate of protons in V–Ti–H alloys was indeed observed to be much faster than that of ^{51}V nuclei for very low temperatures[23] (*Figure 11*).

Again, a quantitative theory of this process is possible near the transition, where the Landau–Ginzburg equations apply, and Maki, Caroli, Eilenberg *et al.* carried out extensive calculations. However, there the effect is very weak. For temperatures much below the transition, we can only make order of magnitude estimates, which seem to agree with experiment. The main difficulty here is that the V–Ti–H system separates into two phases, and the ^{51}V nmr may emphasize one phase and the *H* resonance another one.

10. COEXISTENCE OF SUPERCONDUCTIVITY AND MAGNETISM

Magnetism and SC usually interfere with each other; magnetic impurities, or a magnetic field, destroying SC, by the breakdown of the Cooper pairs. The question arises whether magnetism and SC can coexist. This is a question that is hard to answer by macroscopic experiments, since the SC will prevent the magnetic flux from entering effectively and interacting with the magnetic moments. In principle, nmr can detect the magnetic moments by their effect relaxing the nuclei. A preliminary experiment on the VN(Cr) system by McLaughlin, Ducastelle and Rossier[24] indeed shows an extra relaxation by the Cr impurities (*Figure 12*). From the relaxation rate, it is possible to estimate τ_e, the relaxation rate of the magnetic impurities, and it seems to follow a BCS [$T_1 \propto \exp(2\Delta/kT)$] law. The VN system is 'dirty' (it is hard to get reproducible samples), and also the moments are disordered. It may be interesting to investigate a system that is 'clean' and ordered, ferromagnetically say, like Gd–La.

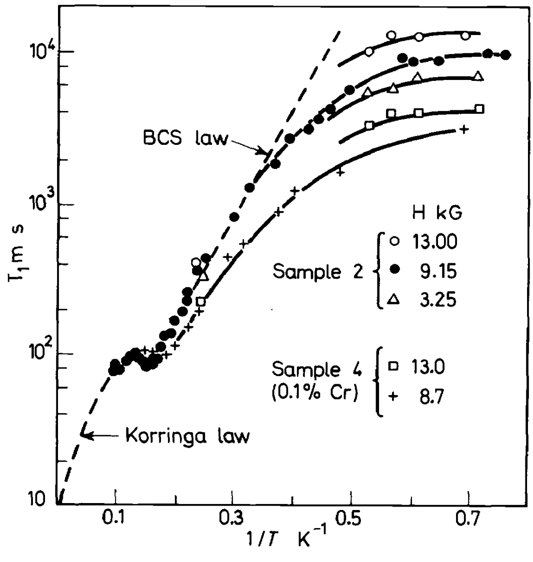

Figure 12. T_1 as function of T in different fields for ^{51}V in VN(Cr). (From Ducastelle, MacLaughlin and Rossier)

11. FLUCTUATIONS IN Δ AT $T \approx T_C$

We mentioned the vibrations of fluxoids. Due to them, $\Delta(r, t)$ is not constant but fluctuates (say, as function of t at a given r). When $T \approx T_c$, these fluctuations become relatively strong; moreover, they cannot be described simply as a fluctuation of the fluxoid lattice (the fluctuations of $\Delta(r, t)$ and $H(r, t)$ are more or less independent). Even when $T > T_c$, $\Delta(r, t)$ does not vanish identically and 'paraconductivity' may be observed. This phenomenon is relatively strong when the mean free path l is very small, since then each electron interacts only with a very small number of other electrons, and the effective field due to them fluctuates wildly; thus it has been observed in some amorphous films (the conductivity increases already at $T > T_c$). Also, fluctuations may be expected to be strong in quasi one-dimensional systems.

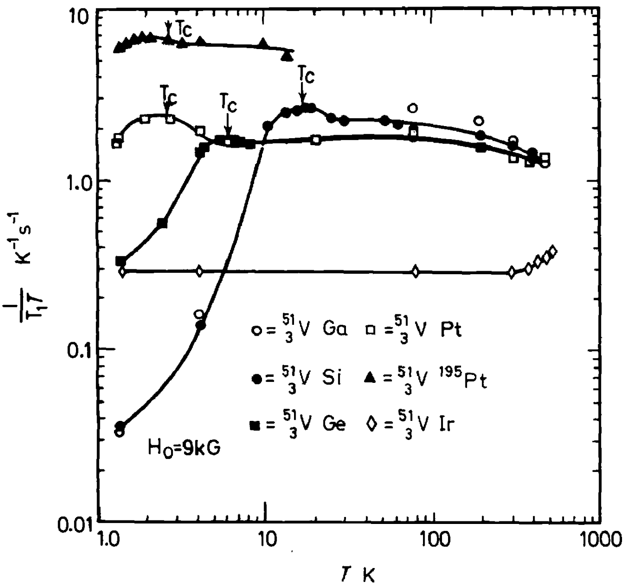

Figure 13. T_1T as function of T in various V_3X compounds. (From Silbernagel, Weger, Clark and Wernick)

Table 1. Summary of properties of superconductors investigated by nmr

Phenomenon	NMR property	Temperature range	Effect	Results
Pairing of spins	KS in thin films	$0 < T < T_c$	KS should vanish	Positive in Al, so so in other materials
Existence of gap	T_1	$T \lesssim \frac{1}{2}T_c$	$T_1 \propto \exp \frac{2\Delta}{kT}$	Excellent
Peak in density of states	T_1	$T \lesssim T_c$	T_1 falls just below T_c	Positive qualitatively
Gapless superconductivity	T_1	$T \approx T_c(H)$	Change in T_1 vs T slope	Positive in V_3Sn Qualitatively right in Nb
Fluxoid lattice	Lineshape	$T < T_c$	Skew line	Indicates triangular lattice
'Normal' core of fluxoid	T_1	$T < \frac{1}{4}T_c$	$1/T_1 \propto H$ $(H \ll H_{c_2})$	Positive
Coexistence of superconductivity, magnetism	T_1	$T < \frac{1}{2}T_c$	T_1 shorter at low H	Positive
Thermal fluctuations of fluxoids	T_1	$T < \frac{1}{2}T_c$	T_1 of protons relatively shorter than T_1 of metal	Tentatively positive
Critical thermal fluctuations of Δ	T_1	$T \approx T_c$	T_1 shortens *above* T_c	Tentatively positive in V_3X, Nb_3X

In an isotropic three-dimensional system, the temperature range over which $\langle \Delta^2 \rangle / \langle \Delta \rangle^2$ is appreciable, is of order $1/(k_F \xi)^2 \approx 10^{-4}$, while in a one-dimensional chain of radius a, it is of order $1/(k_F a)^2$ which is of order unity. In the V_3X system ($X = Ga, Si, Pt, Ge$) an increase in $1/T_1$ has been observed above T_c[7] (at $T \approx 1.2\ T_c$, roughly) and the increase amounts to about 20 per cent at T_c; a similar effect has been observed in Nb_3Al[25]. These systems are quasi one-dimensional since the vanadium (or niobium) atoms are arranged in chains[26] (*Figure 13*). This explanation of the increase in $1/T_1$ well above T_c is as yet only tentative.

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