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MOLECULAR CRYSTALS AND LOCALIZED VIBRATIONAL STATES

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This is an invited book chapter for the NATO conference on dynamical localization. Although we were not invited to this conference, our work has been mentioned so many times that the organizers, after the fact, requested us to at least contribute in writing.

What we describe is a general review of our work on the problem of localization of vibrational energy in solids in general and the molecular crystal L-alanine in particular. We begin with a greatly simplified theoretical model. Then the experimental quantities required by this model of a suitable material for study are outlined. Our measurements of Neutron scattering data, thermal conductivity, thermal expansion, spontaneous Raman intensities versus temperature, spontaneous Raman frequency and linewidths versus temperature are all discussed and related to actual numerical quantities required for the various theoretical scenarios.

Finally we discuss the picosecond experiment we have devised, which will be produced soon, and which has a chance of providing the first unequivocal answer to the question of the existence of local modes.

If P-10 wishes to understand in detail our approach, this article, written for the general physics audience in review form is the one to read.

Molecular Crystals and Localized Vibrational States

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The normal modes arising from a simple linear model of a crystalline solid predict many important properties such as the specific heat, the sound velocity, and the Raman and infrared response. Such a model fails, however, to produce thermal expansion and finite thermal conductivity. The introduction of weak non-linear couplings between the normal modes immediately corrects these simpler problems, while preserving the usual phonon representation of the purely linear system as a useful first approximation for small phonon amplitudes. What we wish to consider here is the next step in the process, taken by keeping the weak non-linearities but introducing large phonon amplitudes. Putting aside, for the moment, the question of how to achieve the necessary amplitudes, we can consider the consequences if certain not unusual conditions obtain which put the phonon equation of motion in correspondence with the non-linear Schrodinger equation. We can then be guided by classical solutions of this equation which predict spontaneous symmetry breaking and vibrational localization. To focus our thoughts, we outline in physical terms the processes leading to the localization of vibrational energy. We use the insight gained to guide our choice of materials, and we describe the measurements we have made to begin the establishment of a rigorous connection between real solids and the theoretical constructs related to this problem.

Introduction

To see in physical terms how the process of localization can work, we begin with a solid having an optical phonon branch with a minimum at the Brillouin zone center. Although not usually the case in simple solids, we take this to be the lowest optical phonon branch, a situation occasionally found in more complex structures. The dispersion curves then look something like Fig.1. Next consider a small non-linear term in the Hamiltonian that couples the optical phonon to the acoustic phonon such that the energy of the solution decreases. Such a term is easy to imagine if we consider a rubber band. The optical branch is a twist in the band, the acoustic branch is a stretch. Clearly a large twist in either direction contracts the rubber band, but a small twist, to first order in the twist angle, has no effect. In a region of the solid large compared to a lattice spacing but small compared to a wavelength of light we imagine the optical mode is sufficiently well populated to have shifted the eigenfrequency downward by some small amount as shown in Fig.1. Thus the new frequency now resides below the bottom of the low-amplitude phonon band, and therefore, below the lowest propagating frequency in the balance of the crystal. The vibrations are, therefore, self-trapped. Again

referring to Fig.1, we see that there is a spread of k -vectors in the high-amplitude dispersion curve, all of which lie below the bottom of the low-amplitude band, and this spread must determine the width of the localized state. The more strongly excited the state, the bigger the spread in k -space, and the smaller the width in real space.

FIG. 1. Schematic dispersion curve of a nonlinear lattice mode. The solid line represents the "eigenmodes" at low vibrational amplitudes. The dashed curve shows the shifted frequencies of these modes at large amplitudes, and extends out to the largest k value for which the shifted frequency is lower than the lowest low-amplitude frequency. A typical acoustic branch that does not couple linearly to the optical mode is the lower solid line.

The possibility of such localized states was first brought into prominence by Davydov and Kislukha¹ in a 1973 paper which proposed that such states might exist on the α -helix because of the interaction of the intramolecular carbon-oxygen amide I stretching modes with low frequency acoustic phonons. This original model has spawned much related work on refined Hamiltonians²⁻⁵ and computer simulations⁶ which have called into question the likelihood of Davydov solitons in polypeptide chains living long enough to be experimentally significant at temperatures much above 10K (although simulations⁷ based on another model by Yomosa⁸ predict stable long lived lattice solitons in these systems). Nevertheless, work on the α -helix system has inspired experimental and theoretical studies of other systems that may stand a better chance of supporting long-lived localized states.

