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Direct Experimental Evidence for Atomic Tunneling of Europium in Crystalline $Eu_8Ga_{16}Ge_{30}$

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Mössbauer-effect and microwave absorption experimental evidence unambiguously demonstrates the presence of slow, ~450 MHz, tunneling of magnetic europium between four equivalent sites in $Eu_8Ga_{16}Ge_{30}$, a stoichiometric clathrate. Remarkably, six of the eight europium atoms, or 11% of the constituents in this solid, tunnel between these four sites separated by 0.55 Å. The off centering of the atoms or ions in crystalline clathrates appears to be a promising route for producing Rabi oscillators in solid-state materials.

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The ability of an atom, ion, or electron to tunnel through a classically impenetrable barrier is one of the most surprising consequences of quantum mechanics. In a solid, most examples of tunneling are restricted to the motion of electrons; there are few examples of the tunneling of whole atoms [1]. Herein we report Mössbauer spectral and microwave absorption experiments that demonstrate the slow ~450 MHz tunneling of magnetic Eu in a stoichiometric clathrate compound, $Eu_8Ga_{16}Ge_{30}$. Remarkably, six of the eight Eu atoms, or 11% of the constituent atoms in this solid, tunnel between four equivalent sites separated by 0.55 Å. The presence of this atomic or ionic tunneling at a well-defined frequency in a crystalline solid may provide an innovative route to new solid-state technological applications of Rabi oscillations, e.g., clocks, quantum computers, low temperature coolers, or masers.

The tunneling of nitrogen in the gaseous ammonia molecule, NH_3, is the most cited example of atomic tunneling in quantum mechanics [2] and this atomic tunneling is fundamental for maser physics [1]. By symmetry the nitrogen can be either above or below the center of an equilateral triangle formed by the three hydrogens and, in accordance with the laws of quantum mechanics, the nitrogen tunnels between the two equivalent positions. This tunneling frequency, ~24 GHz, is independent of temperature and can be detected by the absorption or emission of microwave radiation at this frequency.

In a solid most examples of tunneling involve electrons as is the case in electron field emission, in the Esaki tunnel diode, or in the Josephson junction [3]. Examples of atoms or ions tunneling in a solid are rare and typically are only observed in glasses or involve low concentrations of defects in a crystalline host [1,4]. The off centering of guests in the large cages of clathrates provides a favorable geometric and electronic configuration for the possible tunneling of a large fraction of the atoms in solids [5,6].

$Eu_8Ga_{16}Ge_{30}$, whose schematic structure is shown in Fig. 1, has the cubic type I clathrate structure with space group $Pm\bar{3}n$, [7] and a lattice constant of 10.70 Å. The Ga and Ge atoms are nearly randomly distributed [7,8] among the 20 or 24 vertices of the two different polyhedral cages, X_{20} and X_{24}, that constitute the structure; 1/4 of the Eu is located on the Eu(A) site at the center of the smaller X_{20} cage and 3/4 of the Eu are located on the Eu(B) site near the center of the larger X_{24} cage. A careful analysis of the structure by neutron scattering [7,9] indicates that, in order to improve its bonding with the larger cage, Eu(B) moves to one of the four equivalent bonding sites, sites that are $\simeq 0.4$ Å from the center of the cage and separated by 0.55 Å, see Fig. 1. Indirect measurements such as the temperature dependence of the thermal conductivity, ultra-

