Zeitschrift:	Helvetica Physica Acta
Band:	43 (1970)
Heft:	4
Artikel:	Nuclear magnetic resonance in Be22Re and Be22Tc
Autor:	Bernasson, M. / Descouts, P. / Styles, G.A.
DOI:	https://doi.org/10.5169/seals-114177

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Nuclear Magnetic Resonance in Be₂₂Re and Be₂₂Tc

by M. Bernasson¹), P. Descouts and G. A. Styles²)

Institut de Physique de la Matière Condensée, Université de Genève

(31. I. 70)

Abstract. The N. M. R. Knight shifts, K, and line-widths, ΔH , of the ⁹Be, ¹⁸⁵Re, ¹⁸⁷Re and ⁹⁹Tc resonances have been measured in the intermetallic compounds Be₂₂Re and Be₂₂Tc 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 ¹⁸⁵Re and ¹⁸⁷Re resonances in Be₂₂Re 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 ¹⁸⁵Re (K = -0.880%) and of ⁹⁹Tc (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 vitual 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

¹) Also at At Laboratoire de Spectrométrie Physique de l'Université de Grenoble.

²) Present address: School of Physics, University of Warwick, Coventry, U.K.

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, ¹⁸⁵Re and ¹⁸⁷Re resonances in Be₂₂Re and of the ⁹Be and ⁹⁹Tc resonances in Be₂₂Tc.

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 Be₂₂X structure with the possibility of the presence of a small proportion of the Be₂₀X phase. Finally the samples were ground using a pestle and mortar to produce powders having ar average particle size of 20 μ m 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 linewidth 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 BeCl₂ and of the ¹⁸⁵Re, ¹⁸⁷Re and ⁹⁹Tc resonances in KReO₄ and KTcO₄ 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, ¹⁸⁵Re and ⁹⁹Tc resonances at 300°K are shown in Tables 1 and 2. The results for ¹⁸⁷Re are similar to those for ¹⁸⁵Re except that the Knight shift appears to be slightly more negative for ¹⁸⁷Re (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 ¹⁸⁵Re and ¹⁸⁷Re resonances at room

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A recorder trace of the first derivative of the ¹⁸⁵Re and ¹⁸⁷Re 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

 $v^{(187)}/v^{(185)} = 1.01008 + 0.00008$

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 ⁹⁹Tc is only about 1/10 of that of either ¹⁸⁵Re or ¹⁸⁷Re so that the strength of the interaction is reduced. As a result one can observe a firstorder effect satellite structure in the ⁹⁹Tc resonance. Since both the ¹⁸⁷Re and ¹⁸⁵Re resonances are observable in Be₂₂Re the quadrupole interaction is evidently considerably smaller than in pure Re metal. This we might expect because of the cubic symmetry of the Be₂₂Re 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 Be₂₂Re and Be₂₂Tc and that the ¹⁸⁵Re resonance in Be₂₂Re 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 M. Bernasson, P. Descouts and G. A. Styles H. P. A.

are large and negative, the ⁹⁹Tc 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 Be₂₂Mo. 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 9 Be resonance on the other hand was comparable in width and intensity to those observed in Be₂₂Re and Be₂₂Tc. 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 9 Be resonance is not also affected. Alternatively we cannot neglect the possibility of an electronic structure for the compound Be₂₂Mo different from that in Be₂₂Re and Be₂₂Tc 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 ¹⁸⁵Re 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

$$v_{1/2 \to -1/2} = v_0 + \frac{A_2}{h} (1 - 9 \cos^2 \theta) (1 - \cos^2 \theta)$$
,

where v_0 is the frequency of the unperturbed transition in the metal and

$$A_2 = \frac{9}{64} \frac{2I+3}{4I^2(2I-1)} \frac{e^4 q^2 Q^2}{h v_0}.$$

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 asymmetric peaks broadened by the magnetic dipolar interaction at frequencies of $v_0 - 16/9 A_2/h$ and $v_0 + A_2/h$ 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 asymmetrical 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 Ho, 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/Ho and the Knight shifts given in Table 1 were obtained by extrapolation to infinite magnetic field.