One class of promising systems consists of the pseudo one-dimensional molecular crystals such as l-alanine. Through the non-linear interaction between longitudinal acoustic phonons and low-lying vibrational states, we derive equations of motion appropriate to optical lattice solitons, but with parameters significantly different from the α -helix system. This is because the vibrational spectrum in many crystals composed of long chains of hydrogen-bonded molecular units arises from hindered rotation of the molecules. These librations have much lower frequencies and, in principle, can have a much stronger nonlinear coupling to acoustic phonons. In the molecular crystal l-alanine, two such modes lying near 49

cm^{-1} are particularly interesting because they have an unusually long lifetime even for low level excitations.

A Simplified Model

To study molecular crystals in general as potential candidates for localization, and to help guide and interpret our experimental measurements on l-alanine, we have set up a simple model of a one dimensional chain of molecules based on linear spring constants that exhibit both phonon and vibron degrees of freedom and non-linear coupling between them. The model is designed to preserve only certain relevant features of the l-alanine crystal and can be thought of as a simple molecular dynamics model with all except the essential degrees of freedom suppressed. A form of this model was originally proposed and studied by John C. Wheatley. It turns out to lead to a particular case of the Takeno hamiltonian and therefore includes the possibility of localized states. One advantage of the model is that it enables an estimation of the characteristic parameters of the phonon and vibron systems and the non-linear coupling constant. We can, therefore, use it to make contact with the experimental work.

FIG. 2. The crystal structure of l-alanine (following Simpson and Marsh). The dark circles represent carbon atoms. The dashed lines are hydrogen bonds (hydrogen atoms not shown).

FIG. 3. A section of the ribbon-like chain of molecules in crystalline l-alanine showing the geometric features that enable a nonlinear coupling between a longitudinal acoustic mode and a libration about the c-axis. A hydrogen atom and a $-\text{CH}_3$ group have been deleted for clarity.

The l-alanine crystal consists of long chains of hydrogen bonded l-alanine molecules with the formula $C_3H_7O_2N$ (Fig.2)⁹. The oxygen atoms O_1 and O_2 , the carbon atoms C_1 and C_2 and the nitrogen atom N are approximately coplanar. In addition C_2 is bonded to a hydrogen atom and CH_3 groups lying respectively above and below the plane formed by $N-C_2-C_1-O_1-O_2$. Each nitrogen atom is hydrogen bonded to 3 oxygen atoms, O_1 is bonded to one nitrogen atom and O_2 to two nitrogen atoms.

To model the l-alanine crystal, we retain only the essential features. All internal coordinates of the molecule are assumed to be fixed. The only degrees of freedom allowed for the n^{th} molecule are longitudinal motion along the c-axis with coordinates u_n , and rotation about the principle axis C with coordinate θ_n . Referring to figure 3, the kinetic energy associated with longitudinal motion of the n th molecule is $\frac{1}{2}M\dot{u}_n^2$. In addition to this energy and the potential energy associated with the spring K_0 , we assume that hindering potentials act on the molecules that give rise to energies $(\frac{1}{2}I_c\dot{\theta}_n^2 + \frac{1}{2}I_c\omega_{\theta n}^2\theta_n^2)$ and $(\frac{1}{2}I_a\dot{\phi}_n^2 + \frac{1}{2}I_a\omega_{\phi n}^2\phi_n^2)$ for rotation about the c-axis and a-axis respectively.

