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Nuclear Magnetic Resonance in Be_{22}Re and Be_{22}Tc

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(31. I. 70)

Abstract. The N. M. R. Knight shifts, K , and line-widths, ΔH , of the ^9Be , ^{185}Re , ^{187}Re and ^{99}Tc resonances have been measured in the intermetallic compounds Be_{22}Re and Be_{22}Tc at three different magnetic field strengths. Both K and ΔH were determined at 300°K, 77°K and 4.2°K and were found to be independent of temperature. The line-widths of the ^9Be resonance in both compounds and of the ^{185}Re and ^{187}Re resonances in Be_{22}Re exhibit a field-dependence which is shown to be due to second-order quadrupole effects. The values of the Knight shift of ^9Be ($K = -0.0027\%$), close to that measured in pure Be, together with those of ^{185}Re ($K = -0.880\%$) and of ^{99}Tc ($K = -0.536\%$) appear to indicate localisation of the d-electron wave-functions near to the transition metal ions.

1. Introduction

It is well known that pure Be metal exhibits nuclear magnetic resonance (N.M.R.) characteristics that are somewhat different from those of other metals. The Knight shift, K , is extremely small and negative, the spin-lattice relaxation time, T_1 , is long while the resonance shows a readily measurable first-order quadrupole splitting. These properties have been the subject of a large number of studies, both experimental [1–3] and theoretical [4]. On the other hand to the best of our knowledge there exists only a few publications concerning Be-based alloys [5, 6]. Our interest in the intermetallic compounds Be_{22}Re and Be_{22}Tc was stimulated therefore partly by the scarcity of information on what happens to the ^9Be resonance when alloyed with other metals, but more particularly by the observation that these compounds possess an elevated superconducting transition temperature [7, 8] due to the addition of a small percentage of transition metal to the Be. It was tentatively proposed that the superconductivity may be induced by a virtual bound state on the transition metal ion and the N.M.R. measurements were undertaken in the hope that they would throw some light on this possibility.

The Be_{22}X compounds crystallise in a face-centred cubic system having a very complex structure with 8 formula units per unit cell [9]. Each X atom has 16 Be

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neighbours and one can distinguish 4 non-equivalent sites for the Be atoms. The distance between neighbouring Re atoms in Be_{22}Re is 5 Å which is twice the separation in pure Re metal.

In the present investigation we have studied the Knight shifts and line-widths of the ^9Be , ^{185}Re and ^{187}Re resonances in Be_{22}Re and of the ^9Be and ^{99}Tc resonances in Be_{22}Tc .

2. Experimental

We had at our disposal samples of Be_{22}Re and Be_{22}Tc kindly provided by the group working under Professor J. Müller at the Institut de Physique and whose superconducting properties had previously been measured. In addition the low-temperature specific heat and magnetic susceptibility have been measured in the case of Be_{22}Re [10].

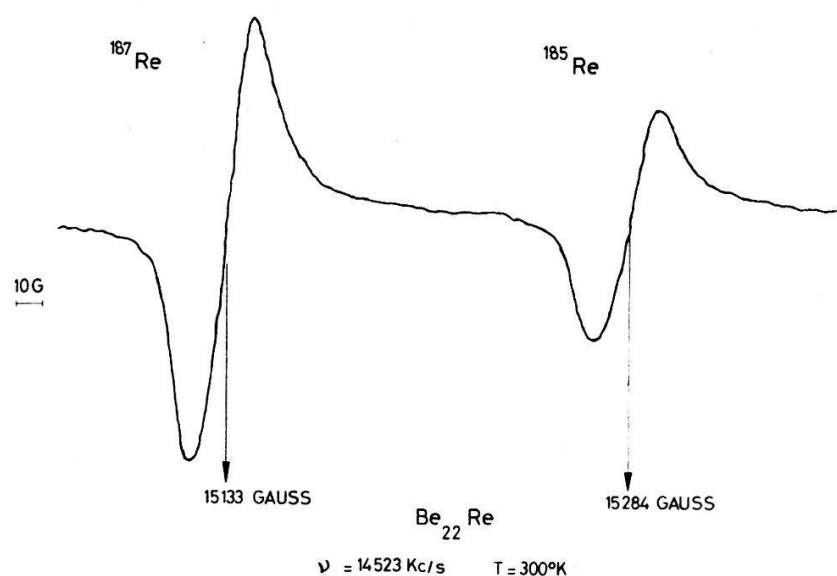
The specimens were prepared from high-purity elements by arc-melting under an argon atmosphere. The ingots were annealed at 900°C for 48 hours and then allowed to cool slowly to room temperature. An X-ray analysis confirmed the Be_{22}X structure with the possibility of the presence of a small proportion of the Be_{20}X phase. Finally the samples were ground using a pestle and mortar to produce powders having an average particle size of 20 μm in order to avoid radio-frequency skin-effect difficulties in the N.M.R. experiment.

