

JAHN-TELLER DISTORTIONS: A NEW STRATEGY IN QUANTUM MECHANICS

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ABSTRACT

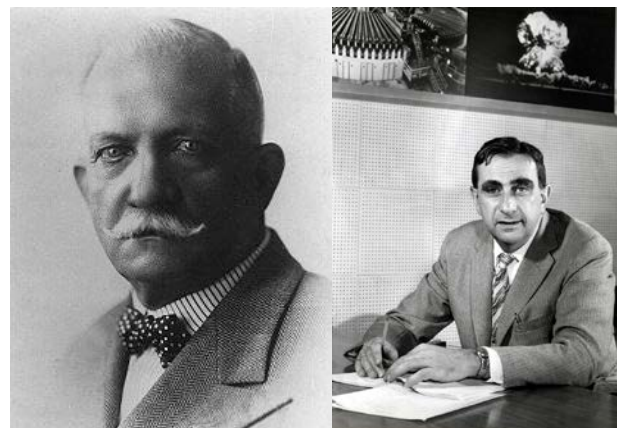
The concepts of the Jahn-Teller effect and vibronic coupling are being applied to more and more systems in both chemistry and physics. Aspects of structural chemistry such as the distortion of the nuclear framework to a lower-symmetry conformation have received an increasing attention, as well as the dynamics on the coupled potential energy surface.

Key words: Quantum mechanics, Vibronic coupling, Molecular Orbital Theory, Alfred Jahn, Edward Teller, Jahn-Teller effect, Electron Spin, Nano chemistry

INTRODUCTION

Sometimes there can be a strong coupling between molecular vibrations and the motion of the electrons. The electrons in the C₆₀ molecule are known to be sensitive to the molecular vibrations. It is believed that this vibronic coupling (known as the Jahn-Teller [JT] effect) plays an important role in determining various aspects of the behaviour of C₆₀ ions and related fullerene compounds. Modes of vibration between fullerene molecules (intramolecular modes) probably play an important role in the relatively high-temperature superconductivity of certain fullerene compounds.

As icosahedral symmetry is extremely rare in nature, vibronic coupling effects were not been investigated in this symmetry until relatively recently. Many interesting new effects due to the vibronic coupling are possible from a theoretical point of view due to the existence of quantum-mechanical states that are four and five fold degenerate. The ground state of a neutral C₆₀ molecule contains a completely filled orbital, so is not subject to a Jahn-Teller effect. However, the ground states of its cationic and anionic states do potentially exhibit strong Jahn-Teller effects. Vibronic coupling is also important from an experimental point of view. However, attempts to explain all the observed data using physically acceptable vibronic coupling models remain in a very underdeveloped state.^[1]



Alfred Jahn

Edward Teller

Figure-1: Jahn-Teller

This paper surveys the present understanding of the Jahn-Teller effect and includes a historical review of the principal advances. The important role of the dynamic Jahn-Teller effect in many experimental phenomena has only recently been recognized and the predicted effects have now been observed in a large number of systems. The dynamic Jahn-Teller effect also explains why a Jahn-Teller distortion does not appear in certain cases for which it was expected and for which its absence was a long-standing puzzle. A Jahn-Teller distortion or static Jahn-Teller effect occurs as a limiting case of the dynamic effect, in the limit of strong coupling and criteria for this transition are presented.

The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among

octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system. The Jahn-Teller effect tells us that a molecule and ions with degenerate states, such as $C60^-$ anions, can spontaneously distort, such that the distorted configuration has lower energy than the undistorted one. The distortions that are allowed are certain combinations of the normal modes of vibration, and group theory can be used to determine the symmetry of the distortions. For $C60^-$ anions, theory tells us that coupling is possible to the eight h_g modes of vibration, and that the distortions can be of $D5d$ or $D3d$ symmetry.^[2]

Molecular Orbital Theory

For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t_{2g} (d_{xz} , d_{yz} , d_{xy}) and e_g (d_z^2 and $d_{x^2-y^2}$). When a molecule possesses a degenerate electronic ground state, it will distort (Jahn-Teller effect) to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the z ligand bonds as shown in **Figure-2** below:

