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Nuclear Magnetic Resonance in Bismuth Metal*

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The nuclear magnetic resonance in bismuth metal powder has been observed from 9 to 19 Mc/sec at 4.2°K. The isotropic and anisotropic Knight shifts and the quadrupole coupling constant have been determined as $(-1.25\pm.30)\%$, $(-0.3\pm0.3)\%$, and $2.10\pm.05$ Mc/sec, respectively. The intrinsic linewidth was found to be 130 ± 20 kc/sec. A technique is developed to take into consideration the broadening of the observed lines due to the combined effects of the magnetic dipolar broadening and the width due to the quadrupolar splitting of each line.

INTRODUCTION

THE use of nuclear magnetic resonance (NMR) for obtaining information about the conduction electron system in metals is a well-established technique. In the presence of an externally applied magnetic field, the field at the nuclear site in a metal is different from the field at the site of the nucleus in a nonmetallic compound of the same material. This difference is usually considered due to two effects; first the electron-spin susceptibility interacting with the nucleus either through a direct contact interaction or through a polarization of the core and second a second-order orbital contribution of the Landau type. Both of these effects change the frequency of the NMR in the metal from the frequency in the non-metallic reference, that is

$$\nu_{\text{metal},}=(1+K)\nu_0 \tag{1}$$

where K is called the Knight shift. In the case of an axially symmetric crystal K may be written to first order as

$$K=K_{\text{iso}}+K_a(3\cos^2\theta-1)\,, \tag{2}$$

where θ is the angle between the symmetry axis of the crystal and the applied magnetic field.[1]

When there is an electric quadrupole interaction of the nucleus with the electric-field gradients in the crystal, the Zeeman levels will be shifted by this quadrupole interaction as has been calculated using perturbation theory.[2] Averaging over angular distributions of powdered specimens,[3] the resulting shape of the NMR absorption spectrum is highly asymmetric. The position of the maximum of the absorption in the asymmetric curve is shifted when the effects of dipole broadening are taken into consideration. For large linewidths an analysis of this shift of the powder pattern maxima is necessary to make precision measurements of the Knight shift and the quadrupole coupling. We have developed a method for this analysis and have applied it to the NMR spectrum in bismuth metal powder.

The recent work in indium[4] was treated in the manner described in this paper and it is shown that good agreement between the value of the quadrupole coupling in that experiment and the value determined by pure nuclear-quadrupole-resonance (NQR) techniques was attained only through the interpretation described here.

THEORY OF LINE-SHAPE ANALYSIS CONSIDERING MAGNETIC DIPOLAR BROADENING

Jones, Graham, and Barnes[3] have discussed the theoretical shape of the NMR lines in powdered metals where there are both a quadrupole interaction and a Knight shift. In the presence of a quadrupole interaction, the single NMR line normally observed is split into a number of components. The frequency of the resonance corresponding to a transition between particular m states is given by

$$\begin{aligned}\nu_{m,m-1}=&[1+K_{\text{iso}}]\nu_0+[K_a\nu_0+(\nu_Q/2)(m-\tfrac{1}{2})]\\&\times[3\cos^2\theta-1]+(\nu_Q{}^2/32\nu_0(1+K))\{1-\cos^2\theta\}\\&\times\{[102m(m-1)-18I(I+1)+39]\cos^2\theta\\&-[6m(m-1)-2I(I+1)+3]\}\,,\end{aligned} \tag{3}$$

where θ is the angle between the symmetry axis of the

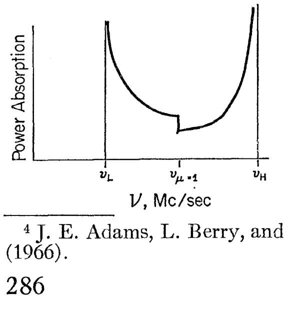

FIG. 1. Broadening of the $\nu_{\frac{1}{2},-\frac{1}{2}}$ due to the angular dependence of the Knight shift and the quadrupole coupling. (a) is $\nu_{\frac{1}{2},-\frac{1}{2}}$ as a function of μ in ν space. (b) is $\nu_{\frac{1}{2},-\frac{1}{2}}$ as a function of ν.