The measurements were made using a Varian VF 16B Wide-Line spectrometer modified for measurements at low temperatures [11]. The magnetic field of the Varian 12" magnet was calibrated for each measurement by determining the frequency of resonance of either the ^1H resonance in water or the ^2D resonance in heavy water using a Watkins-Pound marginal oscillator, and making use of the known gyromagnetic ratios for these nuclei.

In order to enhance the signal to noise ratio all measurements were made by accumulating the signal in a TMC type CAT 400B time-averaging computer connected to the output of the spectrometer. Each measurement of the resonance shift and line-width is the average of several readings. The line-widths determined were the peak to peak widths of the first derivatives of the absorption signals corrected for field modulation broadening while the resonance positions were taken as the magnetic field value midway between these two peaks. The resonance shifts were measured with respect to the positions of the ^9Be resonance in BeCl_2 and of the ^{185}Re , ^{187}Re and ^{99}Tc resonances in KReO_4 and KTcO_4 solutions respectively. In each case the values of the positions of the resonances in the reference solutions were in good agreement with those given in the literature.

3. Results

The measured shifts and line-widths of the ^9Be , ^{185}Re and ^{99}Tc resonances at 300°K are shown in Tables 1 and 2. The results for ^{187}Re are similar to those for ^{185}Re except that the Knight shift appears to be slightly more negative for ^{187}Re ($K = -0.89\%$). A similar difference in shift between the two isotopes is evident in the results of Narath [12]. A recorder trace of the ^{185}Re and ^{187}Re resonances at room



A recorder trace of the first derivative of the ^{185}Re and ^{187}Re resonances at 300°K.

temperature obtained after 10 hours averaging is shown in Figure 1. The ratio of their intensities 1.7 is the same as that of their natural isotopic abundances, and furthermore

$$\nu^{(187)}/\nu^{(185)} = 1.01008 \pm 0.00008$$

in good agreement with the results of Narath on ReO_3 . Measurements were also made at 77°K and 4.2°K but no detectable temperature dependence of either shift or width was observed for any of the resonances in either compound.

This is the first reported observation of the Re resonance in the metallic state using the steady-state method of detection. It is not possible to detect the resonance in pure Re metal because of the very large quadrupole interaction between the Re nucleus and the electric field-gradient of the hexagonal-close-packed lattice which presumably in a polycrystalline material washes out the resonance through the second-order quadrupole effect. Pure Tc also has the hexagonal-close-packed structure but the quadrupole moment of ^{99}Tc is only about 1/10 of that of either ^{185}Re or ^{187}Re so that the strength of the interaction is reduced. As a result one can observe a first-order effect satellite structure in the ^{99}Tc resonance. Since both the ^{187}Re and ^{185}Re resonances are observable in Be_{22}Re the quadrupole interaction is evidently considerably smaller than in pure Re metal. This we might expect because of the cubic symmetry of the Be_{22}Re structure. Quadrupole effects are not, however, entirely absent in these compounds. It will be noted in the tables that the ^9Be resonance shows a field-dependent resonance shift and line-width in both Be_{22}Re and Be_{22}Tc and that the ^{185}Re resonance in Be_{22}Re has a field-dependent line-width. As will be discussed below, these effects are indicative of the presence of second-order quadrupole interactions.

The ^9Be resonance Knight shifts shown in the table were obtained by extrapolating the observed resonance shifts to high field, a procedure which will be justified in the next section. The small negative values thus arrived at are not significantly different from the Knight shift of pure Be metal. Both transition metal shifts on the other hand

are large and negative, the ^{99}Tc shift being considerably different from that observed in the pure metal which exhibits a positive Knight shift [13].