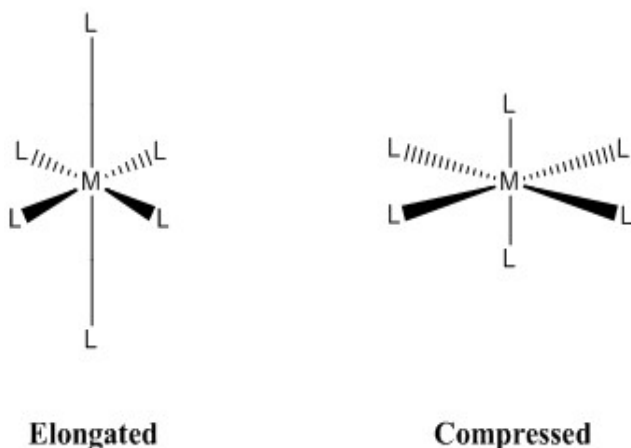


Figure-2: Jahn-Teller distortions for an octahedral complex.

When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.

Elongation

Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, while the orbitals without a z component are destabilized (higher in energy) as shown in **Figure-3** below:

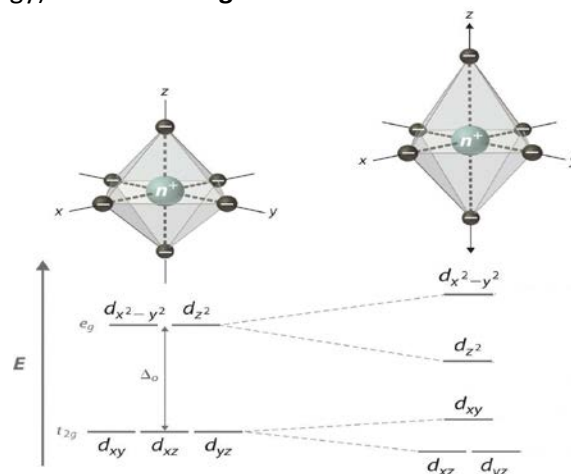


Figure-3: Illustration of tetragonal distortion (elongation) for an octahedral complex.

This is due to the d_{xy} and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding, but is destabilized due to the interactions.^[3]

Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in **Figure-4** below:

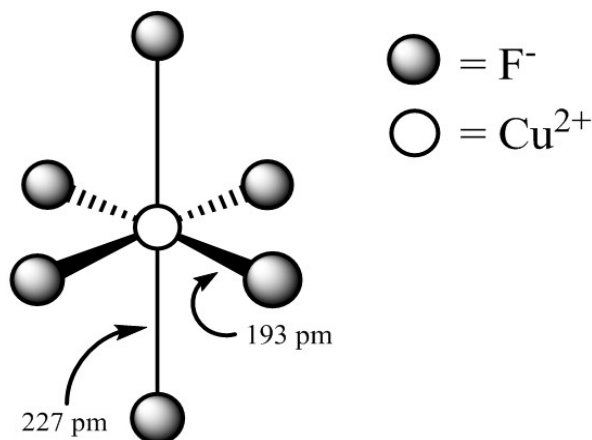


Figure-4: Structure of octahedral copper(II) fluoride.

Notice that the two axial bonds are both elongated and the four shorter equatorial bonds are the same length as each other. According the theorem, the orbital degeneracy is eliminated by distortion, making the

molecule more stable based on the model presented in **Figure-3**.

Compression

Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals *without* a z component, while the orbitals with a z component are destabilized (higher in energy) as shown in **Figure-5** below:

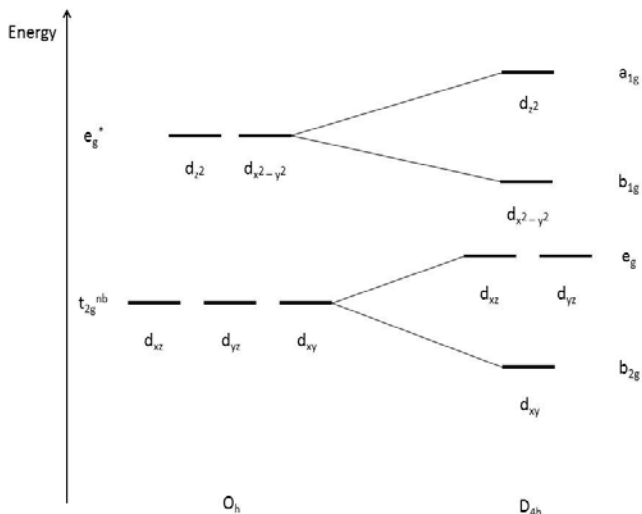


Figure-5: Illustration of tetragonal distortion (compression) for an octahedral complex.