To sketch how we have proceeded, consider rotation about the c-axis. The potential energy associated with the spring K_0 from longitudinal motion and rotation of the molecules is straightforward. For the rotations we introduce a staggered order parameter $Q_n = (-1)^n \frac{1}{2}(r_1 + r_2)$. This places out-of-phase rotation of adjacent molecules, for which the strongest non-linear effects are expected, at the center of the one-dimensional Brillouin zone. The axial motion of the molecules is measured in terms of displacement from their equilibrium position by the variable $q_n = u_n - na$. The potential energy function is then found to be to cubic order in the displacements,

$$U = \frac{K_0}{2} \sum_n \left\{ \left(1 - \frac{r_0}{r_1} + \frac{r_0 D^2}{r_1^3} \right) (q_{n+1} - q_n)^2 - \left(1 - \frac{r_0}{r_1} \right) \frac{4r_1 r_2}{(r_1 + r_2)^2} (Q_{n+1} - Q_n)^2 \right. \\ \left. - \frac{r_0 D}{r_1^3} \frac{4r_1 r_2}{(r_1 + r_2)^2} (q_{n+1} - q_n)(Q_{n+1} + Q_n)^2 \right\} \quad (1)$$

If the kinetic energies and potential energy of hindered rotation are added, this leads to a Hamiltonian of the form

$$H = \sum_n \left[\frac{1}{2M} p_n^2 + \frac{K}{2} (q_{n+1} - q_n)^2 \right] + \frac{m\omega_0}{4\hbar} \chi \sum_n (Q_n + Q_{n+1})^2 (q_{n+1} - q_n) \\ + \sum_n \left[\frac{1}{2m} p_n^2 + \frac{m\omega_0^2}{2} Q_n^2 - \frac{m\omega_0}{\hbar} J Q_n (q_{n+1} - q_{n-1}) \right] \quad (2)$$

where

$$K = K_0 \left(1 - \frac{r_0}{r_1} + \frac{r_0 D^2}{r_1^3} \right) = K_0 \left(\frac{D}{r_1} \right)^2 \quad (3)$$

$$\chi = -\frac{\hbar}{m\omega_0} K_0 \frac{r_0 D}{r_1^3} \frac{4r_1 r_2}{(r_1 + r_2)^2} \quad (4)$$

$$\omega_0^2 = \omega_{\theta}^2 = \frac{2K_0}{m} \left(1 - \frac{r_0}{r_1} \right) \frac{4r_1 r_2}{(r_1 + r_2)^2} \quad (5)$$

$$J = \frac{\hbar}{m\omega_0} \frac{K_0}{2} \left(1 - \frac{l_0}{l_1}\right) \frac{4r_1 r_2}{(r_1 + r_2)^2} \quad (6)$$

and

$$m = I_c \frac{4}{(r_1 + r_2)^2} \quad (7)$$

This hamiltonian is a form of the Takeno hamiltonian and establishes that l-alanine is a useful material for studying the existence and lifetime of localized states in solids. It should be noted that the vibron spectrum determined by ω_0 and J is strongly dependent on whether the spring K_0 is compressed or extended in its equilibrium position. That is, if l_1 is less than or greater than l_0 . If the spring is extended ($l_1 > l_0$) J is positive and the vibron spectrum then has a minimum at $k = 0$, the center of the Brillouin zone (as we observed experimentally, described below). This is also a necessary condition for the formation of localized modes, given the usual softening non-linearities.

All the constants in the hamiltonian (2) can be derived from a knowledge of the geometric factors l_0 , l_1 , r_1 , r_2 , and D , the mass M and moment of inertia I_c of the molecule, and the longitudinal velocity of sound $v = \sqrt{\frac{K}{M}}$. The non-linear coupling constant does not depend on any intrinsically non-linear forces.

L-Alanine

The above model can now be used to justify our choice of l-alanine ($\text{CH}_3\text{-CHNH}_3\text{-CO}_2$), one of the simplest amino acid crystals, as an appropriate material. From the above and other considerations, we can list the important properties and their relevance to l-alanine:

1. Low symmetry. L-alanine is an orthorhombic crystal which, although it certainly exhibits a three dimensional structure, can be approximately modeled as a chain of molecules (oriented along the c-axis of the crystal) coupled by hydrogen bonds at oblique angles. Thus we have at least some justification for treating this as a 1-D system.

2. Simple to model. Although this crystal has 13 atoms per molecule with 4 molecules per unit cell (153 optical phonon modes) the higher energy intra-molecular modes are separated from the 21 lattice modes so that the unit cell can be modeled as four rigid molecules. These low-frequency lattice modes, characteristic of molecular crystals, are quite amenable to simpler models such as the one described above, where all high-frequency vibrations are considered to be unpopulated.