It should be mentioned here that attempts were also made to observe the ^{95}Mo resonance in Be_{22}Mo . These were unsuccessful even after a prolonged heat treatment at 700°C . This is somewhat surprising in view of the ease with which we can detect the resonance in pure Mo metal [14]. The ^9Be resonance on the other hand was comparable in width and intensity to those observed in Be_{22}Re and Be_{22}Tc . The disappearance of the ^{95}Mo resonance is probably caused by a broadening of the resonance line brought about by a very strong second-order quadrupole interaction. This could be related to a strong distortion of the crystal lattice though it is then difficult to see why the ^9Be resonance is not also affected. Alternatively we cannot neglect the possibility of an electronic structure for the compound Be_{22}Mo different from that in Be_{22}Re and Be_{22}Tc which perhaps coupled with a high Sternheimer antishielding factor enhances the electric-field-gradient felt by the Mo nucleus.

4. Discussion

4.1. Quadrupole effects

The behaviour of the ^9Be and ^{185}Re resonances as a function of magnetic field indicates the presence of electric quadrupole interactions sufficiently strong to broaden the powder pattern satellite lines beyond detection leaving only the central $m = 1/2 \rightarrow -1/2$ transition observable.

Second-order perturbation theory shows that the position of the central line in a single crystal with axial symmetry is given by

$$\nu_{1/2 \rightarrow -1/2} = \nu_0 + \frac{A_2}{h} (1 - 9 \cos^2 \theta) (1 - \cos^2 \theta),$$

where ν_0 is the frequency of the unperturbed transition in the metal and

$$A_2 = \frac{9}{64} \frac{2I + 3}{4I^2(2I - 1)} \frac{e^4 q^2 Q^2}{h \nu_0}.$$

In this last expression I is the spin of the nucleus, eq is the electric field gradient of the crystal lattice, Q is the quadrupole moment of the nucleus, h is Planck's constant and θ is the angle between the axis of symmetry of the electric field and the direction of the external magnetic field.

In a powder sample all angles θ are represented and the resulting resonance absorption line shows two assymetric peaks broadened by the magnetic dipolar interaction at frequencies of $\nu_0 - 16/9 A_2/h$ and $\nu_0 + A_2/h$ respectively. If the quadrupole interaction is not sufficiently strong compared with the magnetic dipolar interaction, then this structure will be masked by the dipolar broadening and the two peaks will not be resolved. One will then observe only an assymetrical broadening of the resonant line with a consequent deviation of the measured resonance position (taken as half-way between the position of the peaks of the first derivative of the resonance) from the true value.

The results for the ⁹Be and ¹⁸⁵Re resonances in Be₂₂Re and of the ⁹Be resonance in Be₂₂Tc are consistent with this picture of an unresolved second-order quadrupole splitting. Consider first the ⁹Be resonance. According to the above, the deviation of the measured resonance frequency from the true position will be given approximately by $7/50 A_2/h$. Thus the measured resonance position should vary linearly with the inverse of the frequency and hence the magnetic field H_0 , and extrapolations to infinite field will yield values of the metallic Knight shift. The ⁹Be shifts in both Be₂₂Re and Be₂₂Tc do indeed vary linearly with $1/H_0$ and the Knight shifts given in Table 1 were obtained by extrapolation to infinite magnetic field.

Table 1
The ⁹Be resonance shift and line-width in Be₂₂Re and Be₂₂Tc at 300 °K

H_0 Gauss	⁹ Be in Be ₂₂ Re Shift (%)	Line-width (Gauss)	⁹ Be in Be ₂₂ Tc Shift (%)	Line-width (Gauss)
16500	-0.001 ± 0.003	7.0	-0.005 ± 0.003	7.1
8000	-0.010 ± 0.005	9.3	-0.012 ± 0.003	10.2
4000	-0.022 ± 0.005	10.8	-0.041 ± 0.005	13.2
Extrapolated Knight shift	-0.0004 ± 0.0027		-0.0029 ± 0.0034	