This is due to the z-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the d_{z^2} orbital is antibonding, it is expected to increase in energy due to compression. The d_{xz} and d_{yz} orbitals are still nonbonding, but are destabilized due to the interactions.

Spin States

For Jahn-Teller effects to occur in transition metals there must be degeneracy in either the t_{2g} or e_g orbitals. The electronic states of octahedral complexes are classified as either low spin or high spin. The spin of the system is dictated by the chemical environment. This includes the characteristics of the metal center and the types of ligands.^[4]

Low Spin

Figure-6 (below) shows the various electronic configurations for low spin octahedral complexes:

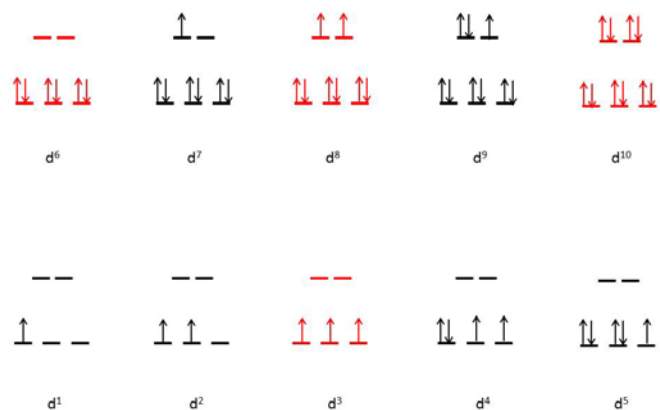


Figure-6: Low spin octahedral coordination diagram (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates that low spin complexes with d^3 , d^5 , d^8 , and d^{10} electrons cannot have Jahn-Teller distortions. These electronic configurations correspond to a variety of transition metals. Many common examples include Cr^{3+} , Co^{3+} , Ni^{2+} , and Cu^{2+} .

High Spin

Figure-7 (below) shows the various electronic configurations for high spin octahedral complexes:

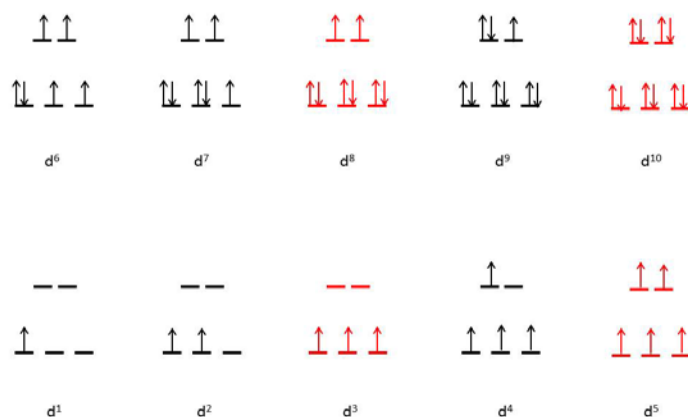


Figure-7: High spin octahedral coordination diagram (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates that low spin complexes with d^3 , d^5 , d^8 , and d^{10} electrons cannot have Jahn-Teller distortions. In general, degenerate electronic states occupying the e_g orbital set tend to show stronger Jahn-Teller effects. This is primarily caused by the occupation of these high energy orbitals. Since the system is more stable with a lower energy configuration, the degeneracy of the e_g set is broken, the symmetry is reduced, and occupations at lower energy orbitals occur.^[5]

Spectroscopy

Jahn-Teller distortions can be observed using a variety of spectroscopic techniques. In UV-VIS absorption spectroscopy, distortion causes splitting of bands in the spectrum due to a reduction in symmetry (O_h to D_{4h}). Consider a hypothetical molecule with octahedral symmetry showing a single absorption band. If the molecule were to undergo Jahn-Teller distortion, the number of bands would increase as shown in **Figure-8** below:

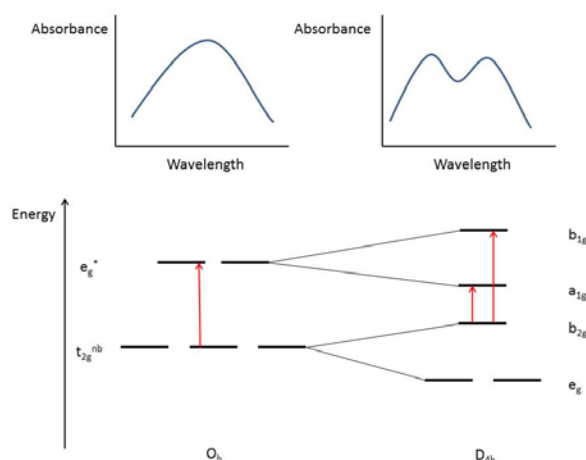


Figure-8: Hypothetical absorption spectra of an octahedral molecule (left) and the same molecule with Jahn-Teller elongation (right). The red arrows indicate electronic transitions.

A similar phenomenon can be seen with IR and Raman vibrational spectroscopy. The number of vibrational modes for a molecule can be calculated using the $3n - 6$ rule (or $3n - 5$ for linear geometry) rule. If a molecule exhibits an O_h symmetry point group, it will have fewer bands than that of a Jahn-Teller distorted molecule with D_{4h} symmetry. Thus, one could observe Jahn-Teller effects through either IR or Raman techniques. This effect can also be observed in EPR experiments as long as there is at least one unpaired electron.

Examples of Jahn-Teller distorted complexes

Table-1: Molecular distortion

$CuBr_2$	4 Br at 240pm 2 Br at 318pm
$CuCl_2$	4 Cl at 230pm 2 Cl at 295pm
$CuCl_2 \cdot 2H_2O$	2 O at 193pm 2 Cl at 228pm 2 Cl at 295pm
$CsCuCl_3$	4 Cl at 230pm 2 Cl at 265pm
CuF_2	4 F at 193pm 2 F at 227pm
$CuSO_4 \cdot 4NH_3 \cdot H_2O$	4 N at 205pm 1 O at 259pm 1 O at 337pm
K_2CuF_4	4 F at 191pm 2 F at 237pm
$KCuAlF_6$	2 F at 188pm 4 F at 220pm
CrF_2	4 F at 200pm 2 F at 243pm
$KCrF_3$	4 F at 214pm 2 F at 200pm
MnF_3	2 F at 209pm 2 F at 191pm 2 F at 179pm

The Jahn-Teller Theorem predicts that distortions should occur for any degenerate state, including degeneracy of the t_{2g} level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the e_g level. Tokyo: Scientists at Tokohu University in Japan have discovered a new state of matter called the 'Jahn-Teller-metal' that resembles an insulator, superconductor, metal and magnet all rolled into one. The discovery came from a team of scientists led by Dr Kosmas Prassides at the Tohoku University in Japan.^[6] While solid, liquids, gases and plasmas occur naturally in nature, the other states of matter must largely be created in the laboratory. The artificial states include superfluids - which can flow without friction - and superconductors, which have zero electrical resistance. An international team of scientists has announced the discovery of a new state of matter in a material that appears to be an insulator, superconductor, metal and magnet all rolled into one, saying that it could lead to the development of more effective high-temperature superconductors



Figure-9: Scientists have discovered a new state of matter, called 'Jahn-Teller metals'

Why is this so exciting? Well, if these properties are confirmed, this new state of matter will allow scientists to better understand why some materials have the potential to achieve superconductivity at a relatively high critical temperature (Tc) - "high" as in -135°C as opposed to -243.2°C . Because superconductivity allows a material to conduct electricity without resistance, which means no heat, sound, or any other form of energy release, achieving this would revolutionise how we use and produce energy, but it's only feasible if we can achieve it at so-called high temperatures.

As Michael Byrne explains at Motherboard, when we talk about states of matter, it's not just solids, liquids, gases, and maybe plasmas that we have to think about. We also have to consider the more obscure states that don't occur in nature, but are rather created in the lab - Bose-Einstein condensate, degenerate matter, supersolids and superfluids, and quark-gluon plasma, for example.