3. Anharmonicity in phonon fields. This is typically demonstrated by large coefficients of thermal expansion. Figure 4 shows the unit cell dimensions of l-alanine as a function of temperature.¹⁰ The steep slopes for the 'a' and 'b' dimensions exhibit the large coefficients of linear expansion expected of a hydrogen bonded molecular crystal. The small, negative slope of the c-axis curve suggests an even more interesting nonlinearity. Remember that the crystal is characterized in all directions by similar hydrogen bonds, and the bonds themselves are expected to show large, positive expansion with increasing temperature. Therefore, the only mechanism for a negative thermal expansion coefficient is a geometric structure in which vibrational or librational motion perpendicular to the c-axis forces a contraction of the lattice along that dimension. It is this type of mechanism that provides the non-linearities of our models.

4. Pure single crystals should be readily available to minimize the presence of impurity- or defect-induced localization. L-alanine is relatively simple to grow in large, defect free, single crystals. The crystals are also transparent and colorless, a valuable property as our most useful probes will be optical.

5. Long lived optical phonon modes. In order to allow enough time

for true, dynamically stable, localized states to distinguish themselves from very-short-mean-free-path phonons as well as to allow for the possibility of observing the dynamics of phonon to local-mode transitions, a long lifetime is important. The lifetimes of the lowest lying optical phonons (usually the longest lived because of a reduced number of decay channels) have been measured by Koscic et al¹¹ to be of order nanoseconds at low temperatures. This corresponds to a quality factor (Q) in excess of 10^3 .

FIG. 4. Thermal expansion of l-alanine. Boxes- Δa , circles- Δb , and triangles- Δc . Data above 150 K are from Forss. Low temperature data are from Vergimini et al¹⁰.

Phonon Dispersion

Crucial to the study of localization described above is knowledge of the dispersion curves of the phonon fields expected to participate in the localization process. As indicated in the discussion of figure 1, knowledge of the curvature at the Brillouin zone center is particularly important. The only way of measuring this is via inelastic neutron scattering, a time-consuming process only to be undertaken after all other criteria have been met. We measured the relevant dispersion curves at the Brookhaven High Flux Beam Reactor¹². The sample was a fully deuterated, single crystal of l-alanine, grown by slow evaporation. The resulting data for the a and c directions at low temperature are shown in figure 5. Although the c direction curves are somewhat tangled, some important observations can be made. First, for the lowest lying optical mode, there is a minimum at the zone center for the dispersion curves in both the a and c directions. This is a crucial point as it is a condition for zone-center localization for systems in which the non-linear term softens the optical mode at high amplitude. Second, the total dispersion in the a direction corresponds to an inter-cell coupling constant, J, of approximately .71 meV (5.7 cm^{-1}). Finally, the initial slope of the c-axis longitudinal acoustic branch of $3.9 \times 10^{-12} \text{ eV} \pm 1.2$ (5.9 km/sec) agrees well with our pulse-echo ultrasound measurements of the speed of sound in undeuterated l-alanine of 6.2 km/sec in the c direction.

Raman Scattering

To further characterize l-alanine, and to test for phase transitions that might complicate our interpretation of the measurements, we conducted a temperature dependent study of the low-frequency Raman modes. Deuterated and undeuterated samples were grown by slow evaporation or slow cooling of a saturated solution, yielding optically clear crystals with

easily identifiable growth habits. The symmetry axes of the crystals were confirmed by Laue diffraction--the well defined diffraction patterns obtained, as well as the optical clarity of the crystals imply a well ordered structure with minimal defects and no twinning.

FIG. 5. Inelastic neutron scattering data on fully deuterated l-alanine, showing the low-lying optical modes and the acoustic branches.

The low-frequency Raman spectrum consists of 21 optical lattice modes, most of which are concentrated in overlapping bands between 90 and 150 cm^{-1} , but the two lowest lying modes, the ones of interest here, are well isolated (figure 6). It is in the intensity of these modes versus temperature (figure 7a) that we observe anomalies that suggest that the two modes are in some way related, and that the appearance of the lower-frequency mode is associated only with high vibrational amplitude.

FIG. 6. Low temperature Raman spectra of l-alanine in c(bb)a orientation.

Note that in the usual picture of Raman scattering off a typical phonon,

the phonon is detectable at low temperatures. For a mode to disappear when cold, something unusual must happen.