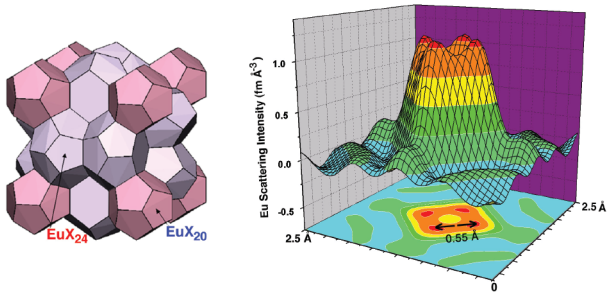

FIG. 1 (color). A schematic of the crystal structure of $Eu_8Ga_{16}Ge_{30}$ is shown on the left. The Eu is located near the center of each polyhedron and X refers to either Ge or Ga. The nuclear density map of the position of the Eu(B) nucleus near the center of the larger polyhedral cage at (1/4, 0, 1/2) of the unit cell is shown on the right. The amplitude along the vertical direction is proportional to the probability of finding the nucleus at a particular position in the cage. The area of the xy plane is 2.5×2.5 Å^2. The Eu nucleus is located at one of the four equivalent positions 0.4 Å from the cage center.

sonic attenuation, and elastic constants [9–12] suggest that Eu on the B-site atoms may tunnel among the four off-center positions. However, none of these techniques directly probe the local environment or the dynamics of the Eu on the B site. For example, the Letter by Zerec *et al.* [11] essentially presents a theoretical model that was developed in order to explain the dip in the elastic constants near 20 K. In this model, only energy levels ~30 K above the ground state contribute to the elastic constants and it is primarily the thermal depopulation of these levels that produces the dip. Although the Zerec model is consistent with previously measured elastic constant, neutron, and heat capacity data, none of these experimental probes are sensitive to the ground state tunneling of Eu(B), with levels separated by only ~50 mK. Our investigation by Mössbauer spectroscopy of the Eu tunneling in $Eu_8Ga_{16}Ge_{30}$ is possible because, first, ^{151}Eu is a Mössbauer active isotope, second, below 32 K $Eu_8Ga_{16}Ge_{30}$ is ferromagnetic and thus exhibits a Mössbauer spectrum with abundant information, and, third, the tunneling time scale is comparable to the Mössbauer-effect time scale of the ^{151}Eu nuclide.

dc magnetization data obtained with a standard SQUID magnetometer indicate that the compound is ferromagnetic below $T_C \sim 32$ K, and has a saturation moment of $7\mu_B$ for each Eu at 5 K [8,9]. Thus all of the Eu is divalent and participates in the ferromagnetism through RKKY indirect exchange coupling via the conduction electrons [8,9]. Neutron scattering measurements [7] also indicate that, in the ferromagnetic phase at temperatures well below 32 K, each Eu has the maximum spin multiplicity moment of $7\mu_B$. The ferromagnetically ordered spin moments of the seven $4f$ electrons of Eu produce an effective hyperfine magnetic field at the Eu-151 nucleus. This effective magnetic field, which is typically ~22 T in most ferromagnetic Eu compounds [13,14], yields an octet spectrum as is shown at the top right of Fig. 2.

The Mössbauer spectra obtained between 32 mK and 30 K on a polycrystalline sample of $Eu_8Ga_{16}Ge_{30}$ are shown on the left of Fig. 2. The Mössbauer measurements used an absorber containing 50 mg/cm^2 of natural isotopic abundance polycrystalline $Eu_8Ga_{16}Ge_{30}$ and a constant acceleration spectrometer which utilized a 400 mCi $^{151m}SmF_3$ source. Between 32 mK and 30 K $Eu_8Ga_{16}Ge_{30}$ is ferromagnetic and the expected spectrum for a "normal" ferromagnetic Eu compound, top right of Fig. 2, is clearly not observed. Rather, the observed spectra indicate that a large fraction of the Eu nuclei shows no resolved magnetic hyperfine interaction on the ^{151}Eu Mössbauer time scale. A fit of the spectra obtained at 15 K and below with a magnetic octet and a broad singlet indicates that only 25% of the Eu nuclei experience a static hyperfine field of ~20 T. This magnetic component may be assigned to Eu(A) and the broad singlet may be assigned to Eu(B), in agreement with the relative Eu(A):Eu(B) occupancies of 1:3.