The ⁹Be resonance also exhibits field-dependent line-widths in both Be₂₂Re and Be₂₂Tc as would be expected from the above if second-order quadrupole effects are present. Casabella [15] has shown how to combine the quadrupole-splitting with the magnetic dipolar broadening of the resonance lines and has obtained relations between the line-width $\delta\nu_2$, as measured between the first derivative peaks, the quadrupole-splitting $\Delta_2 = 25/9 A_2/h$ and the dipolar width 2σ . Using these relations one can estimate the strength of the quadrupole interaction. Assuming that the measured ⁹Be line-widths at the highest-field used (16500 gauss) are purely dipolar in origin, one obtains values for 2σ of 4.19×10^3 Hz and 4.25×10^3 Hz for Be₂₂Re and Be₂₂Tc respectively. The measured ⁹Be line-widths at 4000 gauss of 10.8 gauss for Be₂₂Re and 13.2 gauss for Be₂₂Tc then yield values for $\delta\nu_2$ of 6.46×10^3 Hz and 7.90×10^3 Hz respectively. Using the data calculated by Casabella, these values are found to correspond to Δ_2 values of 4.94×10^3 Hz in Be₂₂Re and 6.16×10^3 Hz in Be₂₂Tc. The quadrupole interaction strengths $e^2 q Q/h$ calculated from these values of Δ_2 using $I = 3/2$ for the Be nucleus are then 3.0×10^5 Hz for Be in Be₂₂Tc and 3.4×10^5 Hz for Be in Be₂₂Re. These values of $e^2 q Q/h$ may in turn be used to calculate the expected deviation $7/50 A_2/h$ of the measured shift from the true Knight shift at 4000 gauss. This procedure predicts deviations of -2.5×10^2 Hz and -3.1×10^2 Hz compared with the measured values of -4.5×10^2 Hz and -9.3×10^2 Hz for Be₂₂Re and Be₂₂Tc respectively. This is considered to be good agreement in view of the approximations made in the calculations and is clear evidence that a second-order quadrupole effect is responsible for the observed behaviour of the ⁹Be shift and line-width as a function of magnetic field. It should be noted that the above values of $e^2 q Q/h$ are much larger than the value of 6×10^4 Hz obtained for pure Be metal [1], and certainly large enough to cause the disappearance of the first-order effect satellite lines.

The ^{185}Re resonance in Be_{22}Re also exhibits broadening at low field but the measured shift is independent of magnetic field. From the line-width at 4000 gauss, using the same procedure as above one obtains $e^2 q Q/h = 8.5 \times 10^5$ Hz. This value gives an expected change of measured shift between 15000 gauss and 4000 gauss of only 0.01% which is within the limits of experimental error. Thus the strength of the quadrupole interaction is such as to produce a line-broadening while having no measurable effect on the shift of the resonance. For this reason the measured shifts may be quoted directly as Knight shifts in Table 2.

Table 2
The ^{185}Re and ^{99}Tc Knight shifts and line-widths in Be_{22}Re and Be_{22}Tc at 300 °K

H_0 Gauss	^{185}Re in Be_{22}Re Knight shift (%)	Line-width (Gauss)	^{99}Tc in Be_{22}Tc Knight shift (%)	Line-width (Gauss)
15 000	-0.880 ± 0.003	5.8	-0.536 ± 0.002	4.7
10 000	-0.880 ± 0.003	5.8	-0.537 ± 0.002	4.6
4 000	-0.881 ± 0.010	8.3	-0.540 ± 0.003	4.6

In Be_{22}Tc both the line-width and shift of the ^{99}Tc resonance exhibit zero field-dependences indicating that the quadrupole interaction with the ^{99}Tc nucleus is considerably smaller than for ^{185}Re in Be_{22}Re . This is to be expected since the electric quadrupole moment of ^{99}Tc is only 0.3×10^{-24} cm² compared with 3×10^{-24} cm² for ^{185}Re .

4.2. Knight shifts

The Knight shift in a metal may be expressed as the sum of a number of terms:

$$K = K_s + K_{cp} + K_{orb} \quad (1)$$

where K_s is the contribution from the hyperfine contact interaction between s-electrons and nucleus, K_{cp} is the core polarisation term contributed by the polarisation of the innercore s-electrons by the conduction electrons and K_{orb} is the contribution from the field-induced orbital motion of the electrons.

