Mössbauer spectroscopy sees atoms tunneling in a crystal

Direct experimental evidence for atomic tunneling of europium in crystalline $Eu_8Ga_{16}Ge_{30}$, Phys. Rev. Lett. 97, 017401 (2006)
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Recommended and a commentary by S. Paschen, Institute of Solid State Physics, TU Vienna, Austria

The quantum mechanical phenomenon of tunneling is well known in the solid state: however, one usually comes across only electron tunneling. Tunneling of whole atoms is a much rarer event and has mostly been investigated in glasses and solid electrolytes which are also quite disordered. The work in the above paper shows unambiguously a perfectly crystalline material in which a large fraction of atoms tunnel from one equivalent position to another. This observation may pave the way for solid-state technological applications of Rabi oscillations.

The material Hermann and co-workers investigated is the extensively studied clathrate $Eu_8Ga_{16}Ge_{30}$. Clathrates are compounds where "host" atoms (here Ga and Ge) form a framework with cavities (or cages) which are filled by "guest" atoms/molecules (here Eu). Current interest in these compounds is due to their potential as thermoelectric materials. It is commonly believed that the guest atoms are only loosely bound in the cages and undergo large, essentially localized oscillations ("rattling") which strongly scatter the heat carrying (acoustic) phonons, leading to low and "glass-like" thermal conductivities. At the same time the rattling does not significantly affect the electronic properties since the charge carriers are confined to the framework. The resulting large electrical to thermal conductivity ratio enhances the thermoelectric figure of merit.

Neutron scattering has revealed (Sales, 2001) that the Eu atoms in the larger of the two different types of cages building up $Eu_8Ga_{16}Ge_{30}$ are not situated in the center of the cage but occupy, instead, four so-called split sites which are separated from each other by 0.55 Å. So far only indirect evidence was available for the tunneling of Eu atoms between these off-center positions, from measurements of elastic constants, ultrasonic attenuation, thermal conductivity, and specific heat.

Hermann and co-workers have investigated this compound by Mössbauer spectroscopy and find that all Eu atoms in the larger cage tunnel at a frequency of about 450 MHz between the equivalent off-center positions. A necessary condition for the experiment to work is that $Eu_8Ga_{16}Ge_{30}$ orders ferromagnetically (below 30 K). From magnetization measurements the ferromagnetism is known to be of local moment type, mediated by the RKKY interaction (all Eu are divalent with a saturation moment of $7\mu_B$). In a "normal" local moment system the ordered spin moments of an atom produces an effective hyperfine magnetic field at its nucleus which then produces a characteristic Mössbauer spectrum (an octet spectrum). However, the most prominent feature of the experimentally observed spectra between 30 K and 32 mK is a broad singlet indicating that a large fraction of Eu nuclei in $Eu_8Ga_{16}Ge_{30}$ show *no* resolved magnetic hyperfine interaction. An excellent fit to the data reveals that only two out of eight Eu atoms experience a static hyperfine field. This is exactly the faction of Eu atoms residing in the smaller cages where no off-center positions are observed and thus no tunneling can take place.

The authors argue that while the absolute value of the magnetic moment is time independent for all the eight Eu atoms of the structure (as known from magnetization measurements), its direction is fluctuating for the six Eu atoms in the larger cages due to their incoherent tunneling. This corresponds to a random fluctuation of the quantization axis for the nuclear spin which can therefore not complete enough Lamor precessions to yield a well-resolved magnetic hyperfine splitting. This interpretation is all the more convincing since the observed temperature independent fluctuation frequency of 450 MHz compares well with theoretical expectations and with microwave absorption measurements presented in the same paper.

These results put a new focus on cage compounds and will, I believe, motivate much more experiments at very low temperatures (dilution fridge range) where quantum-mechanical tunneling can clearly be separated from thermally activated hopping.