A well-defined, resolved, magnetic hyperfine splitting in a Mössbauer spectrum indicates that the hyperfine field in

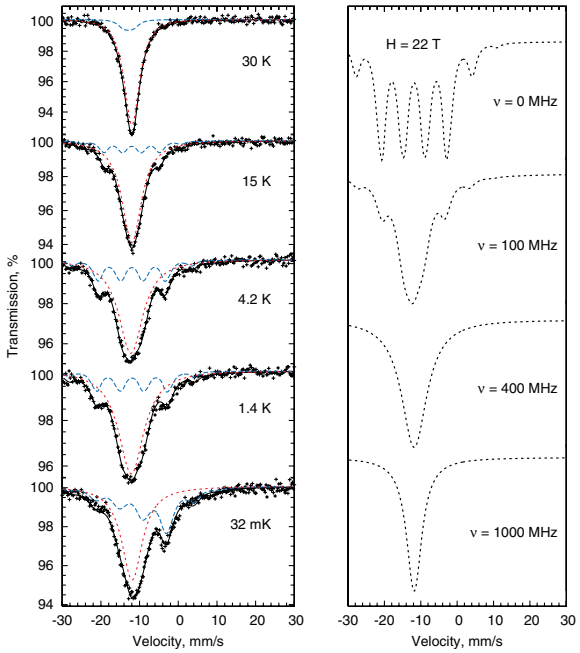

FIG. 2 (color). The Mössbauer spectra of $Eu_8Ga_{16}Ge_{30}$ obtained at the indicated temperatures, left. The solid black line is the total fit obtained from the sum of the magnetic subspectrum assigned to Eu(A), the blue curve, and the relaxation subspectrum assigned to Eu(B) the red curve. The calculated spectra for divalent Eu with a 22 T hyperfine field that is randomly fluctuating at the indicated frequencies, right.

which the nuclear magnetic moment precesses is stationary during several Larmor precessions. The dc magnetization and neutron data indicate that Eu(B) has the full Hund's rule magnetic moment of $7\mu_B$ [9], and the lack of a resolved magnetic pattern for the Eu(B) nuclei cannot be due to actual fluctuations of the hyperfine field. We believe that the incoherent tunneling of Eu(B) perturbs the Larmor precession about the hyperfine field, such that there is no memory of the initial quantum state of the nucleus after the tunneling. This is equivalent to a random fluctuation of the quantization axis for the nuclear spin, i.e., of the hyperfine field direction. The equivalent magnetic relaxation frequency, ν, is that of the tunneling, and must be similar to the typical ^{151}Eu hyperfine Larmor frequency of 1000 MHz in order to collapse the magnetic pattern. The appropriate Mössbauer relaxation line shape is that corresponding to uncorrelated stochastic fluctuations of the hyperfine field in the random phase approximation [15]. Within this model, the spectral line shape is a function of the magnitude and the fluctuation frequency of the hyperfine field. The spectrum evolves from a sharp octet for no fluctuation to a partially resolved magnetic spectrum for a low fluctuation frequency, and then to a narrow single line at high fluctuation frequencies, see the right of Fig. 2.

In fitting the Mössbauer spectra, the magnitude of the Eu(A) and Eu(B) hyperfine fields are constrained to be identical at each temperature. This constraint is reasonable

because the hyperfine field is the sum of the Eu core polarization and the conduction electron self-polarization terms, two terms that should not differ for Eu(A) and Eu(B). Below ~10 K the hyperfine field is constant, but near $T_C \sim 32$ K it becomes much smaller. The fits of the Mössbauer spectra in Fig. 2 yield a fluctuation frequency of 450 ± 50 MHz, a frequency that is independent of temperature between 32 mK and 30 K, see Table I. The lack of any temperature dependence rules out thermally activated hopping of the Eu(B) atoms and strongly suggests tunneling between the four neighboring sites.