To analyze the raw data, intensities were normalized to that of an 851 cm^{-1} mode, well fit by a Lorentzian, which is expected to have an intensity independent of temperature for the temperatures of interest. The two lowest-energy modes were reduced using least-squares fits to Gaussians, with estimated relative intensity errors of $\pm 3\%$. What is surprising is that we could fit the obviously anomalous intensities of both lines to a single very simple model having only one adjustable parameter. To see how this works, note that the sum of the intensities of the 42 cm^{-1} and 49 cm^{-1} bands, shown in figure 7b, obey Maxwell-Boltzmann statistics to well within our expected errors. Thus it must be that the two modes are sharing a single thermal occupation factor. The energy-level scheme for this Maxwell-Boltzmann fit was constructed with a spacing of 49 cm^{-1} between levels from the ground state to the m th excited state of one harmonic potential and a spacing of 49 cm^{-1} for a second harmonic potential from level n up, suggesting that some change or an instability occurs at excitation level m . Such an energy level scheme produces a fit essentially identical to the usual Maxwell-Boltzmann function for a harmonic oscillator with level spacing of 45.5 cm^{-1} , the average value of the two bands. We conclude from this fit that the 49 cm^{-1} and 42 cm^{-1} bands can be considered as representing the same degree of freedom. However, by using two level spacings, two Raman frequencies are present, and the same model predicts the temperature-dependent intensities of each, shown as the solid curves in figure 7a, with n the only adjustable parameter.

FIG. 7a The normalized, integrated intensities of the 49 cm^{-1} (boxes) and the 42 cm^{-1} (X). The solid curves are a fit to a model describing the bands as one degree of freedom with an instability that shifts the oscillator frequency from 49 cm^{-1} at low amplitude to 42 cm^{-1} at high amplitude.

FIG. 7b The sum of the normalized intensities of the 42 cm^{-1} and 49 cm^{-1} Raman bands. The result of the model (solid curve) is not detectably different from a Bose distribution for 45.5 cm^{-1} .

The physical basis for this fit is not entirely clear to us, but having made it, we also see that it has one very interesting imperfection. It is that the predicted intensity of the 42 cm^{-1} line at 20 K is well below our minimum detectable intensity, but we do indeed observe it to be present, although at a level impossible to explain by a simple Maxwell-Boltzmann distribution. Because the model constrains the 42 cm^{-1} intensity to be present only at high temperatures we can conclude that it is large-amplitude motion that makes it appear, and hence the intensity of

this mode is a measure of vibrational amplitude. High vibrational amplitude is, of course, generated by high temperatures in normal modes. But high amplitudes can also be generated if a normal mode at low temperatures localizes. The localization concentrates an energy insufficient by itself to push the normal mode over the 42cm^{-1} threshold. But by concentrating this energy in a few unit cells, large motions can be achieved cold. This evidence for localization is, of course, somewhat tenuous. However, when combined with all the other positive indications that l-alanine is a good candidate for localization, we find it compelling to intensify our studies, eventually leading to the rather complex picosecond coherent Raman measurement we plan, and which is described below.

To prepare for the coherent Raman work, we have attempted to make the best possible study of the non-linear effects observable with conventional means. Figure 8 shows the temperature dependence of the frequency of the 49cm^{-1} mode (the 42cm^{-1} mode shows similar behavior). These data were obtained by scanning through the laser line and then continuously through the band of interest to obtain a repeatable, absolute measure of the frequency. Two important points must be made about this plot:

FIG. 8 The temperature dependence of the frequencies of the 49cm^{-1} (circles) and 42cm^{-1} (triangles) Raman bands in l-alanine.

First, the temperature dependence of the frequency shift is approximately Bose-like, with a characteristic energy of approximately 180cm^{-1} implying that the dominant nonlinearities for this mode involve couplings to other lattice modes rather than intra-mode non-linearity or coupling to acoustic phonons. This suggests that a strict Davydov model is inappropriate for this system, that coupling to optical modes is important, and that the models we propose are valid only below 100 K.

