CLOSE-PACKED FRANK—KASPER COORDINATION AND HIGH CRITICAL TEMPERATURE SUPERCONDUCTIVITY**

A. SZÁSZ[+], D. J. FABIAN and I. JÁNOSI[+]

Department of Physics and Applied Physics,
University of Strathclyde

Received June 27, 1989

Abstract

It has been proposed that a relation exists between close packed Frank—Kasper co-ordination in the layers containing Cu—O planes and high-T_c superconductivity. The origin of the superconductivity in perovskite-type materials is attributed in part to a three dimensional nesting of the Fermi-surface with the boundary of Jones-zone, causing 'partially-gapped' Fermi surface and to a gliding charge density wave arising from a three-dimensional 'breathing' of distorted perovskite structures associated with close-packed seeking symmetry.

MANY QUESTIONS on the mechanism of superconductivity in high-T_c materials are as yet unanswered. Many proposals (Khurana (1987); Proc. Int. Conf. on High T_c materials (1988)) suggest that a non-phonon explanation is needed for their understanding. Mostly, two-dimensional and one-dimensional mechanisms are popular (Mattheiss (1987); Jorgensen et al. (1987)). However some measurements (Inderhees et al. (1988); Tuominen et al. (1988)) and discussions (Chen Chang-feng et al. (1987); Inoue et al. (1987)) have pointed to the reality of a three-dimensional electronic mechanism. We propose a three-dimensional effect arising from close-packing Frank—Kasper coordination (Frank (1958)) in these and earlier (A15) enhanced-T_c materials. Our proposal extends, to 3-dimensions, the Fermi-surface Jones-zone (JZ) interaction invoked in two dimensions (with 'nesting' of Jones zone and Fermi surface) by Mattheiss (1987), Jorgensen (1987) and others (Xu et al. (1987)).

Generally a JZ effect on T_c is well substantiated for metallic materials. An enhancement of T_c arises with Fermi-surface-JZ interaction (Havinga (1986)). The Jones-zone, whose geometry in k-space is strongly related to the symmetry of the real crystalline structure, is a complex polyhedron bounded by a number of planes that is determined by the number of atoms in the elementary cell. The JZ-boundaries correspond to the first X-ray diffraction non-vanishing structure-factor. For complicated crystalline structures the JZ

[+] On leave from the Laboratory of Surface and Interface Physics, Eötvös University, Budapest, Múzeum krt. 6—8. Hungary H-1088

** Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

polyhedron is bounded by more and more planes and becomes nearer and nearer to spherical (Haussler (1983)).

Contact can occur with the Fermi surface over a large proportion of the effectively spherical JZ surface and an accumulated van Hove singularity results. The energy gap produced at the Fermi surface on interaction with the JZ polyhedron is the small and extends over a large part of the Fermi surface, which is said to be 'partially gapped'. At the E_F a hump will appear with a pseudogap, as suggested by others on the different premisses (Zhang (1988); Phillips (1987); Oppermann (1988)). On slight shift of the surface in k-space, within limits set by the JZ inscribed and circumscribed spheres (Szász (1988), the position and direction in k-space in which the gapping occurs will alter but the average 'partial' gap will remain constant and be associated always with the Fermi surface. This, in effect, produces the 'partially gapped' Fermi-surface that Little (1968), Ginzburg (1970) and Allender (1973) have suggested could contribute to high-T_c superconductivity.

We propose that it is close-packed Frank—Kasper coordination with coordination number 12, which creates a distorted icosahedral symmetry in these materials that gives rise to their high T_c by this mechanism. We have observed a relation between metastability and icosahedral-seeking symmetry (Szász (1988)) and note also a relation between the symmetry-based metastability and high-T_c (Soukoulis (1982)).

Turning to the new 'perovskite' high-T_c superconductors, we observe (Figure 1a) that their elongated octahedral basic cell has chemical surrounding with close-packed co-ordination (Figure 1b). It should be noted that in the lanthanum, all the high-T_c superconductors, barium (ReBaCuO), bismuth and thallium (Aurvillius compounds) based structures the characteristic Frank—Kasper co-ordination number is 12; i.e. characteristic of close-packing which therefore taking into consideration the displacements indicates icosahedral-seeking packing (Figure 1c) since the geometry is far from either *fcc* or *hcp*.

Note, that these 'distortions' exist in the single-crystalline materials as well; not have been used any disorder or outgoing stress for this. This behaviour is intrinsic.

The second important fact is that all the compounds can be regarded as mixed — valence metallic system. In La_2CuO_4 the substitution of La^{3+} by Sr^{2+} converts part of the Cu^{2+} ions into Cu^{3+}, in $YBa_2Cu_3O_7$ part of the Cu^{2+} is converted into Cu^{3+} or Cu^{+} by varying the deficiency parameter, or at the Bi-compounds the varying of the Bi-valency is important.