1 200.012

 -0.005 ± 0.003

 -0.012 ± 0.003

 -0.041 ± 0.005

 -0.0029 ± 0.0034

7.1

10.2

13.2

Table 1

 -0.001 ± 0.003

 $-\ 0.010\ \pm\ 0.005$

 $-\ 0.022 \pm 0.005$

Extrapolated -0.0004 ± 0.0027

The 9De

16500

8000

4000

Knight shift

The "Be resonance shift and line-width in $Be_{22}Re$ and $Be_{22}Ic$ at 300 °K					
H_0	⁹ Be in Be ₂₂ Re		⁹ Be in Be ₂₂ Tc		
Gauss	Shift (%)	Line-width (Gauss)	Shift (%)	Line-width (Gauss)	
		· · · · · · · · · · · · · · · · · · ·	(707	,	

7.0

9.3

10.8

The ${}^{9}\text{Be}$ resonance also exhibits field-dependent line-widths in both Be_{22} Re and
$Be_{22}Tc$ 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 δv_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 ⁹ Be
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 Be ₂₂ Re and Be ₂₂ Ic
respectively. The measured "Be line-widths at 4000 gauss of 10.8 gauss for Be_{22} Re and 12.0 models of E_{22} Re and E
13.2 gauss for Be_{22} is then yield values for ∂v_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° Hz in Be ₂₂ Ke and 0.10 × 10° Hz in Be ₂₂ Ic. The
quadrupole interaction strengths $e^2 q Q/h$ calculated from these values of Z_{12} using $L = 3/2$ for the Be nucleus are then 3.0×105 Hz for Be. To and 3.4×105 Hz for
$T = 5/2$ for the be nucleus are then 5.0×10^{5} Hz for be in Be_{22} is and 5.4×10^{5} Hz for Be in Be are calculate the expected
deviation $7/50$ A /k 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 Be ₂₀ Re and Be ₂₀ Tc
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 ⁹ Be 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 ¹⁸⁵Re resonance in Be₂₂Re 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	99Tc Knight	shifts and	line-widths in	Be ₂₂ Re and	Be _{so} Tc at 30	0°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)
15000	-0.880 ± 0.003	5.8	-0.536 ± 0.002	4.7
10000	$-$ 0.880 \pm 0.003	5.8	$-$ 0.537 \pm 0.002	4.6
4000	-0.881 ± 0.010	8.3	$-$ 0.540 \pm 0.003	4.6

In Be₂₂Tc both the line-width and shift of the ⁹⁹Tc resonance exhibit zero fielddependences indicating that the quadrupole interaction with the ⁹⁹Tc nucleus is considerably smaller than for ¹⁸⁵Re in Be₂₂Re. This is to be expected since the electric quadrupole moment of ⁹⁹Tc is only 0.3×10^{-24} cm² compared with 3×10^{-24} cm² for ¹⁸⁵Re.

4.2. Knight shifts

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

$$K = K_s + K_{cp} + K_{orb} \tag{1}$$

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 suspectibility 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 dwave-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 ¹⁸⁵Re and ⁹⁹Tc nuclear moments determined by measuring the resonance positions in KReO₄ and KTcO₄ 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 ⁵⁵Mn 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 ¹⁸⁵Re nuclear moment may be in error by as much as was found for ⁵⁵Mn. Thus all we can say with certainty is that $-0.88\% < K(^{185}Re) \leq -0.38\%$. As can be seen, however, even the largest estimate of the correction required to the ¹⁸⁵Re moment still leaves the Knight shift negative. A similar correction may be required for ⁹⁹Tc so that one has $-0.54\% < K(^{99}Tc) \leq -0.04\%$ and again it seems certain that the ^{99}Tc shift is negative. Furthermore the Knight shift in pure Tc metal, measured using a CsTcO₄ 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 Be₂₂Tc 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

$$K = lpha_s \, \chi^s_{
ho} + lpha_d \, \chi^d_{
ho} + eta \, \chi_{orb}$$
 ,

(2)

the total susceptibility being given by

$$\chi = \chi_p^s + \chi_p^a + \chi_{orb} + \chi_{dia} \,. \tag{3}$$

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 $\beta = (2/A) < 1/r^3 >$ for the metal where *A* is Avogadros' 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 $K_{cp} = \alpha_d \chi_p^d = 0.895 \times 10^{-4} H_{h/s}^d \chi_p^d$ where $H_{h/s}^d$ 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 $H_{h/s}^d$ 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.

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

Table 3 Magnetic susceptibilities of pure Be, Tc and Re and of $Be_{22}Re$

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

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An estimate of K_{cp} cannot be made for ⁹⁹Tc in Be₂₂Tc 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 Be₂₂Re will be equally applicable to Be₂₂Tc.

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 ⁹⁵Mo resonance in Be₂₂Mo. This last problem is to be studied further, and it is also hoped to obtain supplementary information on Be₂₂Re and Be₂₂Tc and other allied systems by making measurements of the spin-lattice relaxation times T_1 .

Acknowledgments

The authors wish to thank Professor J. Müller and Professor A. J. Heeger for many fruitful discussions and the Fonds National Suisse de la Recherche Scientifique for the provision of a research grant.

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