By introducing rubidium into carbon-60 molecules - more commonly known as 'buckyballs' - a team led by chemist Kosmas Prassides from Tokohu University in Japan was able to change the distance between them, which forced them into a new, crystalline structure. When put through an array of tests, this structure displayed a combination of insulating, superconducting, metallic, and magnetic phases, including a brand new one, which the researchers have named 'Jahn-Teller metals'.

Named after the Jahn-Teller effect, which is used in chemistry to describe how at low pressures, the geometric arrangement of molecules and ions in an electronic state can become distorted, this new state of matter allows scientists to transform an insulator - which can't conduct electricity - into a conductor by simply applying pressure. Byrne explains at Motherboard:

"This is what the rubidium atoms do: apply pressure. Usually when we think about adding pressure, we think in terms of squeezing something, forcing its molecules closer together by brute force. But it's possible to do the same thing chemically, tweaking the distances between molecules by adding or subtracting some sort of barrier between them - sneaking in some extra atoms, perhaps. What happens in a Jahn-Teller metal is that as pressure is applied, and as what was previously an insulator - thanks to the electrically-distorting Jahn-Teller effect - becomes a metal, the effect persists for a while. The molecules hang on to their old shapes. So, there is an overlap of sorts, where the material still looks an awful lot like an insulator, but the electrons also manage to hop around as freely as if the material were a conductor."

And it's this transition phase between insulator and conductor that, until now, scientists have never seen before, and hints at the possibility of transforming insulating materials into super-valuable superconducting materials. And this buckyball crystalline structure appears to be able to do it at a relatively high TC.^[7] "The relationship between the parent insulator, the normal metallic state above Tc, and the superconducting pairing mechanism is a key question in understanding all unconventional superconductors," the team writes in *Science Advances*.

There is a whole lot of lab-work to be done before this discovery will mean anything for practical energy production in the real world, but that is science for you. And it is got people excited already, as chemist Elisabeth Nicol from the University of Guelph in Canada told Hamish Johnston at Physics World: "Understanding the mechanisms at play and how they can be manipulated to change the Tc surely will inspire the development of new [superconducting] materials".

Table-2: Electronic effect

	Jahn-Teller effect									
Number of d electrons	1	2	3	4	5	6	7	8	9	10
High/Low Spin				HS	LS	HS	LS	HS	LS	HS
Strength of J-T Effect	w	w		s	w		w	w		w

w: weak Jahn-Teller effect (t_{2g} orbitals unevenly occupied)

s: strong Jahn-Teller effect expected (eg orbitals unevenly occupied)

blank: no Jahn-Teller effect expected.

The **Jahn-Teller effect**, sometimes also known as **Jahn-Teller distortion**, describes the geometrical distortion

of molecules and ions that is associated with certain electron configurations. This electronic effect is named after Hermann Arthur Jahn and Edward Teller, who proved, using group theory, that orbital nonlinear spatially degenerate molecules *cannot* be stable. The **Jahn-Teller theorem** essentially states that any nonlinear molecule with a spatially degenerate electronic ground

state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species. For a description of another type of geometrical distortion that occurs in crystals with substitution impurities see article off-center ions.

The Jahn-Teller effect is most often encountered in octahedral complexes of the transition metals. The phenomenon is very common in six-coordinate copper (II) complexes. The d^9 electronic configuration of this ion gives three electrons in the two degenerate e_g orbitals, leading to a doubly degenerate electronic ground state. Such complexes distort along one of the molecular fourfold axes (always labelled the z axis), which has the effect of removing the orbital and electronic degeneracy and lowering the overall energy. The distortion normally takes the form of elongating the bonds to the ligands lying along the z axis, but occasionally occurs as a shortening of these bonds instead (the Jahn-Teller theorem does not predict the direction of the distortion, only the presence of an unstable geometry). When such an elongation occurs, the effect is to lower the electrostatic repulsion between the electron-pair on the Lewis basic ligands and any electrons in orbitals with a z component, thus lowering the energy of the complex. If the undistorted complex would be expected to have an inversion centre, this is preserved after the distortion.