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[1] N. Bloembergen and T. J. Rowland, Acta Met. **1**, 731 (1953).

[2] R. Bersohn, J. Chem. Phys. **20**, 1505 (1952).

[3] W. H. Jones, T. P. Graham, and R. G. Barnes, Phys. Rev. **132**, 1898 (1963).

[4] J. E. Adams, L. Berry, and R. R. Hewitt, Phys. Rev. **143**, 164 (1966).

crystal and the applied magnetic field. $\nu_Q=(3eQq/2I(2I-1))$ is a measure of the quadrupole coupling. For a powder, where all θ are present, the absorption takes place over a wide region. Let $\mu=\cos\theta$. Figure 1 shows the splitting of the $(\frac{1}{2}, -\frac{1}{2})$ transition in the NMR pattern resulting from the angular dependence of the Knight shift and the quadrupole interaction. In the experiment, only the regions around the singularities are observable. For this central line these positions are given by

$$\nu_H=[1+K_{\text{iso}}-K_a]\nu_0+3\nu_Q^2/2(1+K)\nu_0, \tag{4}$$

$$\nu_L=[1+K_{\text{iso}}+2K_a/3]\nu_0-(8\nu_Q^2/3\nu_0(1+K)) \\ -(K_a^2\nu_0^3(1+K)^3/6\nu_Q^2). \tag{5}$$

We now treat the problem of the shift of the observed maxima positions due to dipole broadening of the resonance. The data are taken in terms of the derivatives of the power absorption. The position of the singularity in the original line falls somewhere between the points of maximum and zero derivative in the observed curve. The width of the line as it appeared in the data was about 400 G, which represents 2% of the total field. Since two of the quantities to be measured are shifts in the field of that order, a quantitative technique must be devised to determine the location of the original singularity.

Consider an arbitrary power absorption function $P(t)$ to be made up of the superposition of delta functions of varying amplitudes. $P(t_0)$ then describes the "amplitude" at the point t_0. The contribution to the absorption at the point t due to the absorption at t_0 is zero if there is no broadening of the individual components of the line. If each component is broadened, however, the contribution at t from the original absorption at t_0 is given by $p(t)=P(t_0)e^{-[(t-t_0)/\sigma]^2}$. To find the contribution at t from the absorption at all t_0, we integrate over the variable t_0. In this case $P(t)$ becomes $P(t)=\int P(t_0)e^{-[(t-t_0)/\sigma]^2}dt_0$. This is the expression which was used to determine the broadened line shape in the following cases.

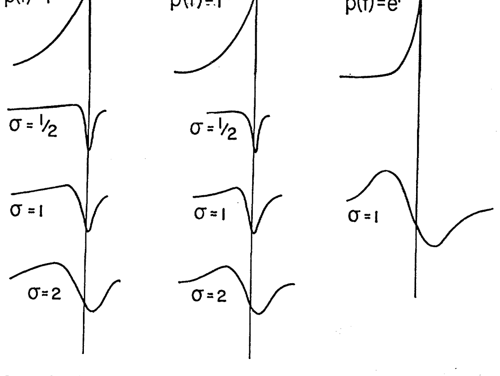

FIG. 2. Dipolar-broadening effects on various curves and their derivatives as discussed in the text.

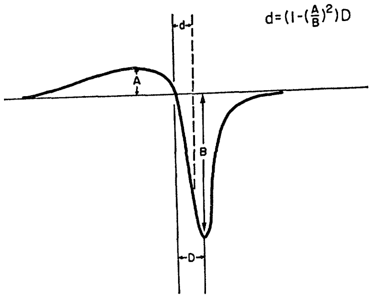

FIG. 3. Asymmetric curve labeled for analysis of frequency shifts from line broadening. The dashed line is the position of the original singularity.