Second, the total frequency shift may be used as an estimate for the eigenfrequency softening and thus provide a very rough limit on the maximum degree of localization of vibrational energy possible in this system. The total frequency shift from 0 K to 295 K is approximately 2cm^{-1} . Because the lattice breaks up near 450 K, we may take 2cm^{-1} as an order-of-magnitude estimate of the maximum available softening of these low-energy lattice-mode eigenfrequencies. In the introduction to this work, we demonstrated in figure 1 how a softening of the dispersion curve of an excitation allows for the possibility of self trapping of that excitation. The dotted line under the lowest-energy modes near zone center in figure 5 represents a dispersion curve softened by 2cm^{-1} (.25

meV). This softened curve is presumed to have the same shape as the low temperature curve represented by the data points. This figure is the experimental analog of the schematic figure 1. From figure 5 we can now see that the spread in k-states used to form a localized state must extend in k-space no further than approximately one tenth of the Brillouin zone. Thus the minimum possible width of a dynamically stable localized state is of the order of 10 lattice constants in this system. It should be reiterated that since the 2 cm^{-1} softening is a result of all nonlinear couplings and that not all of these couplings may be useful in self trapping the excitation, this estimate is very much a lower bound on the real space size of the localized state and the actual state, if it exists, will almost certainly be larger.

Picosecond Coherent Raman Scattering

In order to obtain greater insight into the detailed behavior of the 49 cm^{-1} mode of l-alanine at both high and low excitation levels, time-resolved measurements using the technique of ps CARS can be performed. Ps CARS (picosecond coherent anti-stokes raman spectroscopy) is a four-wave mixing technique whereby three laser beams are overlapped in a solid in order to generate a fourth¹⁴ (figure 9). This technique can be utilized in either the time-domain or the frequency domain. In the time domain, two laser pulses (from two sync-pumped, cavity-dumped tunable dye lasers driven by a mode-locked, Q-switched, frequency-doubled Nd-YAG laser) are overlapped in the sample to pump coherently the phonon (Vibron) of interest. At some later time another dye-laser pulse is used to interrogate the coherently excited ensemble. This probe pulse interacts with the coherence remaining in the ensemble to produce a fourth pulse, spectrally and spatially resolved. In the time domain, the intensity of the fourth pulse is a measure of the decay rate of the phonon. Because decay times as long as several nanoseconds are easily resolved, the corresponding linewidth resolution is many orders of magnitude smaller than the resolution limit of the best spectrometer¹⁵.

Fig. 9 Spatial arrangement and transitions excited in a time delayed CARS experiment. Simultaneous pulses ω_1 and ω_2 excite a Raman active vibration V. At time τ later a probe pulse at ω_1 stimulates anti-Stokes emission $\omega_{AS} = 2\omega_1 - \omega_2$. The conservation of both energy as well as momentum (for a system having translational invariance) causes the emitted ω_{AS} pulse to be spatially as well as spectrally resolved.

By using Ps CARS, we hope that the onset of dynamic localization can be followed in time, perhaps enabling us to observe the growth of localization from an extended (phonon) initial state, and then the subsequent decay back to that state. Because the generated optical signal is spatially resolved only if k-vector (crystal momentum) is conserved, a local mode that breaks the translational symmetry of the solid, thereby relaxing the condition for k-vector conservation, may cause the fourth

beam to spread from a narrow beam to a cone, the cone angle inversely proportional to the spatial extent of the mode. The use of two sets of detection optics, one on axis and one off axis, can be used to measure the cone angle and hence the degree of localization. Within limits mostly determined by lifetimes and local-mode density, this measurement is completely unambiguous. For l-alanine, we know that the lifetimes of the excited states at 42cm^{-1} and at 49cm^{-1} exceed nanoseconds at 10K^{16} , a long enough time for anything we might hope to observe. We can also estimate the density by noting that the inverse k-vector for light in l-alanine is about 30 unit cells (including the effects of the index of refraction), and as discussed above, the neutron and Raman data imply a minimum soliton size of approximately 10 unit cells. Thus the local mode, if it is there and can be optically excited, is somewhat bigger than 10 unit cells and smaller than 30. If (for example only) it were formed from regions 30 unit cells in size, then the density of these objects would be of order $(1/30)^3$ or about 0.003%, a value easily low enough to prevent the formation of coherent arrays. This is important because coherent arrays would produce beam-like scattering instead of cone-like scattering. This experiment, though not yet running, is in the final stages of development.

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