In octahedral complexes, the Jahn-Teller effect is most pronounced when an odd number of electrons occupy the e_g orbitals. This situation arises in complexes with the configurations d^9 , low-spin d^7 or high-spin d^4 complexes, all of which have doubly degenerate ground states. In such compounds the e_g orbitals involved in the degeneracy point directly at the ligands, so distortion can result in a large energetic stabilization. Strictly speaking, the effect also occurs when there is degeneracy due to the electrons in the t_{2g} orbitals (*i.e.* configurations such as d^1 or d^2 , both of which are triply degenerate). In such cases, however, the effect is much less noticeable, because there is a much smaller lowering of repulsion on taking ligands further away from the t_{2g} orbitals, which do not point *directly* at the ligands (see the table below). The same is true in tetrahedral complexes (e.g. manganate: distortion is very subtle because there is less stabilization to be gained because the ligands are not pointing directly at the orbitals).

The Jahn-Teller effect is responsible for the tetragonal distortion of the hexaaquacopper (II) complex ion, $[\text{Cu}(\text{OH}_2)_6]^{2+}$, which might otherwise possess octahedral geometry. The two axial Cu–O distances are 238 pm, whereas the four equatorial Cu–O distances are

~195 pm. A recent study shows that the copper(II) ion coordinates five water molecules in an elongated square pyramid with four Cu–O_{eq} bonds (2x1.98 Å and 2x1.95 Å) and a long Cu–O_{ax} bond (2.35 Å). The four equatorial ligands were distorted from the mean equatorial plane by $\pm 17^\circ$.^[8]

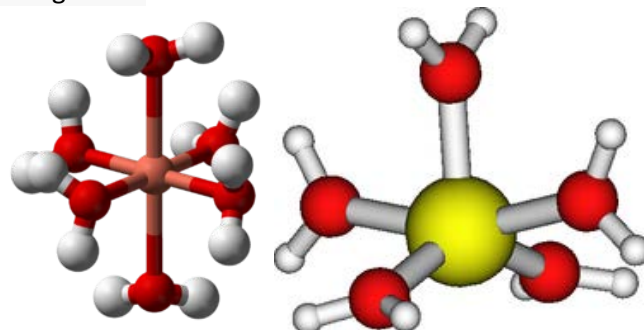


Figure-10: 3D structure of crystal lattice

The Jahn-Teller effect is manifested in the UV-VIS absorbance spectra of some compounds, where it often causes splitting of bands. It is readily apparent in the structures of many copper (II) complexes. Additional, detailed information about the anisotropy of such complexes and the nature of the ligand binding can be however obtained from the fine structure of the low-temperature electron spin resonance spectra. In the latest research, researchers took a crystalline arrangement of carbon-60 molecules - known as buckyballs and inserted atoms of rubidium. When the pressure between the buckyballs was increased by adding more rubidium atoms, the material changed from being an insulator into a superconductor.

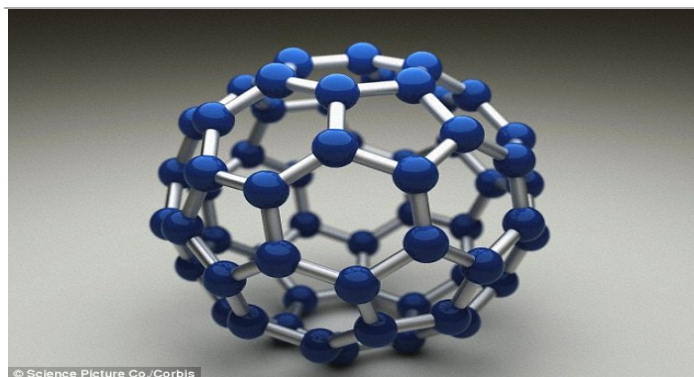


Figure-11: Buckyball

In so doing, they created a material that had the properties of an insulator, superconductor, metal and a magnet, all in one. The change from an insulator to a conductor is known as the Jahn-Teller effect, and it was first predicted in 1937 - but had not been found until now - earning the new material the moniker of Jahn-Teller metal. The surprising thing about this metal-insulator transition is that it involves an intermediate state never

seen before, wrote Hamish Johnston, editor of physicsworld.com. And it is this intermediate state that has scientists interested, as it seems that just applying pressure can turn the material from an insulator into a conductor. Superconductors are incredibly useful because they efficiently transport electric charge with zero resistance. Regular conductors like copper and aluminium lose energy to resistance when they transport electricity, about six per cent in your home, according to Business Insider. And because superconductors have this ability, they also make almost perfect magnets, and can thus be used to make powerful superconducting electromagnets.