A comparison of Fig. 1 and Fig. 2 shows that a good approximation to the actual absorption curve shown in Fig. 1 is the expression shown in Fig. 2. This function was evaluated up to the constant b and then cut off. For $n=2$ & 3, the function below is plotted in Fig. 2.

$$\frac{d}{dt}P(t)=\frac{d}{dt}\int t_0^n e^{-(t-t_0/\sigma)^2}dt_0.$$

The curves in Fig. 2 were determined by performing the above integration and taking the derivative. These curves were then plotted below the original absorption pattern. Since the location of the discontinuity is known, a scheme can now be determined which gives this location in terms of the positions of the maximum and zero of the derivative curve. It is impractical to write down an analytic expression for the position since the integral involves the error function, $\int_a^b e^{-s^2}ds$, and there is no closed expression for this integration. Instead, an empirical technique was developed which gave the position of the discontinuity to less than 2% of the linewidth in all cases tried. This expression involves the relative heights of the two sides of the curve (A and B) and its width (D). Figure 3 is an asymmetric curve labeled in the appropriate fashion. When A/B is 0, the unbroadened curve was a step and the experimental curve should be measured at the peak. When A/B is 1, the unbroadened curve was a delta function and the experimental curve should be measured at the zero. If we write $d=[1-P_n(A/B)]D$ where P_n is a polynomial such that $P_n(0)=0$ and $P_n(1)=1$ and d is the distance from the zero derivative to where the curve should be measured, we have the desired behavior at the end points. It was determined empirically that the expression $d=[1-(A/B)^2]D$ provides a good approximation to where the lines should be measured.

This expression gives the better than 2% accuracy cited above. All of the results of this work make use of this approximation.

EXPERIMENTAL METHOD

325 mesh 99.9999% pure bismuth powder was obtained from Cominco, Ltd. It was annealed at 210°C for 6 h in a carbon boat at a pressure of 10^{-5} mm of Hg. Thirteen grams of the powder were used for the measurement. This filled a vial 1 in. long and $\frac{1}{2}$ in. in diameter.

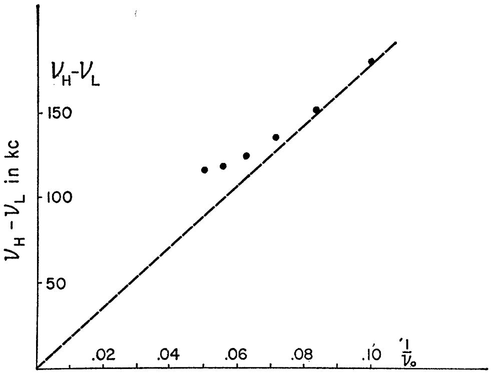

FIG. 4. Splitting of the $\nu_{\frac{1}{2}',-\frac{1}{2}}$ versus $(\nu_0)^{-1}$. The dashed line is the asymptotic limit of $\Delta\nu_{HL}$.

The experiment was done at the boiling point of liquid helium at 1 atm. The size of the electromagnet allowed a 1-in.-diam helium space for runs at 30 kG. This enabled enough helium to be stored to allow 12 h of continuous running which was necessary because of the very large width of the bismuth spectrum. The magnet itself was a Pacific Electric Motors 120-kW water-cooled low-impedance electromagnet.

At 30 kG, the frequency of the Bi NMR in nonmetallic, nonmagnetic bismuth nitrate is 20 Mc/sec.[5] The rf energy was provided by an oscillator similar to the Pound-Knight[6] oscillator.

In this work the oscillator frequency was held fixed and the magnetic field was varied. The rf frequency was measured with a Hewlett-Packard 524 C frequency counter and the magnetic field was measured by the voltage developed across a shunt in series with the magnet coil. This voltage was calibrated to the field at low field using the NMR of ^{23}Na in sodium chloride, and above 20 kG the NMR of ^{6}Li in lithium metal was used. In the region of overlap of the two calibrations there is excellent agreement. Lithium has a measured Knight shift of 5 G at 20 kG which was taken into consideration. The field measurements are good to ±20 G.

The field was modulated at 40 cps with an amplitude of 60 G. The output of the oscillator was detected and fed into a phase sensitive detector with the final signals displayed on a strip-chart recorder. The final signal-to-noise ratio was 10:1 with the use of a 180-sec time-constant in the phase-sensitive detector and with 1-kG/h sweeping.