Let us consider a Cu-oxide layer spanned by the Ba-sublattice in YBaCuO. In this arrangement the Cu ions as we described before have the Frank—Kasper coordination number is close-packed, equals 12. Some of the Cu^{2+} ions may have extra holes, so the oxygen coordination of Cu^{3+} will be deformed with respect to that of Cu^{2+}. The ionic radius of Cu^{3+} will be

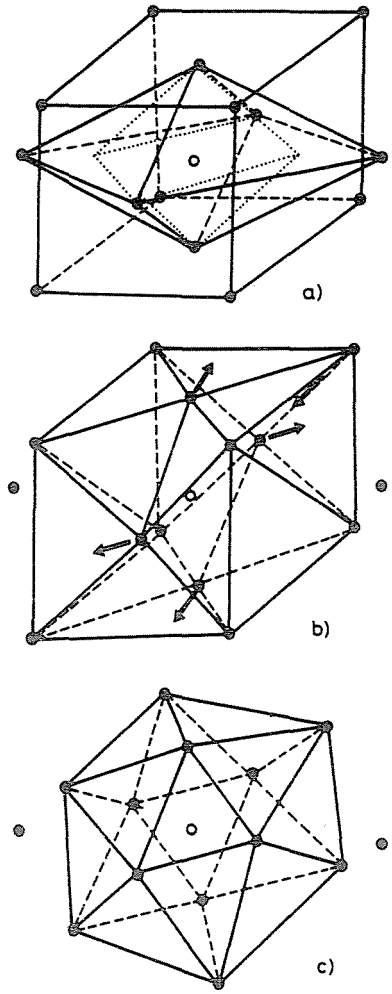

Fig. 1. a) An orthorombic cell of the high T_c superconductors perovskite structure showing basic cube and elongated octahedron. At the centre of these octahedron is the copper atom (not shown); b) Same structural arrangement as (a) but highlighting the icosahedral five-fold co-ordination (chemical bonding) for atoms in the basic cell; c) The icosahedral co--ordination 'cell' formed by displacements indicated in (b)

smaller, implying that the oxygen octahedron should contract isotropically. The extra hole of the Cu^{3+} ion may have a high mobility trough the lattice, when there is sufficient overlap of the Cu^{2+} wave functions with the oxygen wave functions. The tunneling probability may be enhanced by vibronic effects as well, e.g. by the "breathing-mode" deformations of the oxygen octahedron or by the soft optical phonon assisted charge carrier hopping, which are common feature of the compounds considered. The result of these local

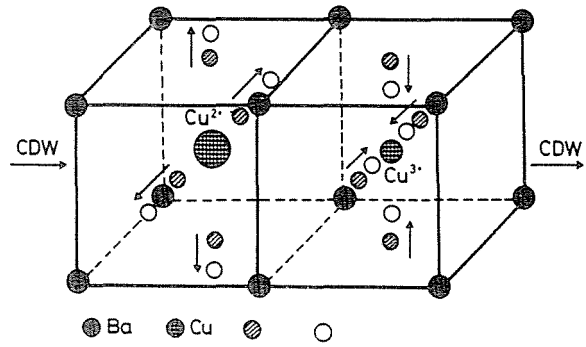

Fig. 2. The changes of the oxygen-environment around the Cu-ions having different valency

deformations would be a long range layer distortion, where the environment of the Cu^{2+} ions may have distorted icosahedral coordination symmetry (Soukoulis (1982)), (Figure 2).

Based on these facts a 3-dimensional charge density wave (CDW) would be produced; not a 2-dimensional CDW as proposed by Mattheiss, followed by others (Stavola (1987)), for the lanthanum-based LaMCuO-type system. The Mattheiss calculation for pure La_2CuO_4 involves a two-dimensional Peierls distortion (or frozen in CDW), with either a planar or a 2-dimensional quadripolar 'breathing' of the oxygen atoms, which would allow a *semiconductor* gap to open at E_F and would, as described by Stavola et al. (1987), destroy the potential superconductivity. The presence of the divalent metal atom (Ba or Sr) prevents the CDW from being 'frozen in'; it essentially stabilizes the metallic phase (by lowering E_F) and, in the Mattheiss model, allows oxygen-atom 'breathing' in two dimensions (a 'warping' of the CuO crystal planes) without spoiling the superconductivity. Evidence for Peierls distortion was found in vibrational spectra by Stavola et al., who proposed that doping with the divalent metal 'tunes' the planar-oxygen 'greathing' distortion. Weber however, discounts the two-dimensional warping of the CuO plane as the sole explanation of the Peierls distortion, which again supports our suggestion that a 3-dimensional icosahedral 'warping' or 'breathing' could be occuring. Other investigations (Jacak (1988); Bruder (1988)) are also support these ideas. It is further important to note that a Peierls distortion, hitherto accepted only in 1- and 2-dimensional models, has recently been observed experimentally in π-bonding in liquid arsenic (Matsuura (1987)). Here it must be a 3-dimensional effect, since this is an amorphous state, supporting our contention that 3-dimensional 'breathing' distortions can occur in the solid, located into the layer, containing the Cu—O planes. The displacements would bring about a close-packed tetrahedral arrangement, producing (microscopic) icosahedral-seeking co-ordination regions with tetrahedral Frank—Kasper packing, which is observed having important role in the stabilization of the metastable sys-