In pure Be metal in considering the complex form of the Fermi surface it has been possible to explain the very small negative Knight shift observed by postulating an almost complete compensation between the positive contact term K_s and two negative terms K_{cp} and K_{orb} , the latter resulting from a Landau-type orbital diamagnetism of the conduction electrons [4]. This term is crucial in accounting for the observed sign and magnitude of the Knight shift.

The results for the ^9Be Knight shifts in Be_{22}Re and Be_{22}Tc suggest no change in the above situation. The principal modification to the electronic structure brought about by the addition of a transition element to pure Be should be, in adopting a rigid-band model, the appearance of a relatively narrow *d*-band. This would be expected to augment the negative core-polarisation term in the Knight shift and also to introduce a positive contribution from the Van Vleck-type temperature-independent orbital susceptibility of the *d*-electrons. That no change of ^9Be shift occurs indicates

that either these two contributions cancel out, or that the effects are too small to be observed because of a very low d -electron density near the Be sites. This second hypothesis seems to be confirmed by the results for the transition element nuclei as will be discussed below.

It is interesting to note that in the compounds TiBe_2 , CrBe_2 and MnBe_2 the negative ^9Be shifts have been found to be much larger than in pure Be [5]. It was proposed that this was due to the inner core s -electron polarisation produced by the s - p exchange interaction with the 2 p electrons of Be which themselves are polarised through a strong admixture of their wave-functions with the transition metal 3 d wave-functions. This effect is evidently considerably smaller in Be_{22}Re and Be_{22}Tc presumably because of the greater dilution of the transition metal ions.

The transition metal resonances show two important properties; firstly the Knight shifts are large and negative both for ^{99}Tc ($K = -0.536\%$) and for ^{185}Re ($K = -0.880\%$), and secondly the shifts are independent of temperature. Before discussing these results further it should be pointed out that there may be uncertainty in these Knight shift values because of possible errors in the ^{185}Re and ^{99}Tc nuclear moments determined by measuring the resonance positions in KReO_4 and KTcO_4 respectively. This arises because of paramagnetic shielding in the ReO_4^- and TcO_4^- complex ions. For example, recent ENDOR experiments have shown that the ^{55}Mn nuclear moment is some 0.5% smaller than that indicated by NMR measurements on paramagnetic ions. Narath [12] has discussed the situation in KReO_4 and concludes that the ^{185}Re nuclear moment may be in error by as much as was found for ^{55}Mn . Thus all we can say with certainty is that $-0.88\% < K(^{185}\text{Re}) \lesssim -0.38\%$. As can be seen, however, even the largest estimate of the correction required to the ^{185}Re moment still leaves the Knight shift negative. A similar correction may be required for ^{99}Tc so that one has $-0.54\% < K(^{99}\text{Tc}) \lesssim -0.04\%$ and again it seems certain that the ^{99}Tc shift is negative. Furthermore the Knight shift in pure Tc metal, measured using a CsTcO_4 solution as reference, is $+0.61\%$ and since this value would require an identical correction it is clear that regardless of the uncertainties in the absolute magnitude of the Knight shift there must be a large negative contribution in Be_{22}Tc that is not present in pure Tc metal. Although no value is available for the Knight shift in pure Re metal it is likely to be comparable to that of Tc because of the similarities in their electronic and crystal structures. Thus it can be assumed with some confidence that there is a negative contribution to the transition metal Knight shifts of the order of or slightly greater than 1% in both Be_{22}Re and Be_{22}Tc which is not present in the respective pure metals.

This result confirms the above postulate that electrons near the Fermi level in Be_{22}Re and Be_{22}Tc have strong d -character. The negative contribution to K results then from a large core polarisation term K_{cp} in the Knight shift equation arising from the exchange interaction between the d -electrons and the inner core s -electrons of the Re and Tc ions. There will also be a positive term K_{orb} resulting from the orbital interaction of the d -electrons but the results indicate that this is much smaller than the core polarisation term.