EFFECTS OF LINE-SHAPE ANALYSIS IN INDIUM

Until the NMR in a single crystal of some metal with large spin and large quadrupole coupling is done and compared with this powder technique, there is no way to test directly the accuracy of the method for the determination of the Knight shift. However, just as the Knight-shift value depends on the proper interpretation of the absorption curves, the value for the quadrupole coupling is also sensitive to the point in the curves at which the discontinuity is assumed to occur. The value of the quadrupole coupling can be measured by pure nuclear quadrupole resonance and a comparison of the NMR and the NQR results provides a test of the line measurement scheme. The NQR value for ν_Q in indium is 1.886±0.003.[7] Recent work[4] on indium NMR gives the value of ν_Q as 1.885±0.002 using the technique described in this paper. Assuming the absorption maximum to be the point of original discontinuity $\nu_Q=1.845\pm0.002$. The linewidth shifts will be much greater in bismuth since the width of the lines is six times larger than in indium (20 kc/sec).

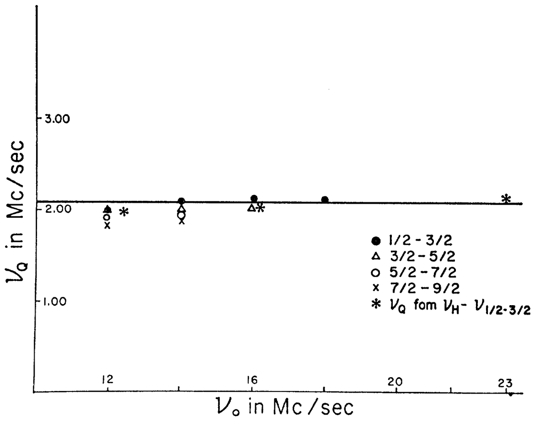

FIG. 5. ν_Q versus ν_0 from the $m>\frac{1}{2}$ satellites. Solid line is the result from the central line splitting.

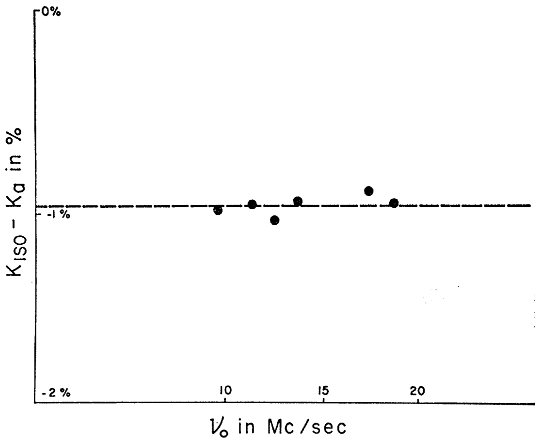

FIG. 6. The difference between isotropic and anisotropic Knight shifts $(K_{\rm iso}-K_a)$ versus the resonance frequency ν_0 as obtained from the ν_H & $\nu_Q=2.10$ Mc/sec.

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[5] W. G. Proctor and F. C. Yu, Phys. Rev. **78**, 471 (1950).

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EFFECTS OF LINE-SHAPE ANALYSIS IN BISMUTH

Earlier, the results of the preliminary work in bismuth NMR were reported.[8] In the present paper we have applied the line analysis described above to the broad lines in the bismuth spectrum.

The original paper assumed that the maximum in the observed absorption was the maximum in the theoretical curves. That this is not the case can be seen by considering the splitting of the $(\frac{1}{2},-\frac{1}{2})$ transition. From Eqs. (4) and (5) this separation as a function of frequency is

$$\Delta\nu_{HL}=\frac{25\nu_Q^2}{6(1+K)}(\nu_0)^{-1}-\frac{5K_a}{3}\nu_0-\frac{K_a^2(1+K)^3}{6\nu_Q^2}\nu_0^3. \quad (6)$$

For $(\nu_0)^{-1}$ large, this curve is a straight line and since there is no constant term, when it is extrapolated to $(\nu_0)^{-1}=0$ the splitting is zero. This condition is satisfied for the corrected bismuth data as is shown in Fig. 4. If the absorption is measured at the peaks, the intercept is a combination of the width due to dipole broadening and the quadrupole effects that do exist at the low field points from which the extrapolation is made. The zero value for this splitting in the present interpretation and the high degree of internal consistency of the data provide internal consistency checks of the technique.