tems (Szász 1988)). Based on these, a 'non-frozen-in' or gliding CDW in *three dimensions* could be caused by a 'breathing' of microscopic closepacked cluster regions. In the crystal periodically occurring distorted icosahedral-like 'neighbourhood' regions would allow for the complete filling of real space needed. We illustrate schematically the way in which this short-range icosahedral 'breathing' could occur in Figure 3. The oxygen atoms, as in the Mattheiss model, would be primarily involved in the breathing; their displacement (for rotation of CuO octahedra, as appropriate to a distorted icosahedral cluster packing) has been observed in crystal structure determinations of KaMCuO-type superconductors by Onoda et al. (1987). The solid-line regions are 'momentarily' icosahedrally close-packed (cf. Figure 1c), with the not so dense, non-icosahedral regions linking them in 3-dimensions (for example through corner atoms as here) to the next neighbouring close-packed region. This example illustrate a 'commensurate' breathing in the layers containing the Cu—O planes. Complex 'non-commensurate' forms of breathing are also possible in which the closepacked regions, highlighted in Figure 3, in fact overlap. This is in good agreement with the models based on the highly anharmonic oxygen vibrations in superconductive oxides (Bogoljubov (1988)), and well corresponds with the role of the shear distortions (Bhattacharya (1988)). We note, that the CDW is located to the thick layers containing the Cu—O planes, and they are not extended into the whole elementary cell. The meaning of three-dimensionality covers the changes in the 3D-neighbourhoud in these layers. Figure 3 (as an example) is showing the case of an Aurvillius-phase containing double Cu—O planes in one cell.

On the other hand, the icosahedral close-packing causes special effects at the Fermi-energy (E_F) (Szász (1988)). Due to the spherical-like JZ the

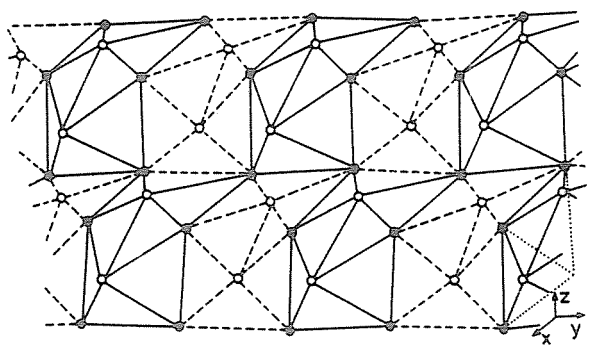

Fig. 3. A schematic of the proposed 3-dimensional icosahedral (solid lines) to non-icosahedral (dotted) breathing displacements of oxygen atoms in perovskite-type materials (o-oxygen; o-Ba(La)Y). Note the two-dimensional planar warping, proposed previously by Mattheiss and others (Proc. Int. Conf. on High T_c (1988); Mattheiss (1987); Jorgensen (1987); Inderhees (1988); Tuominen (1988); Chang-feng (1987); Inoue (1987)), can be observed

van-Hove singularity is enhanced and a pseudogap appears at E_F. Relative enhancement of $N(E)$ at the vicinity of E_F has been observed experimentally in studies of high-T_c materials by UPS (Takahashi (1987)) and XPS (Mingrong (1987); Ihara (1987); Rietschel (1987)), as well as in measurements of their specific heat (Kitazawa (1987)) and thermo electric power (Cooper (1987)). The pseudogap also has been proofed (Zhang (1988); Phillips (1987); Oppermann (1988)), which is the analog of the Nagel—Tauc theory (Nagel (1975)) for metallic glasses. Indeed the glassy-behaviour also have been measured (Legreid (1988)), and simulated by computer as well.