The Knight shift may be related to the magnetic susceptibility using

$$K = \alpha_s \chi_p^s + \alpha_d \chi_p^d + \beta \chi_{orb}, \quad (2)$$

the total susceptibility being given by

$$\chi = \chi_p^s + \chi_p^d + \chi_{orb} + \chi_{dia} \quad (3)$$

The three terms in equation (2) correspond to those in equation (1). χ_p^s and χ_p^d are the Pauli spin susceptibilities of the *s* and *d* electrons respectively, χ_{orb} is the orbital susceptibility, χ_{dia} is the diamagnetic susceptibility including contributions from the core electrons and the conduction band, α_s and α_d are 0.895×10^{-4} times the hyperfine field per spin for the *s*-contact and *d*-core-polarisation processes respectively and $\beta = (2/A) \langle 1/r^3 \rangle$ for the metal where *A* is Avogadro's number.

The data available does not allow a separation of *K* and χ into their various contributions using the method of Clogston et al. [16]. However, a crude estimate can be made of the expected core polarisation term in the Knight shift. For Be₂₂Re the measured magnetic susceptibility is $\chi = -5 \times 10^{-6}$ e.m.u./mole and is independent of temperature compared with the value $\chi = -9 \times 10^{-6}$ e.m.u./mole in pure Be. The observed temperature-independence of the Knight shift then follows from equation (2) since it would be expected that each of the susceptibility terms is itself temperature-independent. If it is assumed that for pure Be $\chi = \chi_p^s + \chi_{dia}$ and that these two contributions remain approximately the same in Be₂₂Re then provided we can ignore χ_{orb} in Be₂₂Re the difference between the above two susceptibility figures represents the *d*-electron spin susceptibility in Be₂₂Re (if χ_{orb} cannot be neglected then the estimated χ_p^d will be somewhat smaller).

This value³⁾ of $\chi_p^d = 4 \times 10^{-6}$ e.m.u./mole may then be used to calculate $K_{cp} = \alpha_d \chi_p^d = 0.895 \times 10^{-4} H_{hfs}^d \chi_p^d$ where H_{hfs}^d is the hyperfine field per *d*-spin at the Re nucleus, and is taken to have the value 2.8×10^6 gauss which is comparable to that found in Ir or Pt. One thus obtains $K_{cp} = -0.1\%$ which is very much smaller than that observed experimentally. This value would be reduced if χ_{orb} were taken into account. Thus in Be₂₂Re in order to arrive at the correct value of K_{cp} it would be necessary to postulate either a reinforcement of H_{hfs}^d or alternatively a *d*-electron susceptibility in the region of the Re ions augmented by a factor of about 10 and thus close to the value for pure Re (Table 3). Either hypothesis leads to the conclusion of a localisation of the *d*-electron wave-functions near the Re ions which is perhaps justified by the large separation of the latter. This localisation may be associated with the creation of a virtual bound state on the Re ion.

Table 3

Magnetic susceptibilities of pure Be, Tc and Re and of Be₂₂Re

	(10^{-6} emu/mole)	T (°K)
Be	- 9	290
	- 7	95
Tc	120	300
Re	68	300
	67	93
Be ₂₂ Re	- 5	300

³⁾ An estimation based on the electronic specific heat gives a χ_p^d value of the same order.

An estimate of K_{cp} cannot be made for ^{99}Tc in Be_{22}Tc because of the lack of magnetic susceptibility data. There are obvious similarities in the results for both compounds, however, and it is probable that any explanation of the Knight shift in Be_{22}Re will be equally applicable to Be_{22}Tc .

5. Summary

The present investigation has yielded evidence that the electronic structures of the intermetallic compounds Be_{22}Re and Be_{22}Tc are very similar. The Knight shift results suggest strongly that the d -electrons of the transition metal ions are localised. This may be taken as giving support to the proposition of the formation of a virtual bound state originally put forward to account for the superconductivity results, although it is not yet possible to elucidate the mechanism by which the superconducting transition temperature is augmented.

Second-order quadrupole interactions are also clearly in evidence in both compounds and are thought to be responsible for the absence of a detectable ^{95}Mo resonance in Be_{22}Mo . This last problem is to be studied further, and it is also hoped to obtain supplementary information on Be_{22}Re and Be_{22}Tc and other allied systems by making measurements of the spin-lattice relaxation times T_1 .

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