The Eu(A) component in the Mössbauer spectrum recorded at 32 mK exhibits an increased and decreased spectral weight toward higher velocities and lower velocities, respectively, a difference that arises from the different Boltzmann populations of the nuclear levels of the ^{151}Eu nuclear ground state. The energy splitting between the nuclear ground states $m_I = -5/2$ and $+5/2$ in a field of 22 T is ~56 mK. The temperature has been explicitly taken into account in calculating the spectral line shape and in weighting the spectral area for Eu(A) at 32 mK. The Eu(B) spectral component does not exhibit a similar asymmetry at 32 mK because precession about the magnetic field is perturbed by the tunneling and a mixing of the population of the nuclear levels occurs yielding a symmetric spectrum. The absence of asymmetry in the Eu(B) spectral component at 32 mK supports the proposed tunneling in $Eu_8Ga_{16}Ge_{30}$.

The temperature independence of the measured fluctuation frequency is indicative of tunneling, but is the frequency of 450 MHz reasonable? A simple estimation of the Eu(B) tunnel energy splitting in $Eu_8Ga_{16}Ge_{30}$ may be obtained by assuming that Eu(B) resides in a double-well potential approximated by a double harmonic oscillator with $V(x) = \frac{k}{2}(|x| - a)^2$, where k is the force constant and $2a$ is the distance between the two minima. The distance, $\simeq 2a$, between neighboring Eu(B) sites is 0.55 Å, see Fig. 1, and the force constant for a harmonic oscillator is given by $k = m\omega^2$, where m is the mass of Eu and ω is the Einstein frequency for the harmonic oscillator. From previous heat capacity, elastic constant, and Raman and nuclear inelastic scattering studies [9,11,16,17], an Einstein temperature of ~30 K has been obtained for Eu(B), corresponding to an Einstein energy of 2.7 meV. With no adjustable parameters the textbook solution of this model [18] predicts a splitting between the two lowest energy levels of the double oscillator of 5.5 μeV or a splitting frequency of ~1300 MHz, and an 11 meV or 120 K potential barrier. Hence, below ~15 K, thermally activated hopping over the barrier can be neglected and, as observed, tunneling dominates. A more sophisticated model [11] that considered all four Eu sites was developed to account for elastic constant anomalies in $Eu_8Ga_{16}Ge_{30}$. Although there was no direct experimental evidence of tunneling in this earlier work [11], their model predicts a splitting between the two lowest energy levels of the four level system, Δ_1, of 0.05 K or 4.3 μeV or a splitting frequency of ~1050 MHz, close to the splitting between the two lowest energy levels of the double oscillator. These calculated frequencies are extremely sensitive to both the Einstein temperature and the distance between neighboring Eu(B). Indeed, for Einstein temperatures between 25 and 35 K and distances between 0.51 and 0.60 Å, the calculated frequency varies between 2000 and 200 MHz. Hence, the observed frequency of 450 MHz is well within this range.

TABLE I. The relative area of the Eu(A) magnetic spectral absorption, r, the Eu(A) and Eu(B) hyperfine field, H, and the fluctuation frequency, ν.

T (K)	r (%)	H (T)	ν (MHz)[a]
30	25 ± 5	5.2 ± 0.4	450 ± 120
15	25 ± 3	17.5 ± 0.2	480 ± 30
4.2	27 ± 2	21.3 ± 0.2	440 ± 20
1.4	25 ± 1	22.4 ± 0.2	460 ± 20
0.032	25 ± 2	22.7 ± 0.2	480 ± 30

[a]A constrained linewidth of 2.3 mm/s, as is observed at 100 K, has been used for all fits.