Magnetic levitation (maglev) trains make use of this by having superconducting magnetic coils on their base, which causes them to float on a track. But while superconductors have this ability, the drawback at the moment is that they have to be cooled to extremely low temperatures, approaching -243.2°C (-405.8°F). The reason why a material needs to be cold for superconductivity to occur is poorly understood. But the Jahn-Teller metal suggests that materials can be turned into superconductors without having to chill them to extreme temperatures, and instead allow superconductivity to occur at -135°C (-211°F). If the process can be replicated in other materials, it could make superconductors much more accessible - and useful. This could allow for wider applications, possibly making electrical devices in your home and elsewhere more energy efficient. It is hoped that the Jahn-Teller metal could be this 'holy grail' of superconductors.^[9]

Conclusion:

This tutorial review discusses the structural and electronic consequences of the Jahn-Teller effect in transition metal complexes, focussing on copper (II) compounds which tend to be the most studied. The nature of a Jahn-Teller distortion in molecular complexes and extended lattices can be manipulated by application of pressure or temperature, by doping a molecule into a host lattice, or simply by molecular design. Many of these results have been achieved using compounds with a trans-[CuX_4Y_2] coordination sphere, which seems to afford copper centres that are particularly sensitive to their environment. Jahn-Teller distortions lead to some unusual phenomena in molecular magnetism, and are important to the functionality of important classes of conducting and superconducting ceramics. An international team of scientists has announced the discovery of a new state of matter in a material that appears to be an insulator, superconductor, metal and magnet all rolled into one, saying that it could lead to the

development of more effective high-temperature superconductors. Why is this so exciting? Well, if these properties are confirmed, this new state of matter will allow scientists to better understand why some materials have the potential to achieve superconductivity at a relatively high critical temperature (T_c) - "high" as in -135°C as opposed to -243.2°C . Because superconductivity allows a material to conduct electricity without resistance, which means no heat, sound, or any other form of energy release, achieving this would revolutionize how we use and produce energy, but it is only feasible if we can achieve it at so-called high temperatures. As Michael Byrne explains at Motherboard, when we talk about states of matter, it is not just solids, liquids, gases, and maybe plasmas that we have to think about. We also have to consider the more obscure states that don't occur in nature, but are rather created in the lab - Bose-Einstein condensate, degenerate matter, super solids and super fluids and quark-gluon plasma, for example. By introducing rubidium into carbon-60 molecules - more commonly known as 'buckyballs' - a team led by chemist Kosmas Prassides from Tokohu University in Japan was able to change the distance between them, which forced them into a new, crystalline structure. When put through an array of tests, this structure displayed a combination of insulating, superconducting, metallic, and magnetic phases, including a brand new one, which the researchers have named 'Jahn-Teller metals'. Named after the Jahn-Teller effect, which is used in chemistry to describe how at low pressures, the geometric arrangement of molecules and ions in an electronic state can become distorted, this new state of matter allows scientists to transform an insulator - which can't conduct electricity - into a conductor by simply applying pressure. Byrne explains at Motherboard: "This is what the rubidium atoms do: apply pressure. Usually when we think about adding pressure, we think in terms of squeezing something, forcing its molecules closer together by brute force. But it's possible to do the same thing chemically, tweaking the distances between molecules by adding or subtracting some sort of barrier between them - sneaking in some extra atoms, perhaps. What happens in a Jahn-Teller metal is that as pressure is applied and as what was previously an insulator - thanks to the electrically-distorting Jahn-Teller effect - becomes a metal, the effect persists for a while. The molecules hang on to their old shapes. So, there is an overlap of sorts, where the material still looks an awful lot like an insulator, but the electrons also manage to hop around as freely as if the material were a conductor." And it is this transition phase

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