The magnitude of the quadrupole interaction is nominally the same as that reported earlier 2.10±0.05 Mc/sec compared to the earlier result of 2.40±0.07 Mc/sec. The errors quoted in both of these numbers show the scatter in the data and do not reflect the possibility of a systematic error.

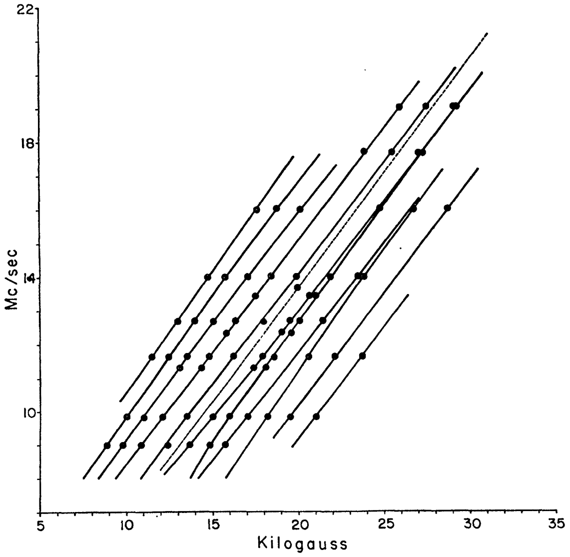

FIG. 7. The field dependence of bismuth spectrum at 4.2°K.

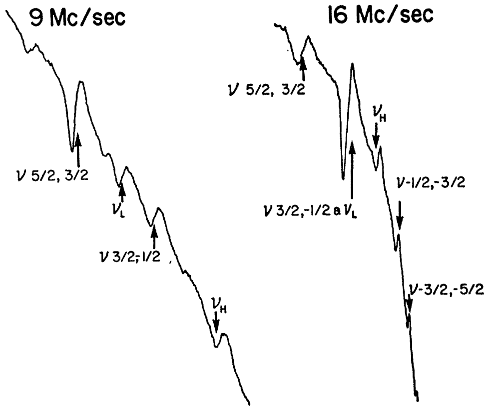

FIG. 8. Magnetic-field sweeps of the derivative of a partial spectrum of a power absorption in bismuth at two rf frequencies, 9 Mc/sec on the left and 16 Mc/sec on the right.

The quadrupole coupling may be measured by three essentially independent techniques. The positions of the satellites are given by

$$\begin{aligned}\nu_{m,m-1}=(1+K_{\text{iso}}-K_a)\nu_0-(\nu_Q/4)(2m-1)\\-(\nu_Q^2/16(1+K_{\text{iso}}-K_a)\nu_0)\\\times[3m(m-1)-I(I+1)+\tfrac{3}{2}]. \quad (7)\end{aligned}$$

Then the separation between corresponding pairs is

$$\nu_{-m+1,-m}-\nu_{m,m-1}=(\nu_Q/2)(2m-1). \quad (8)$$

The experimental values are plotted in Fig. 5 as a function of field for all the satellites available.

In addition, the slope of Eq. 4 for large $(\nu_0)^{-1}$ gives ν to within $(K/2)\%$. The solid line in Fig. 5 is this value.

Finally, using the ν_H line and the $(-\frac{3}{2}\text{-}-\frac{1}{2})$ satellite and eliminating $K_{\text{iso}}-K_a$ between them, we get a third expression for ν_Q.

$$\nu_{-\frac{3}{2}-\frac{1}{2}}-\nu_H=(\nu_Q/2)-(3\nu_Q^2/16\nu_0(1+K)). \quad (9)$$

This expression, like the first, is independent of any of the other parameters to be measured. While it is true

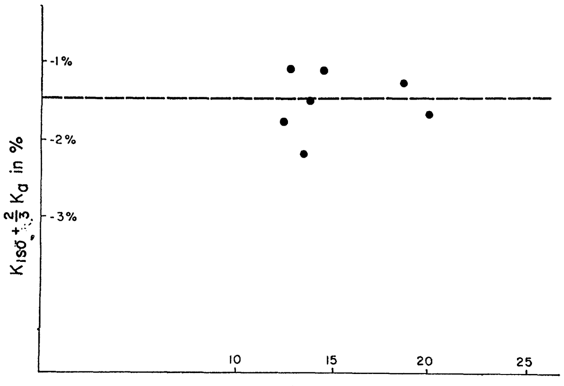

FIG. 9. $K_{\text{iso}}+\frac{2}{3}K_a$ versus ν_0 as found from ν_L & $\nu_Q=2.10$ Mc/sec.