In analogy with the microwave absorption measurements [2] on the nitrogen tunneling in NH_3, similar measurements have been performed on $Eu_8Ga_{16}Ge_{30}$ in order to support the validity of the conclusions reached by the Mössbauer spectral analysis. The absorption by $Eu_8Ga_{16}Ge_{30}$ of a microwave signal with a frequency between 0.3 and 3000 MHz was measured with a Hewlett-Packard 8714ES network analyzer. A single crystal of $Eu_8Ga_{16}Ge_{30}$ with dimensions of $1.5 \times 2 \times 3$ mm^3 was inserted in a loop of ~3 mm diameter, located during operation in the sample space of a Physical Property Measurement System from Quantum Design. The loop formed a short at one end of a semirigid 1.7 m long coaxial cable connected to the network analyzer. The loss factor on the coaxial line was determined in a one port setup by measuring the reflectance coefficient, S_{11} [19]. This measurement was performed in the absence of any external magnetic field, except for determining whether the absorption is related to ferromagnetic resonance. A broad absorption of microwave energy centered near 500 MHz is observed between 5 and 25 K, see Fig. 3; the frequency of this peak is essentially independent of temperature as expected for the absorption of energy due to the Eu(B) tunneling. The possibility that the microwave absorption is related to ferromagnetic resonance [20] was considered but eliminated, first, because the frequency of such a peak would exhibit at strong temperature and field dependence just below T_C, and second, because the resonance should appear at a much higher frequency. Indeed such a peak is observed between 32 and 30 K, at a frequency of about 2.5 GHz, and rapidly moves outside the observation window as the sample is cooled, see the right portion of Fig. 3. Above ~30 K, there is no measurable absorption of microwave energy, presumably because Eu(B) thermally hops over the 120 K barrier between adjacent sites or

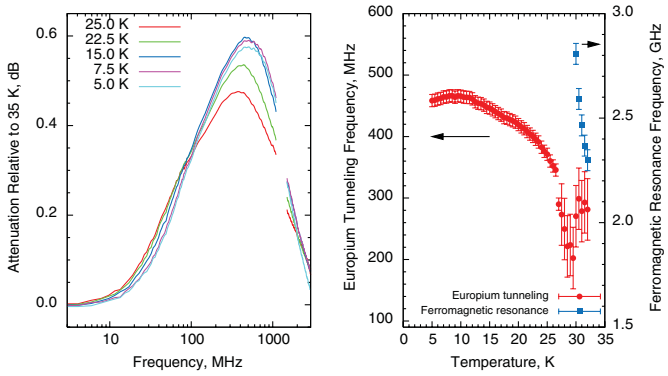

FIG. 3 (color). The microwave attenuation in $Eu_8Ga_{16}Ge_{30}$ at different temperatures, left. A resonant cavity in the instrument prevents measurements at ~1300 MHz. The frequency of both the maximum in power absorption attributed to the Eu tunneling, in red, and the ferromagnetic resonance, observed near T_C, in blue, are shown on the right.

because the microwave field is better coupled to the tunneling states when the material is ferromagnetic. Because the Eu is ionic [21] in $Eu_8Ga_{16}Ge_{30}$, the most likely coupling mechanism between the electromagnetic field and the tunneling states is through the electric dipole moment resulting from the off centering of the Eu(B); however, coupling with the Eu(B) magnetic moment cannot be excluded.

As the temperature is increased from 20 to 30 K, a decrease in the microwave absorption frequency from 400 to 300 MHz is observed, see the right portion of Fig. 3, a decrease that is incompatible with a thermally activated process for which the frequency would increase with temperature. The temperature dependence of the tunneling frequency can be related to the thermal expansion of the lattice because the resulting slight increase in the separation of the off-center positions yields a decrease in the tunneling frequency, a frequency which is a very sensitive function of the Einstein energy and the off-centering distance [1]. An increase of ~5% in separation reduces the tunneling frequency by a factor two. In contrast, physical pressure on the system is likely to increase the tunneling frequency and may well permit its tuning.

A combination of the Mössbauer spectra and microwave absorption of $Eu_8Ga_{16}Ge_{30}$ provides exceptionally clear support for the tunneling of 75% of the Eu in a ferromagnetic crystalline solid with a well-defined frequency. The observed frequency of 450 ± 50 MHz in both the microwave absorption experiment and the Mössbauer relaxation spectra is within the range of tunneling splitting calculated for a double harmonic oscillator with an Einstein temperature of 31 ± 4 K and a distance between the well minima of 0.58 ± 0.03 Å. The agreement found herein between the frequency measured in a ferromagnetic solid and the frequency calculated for an isolated tunneling atom is indeed quite surprising because of the ferromagnetic interactions between the Eu ions.

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