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[8] R. R. Hewitt and B. F Williams, Phys. Rev. Letters 12, 216 (1964).

that K appears in this expression, $(3\nu_Q^2/16\nu_0)$ is on the order of 0.05 and the change of approximately 1% in this number is not significant. The results of solving this quadratic for ν_Q are also shown as a function of field in Fig. 5.

Since the magnitude of the Knight shift is small and since the lines are very broad in the bismuth powder spectrum (400 G), a reinterpretation of the line shape will result in fairly large changes in the value of K_{iso} and K_a. Figure 6 shows the field dependence of $K_{\text{iso}}-K_a$ found by substituting the value of ν_Q obtained as described above into Eq. 5. In order to separate these two quantities it is necessary to use the ν_L line since this is the only one in which K_{iso} and K_a do not appear in the combination $K_{\text{iso}}-K_a$. Unfortunately the ν_L line crosses over the $\frac{1}{2}$-$\frac{3}{2}$ satellite, making an accurate measurement of the line difficult. Figure 7 shows the entire spectrum from 9 to 19 mc/sec and Fig. 8 is a recorder trace of the absorption at 9 and 16 mc/sec. Both of these figures show this crossing. Figure 9 is the field dependence of the quantity $K_{\text{iso}}+(2K_a/3)$ as determined from ν_L by substituting ν_Q into Eq. 4. The solution of $K_{\text{iso}}-K_a$ and $K_{\text{iso}}+\frac{2}{3}K_a$ for K^*_{iso} and K_a gives

$$K_{\text{iso}}=(-1.25\pm0.3)\%, \quad K_a=(-0.3\pm0.3)\%.$$

CONCLUSIONS

The -1% value for K_{iso} is the most interesting result of this work. A negative value for the Knight shift can result from two mechanisms. If there is a change in the chemical shift in the bismuth ion from salt to metal then the apparent shift is not due to a conduction-electron effect. Since chemical shifts are normally two orders of magnitude smaller than this bismuth metal result, it would be surprising to find a change in the chemical shift of this size. The Knight shift has been measured in liquid bismuth as $+1.4\%$.[9] The presence of a large negative chemical shift in the metal ion would probably not allow such a large positive value in the liquid. The difference between the liquid and the solid value for the Knight shift can be understood qualitatively if we consider the valence electrons in the liquid to be essentially free. When the metal solidifies, the number of electrons at the Fermi surface changes dramatically and hence so does the direct contact Knight shift. The remaining conduction electrons provide the negative shift as is described below.

A second mechanism for negative Knight shifts is a polarization of the core s states by the conduction electrons through the exchange interaction. If we consider the conduction electrons to be entirely of p and d character then there will be no direct contact Knight shift. The polarization of the core from s state conduction electrons, which seems to be always positive,[10] will also be missing. The Knight shift in this case will be due to a polarization of the core states by the remaining conduction electrons which can be negative.[10] The large negative hyperfine field present in the bismuth atom[11] indicates the large negative exchange polarizability of the core s states is a reasonable result.

The large widths of the lines in the spectrum cannot be explained in terms of a normal dipole-dipole-type broadening. A comparison with the dipole widths in antimony, which has the same structure, gives a value of 30 G in bismuth while the measured linewidth is 200 G. The 1% magnitude for the Knight shift indicates a strong coupling between the nuclei and polarizable electrons and perhaps an indirect exchange of the Rudermann-Kittel type is the explanation. The large size of the bismuth ion itself may be the cause since in the case of $BiCl_3$ the width of the Bi NQR is about 70 kc/sec[12] which is an order of magnitude larger than the result in the same antimony salt.[13]

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[9] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) 8, 173 (1959).

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