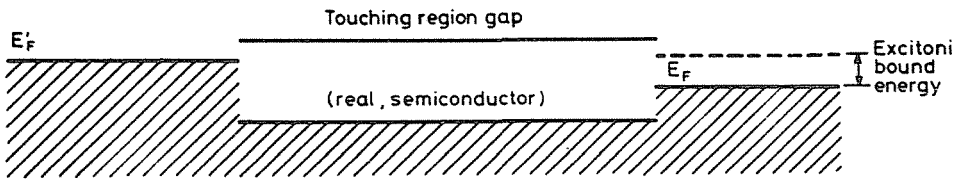

Fig. 4. The schematic diagram of the touching-region caused by the Fermi-surface—Jones-zone interaction. In the touching positions a real semiconductor gap are created, while in their neighbourhoud the Fermi-surface is free in localised disjunct areas

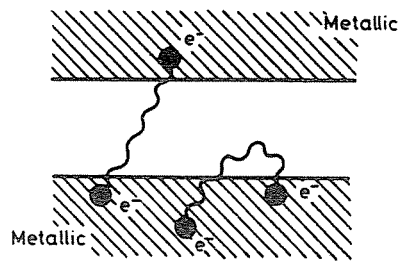

Fig. 5. The pairing mechanisms mediated by the excitonic-like polarization: a) on the same side of the gap; b) on the different side of the gap

Due to the partially-gapped Fermi-surface (causing the pseudogap as well), between the touching (so gapped) areas well distinguisable, disjunct non-gapped areas are exist on the Fermi-surface (Figure 4). At an excitation of the electron-sea in one direction of the k-space, a slightly different (but limited by the gap size) E_F could be created due to the barrier caused by the semiconductor gap-region. This is as a polarization effect (or as an exciton, involving the electron in the region of the higher E_F region, and a hole-state from the lower one) could be the reason of the pairing effect for the superconductivity. This polarization is effective by the tunneling of the electron into the gap-region, and could be create a pair either on the same region of the "free"-Fermi surface or on the neighbourhoud (See Figure 5). The observed hole-like transport (Gezel (1987)) is also supports these ideas.

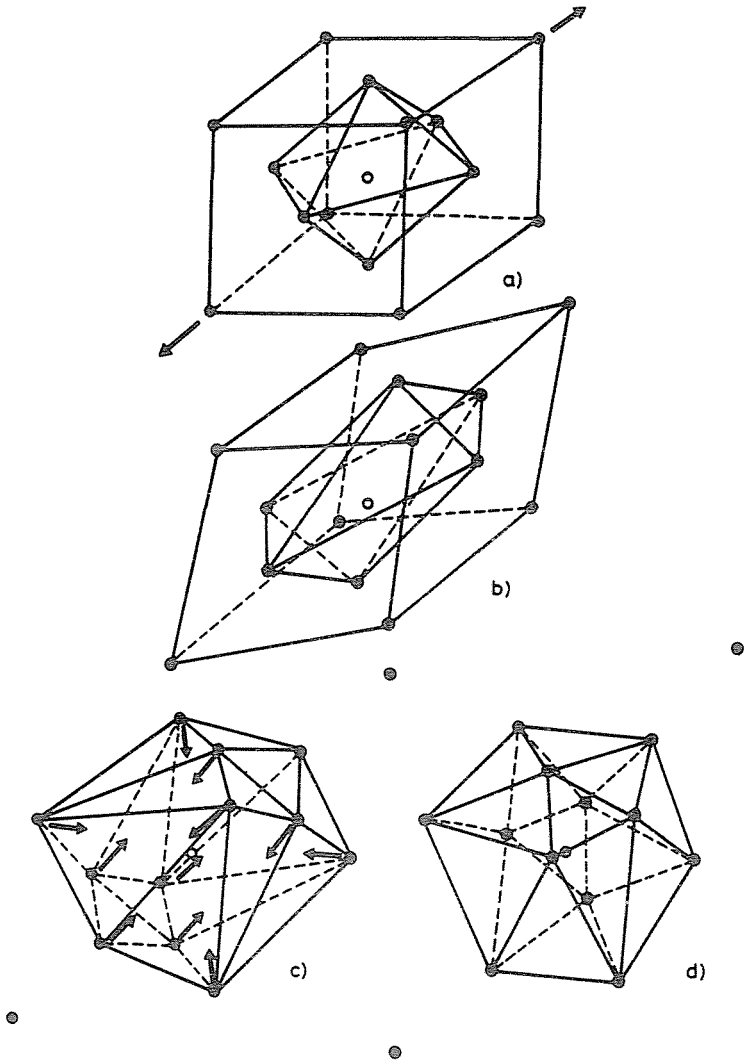

Fig. 6. The changes of the Frank-Kasper coordination polyhedra in a mechanically distorted perovskite structure: a) Non-distorted perovskite; b) Diagonally elongated perovskite by external mechanical stresses; c) The Frank-Kasper coordination polyhedra in the distorted case very close to a distorted icosahedron

Supporting evidence for the partial-gapping is found in far infra-red measurements of the superconductor energy gap, showing it to be highly anisotropic (Maekawa (1987); Frank (1958)) and to vary with direction in k-space; while its temperature dependence — characterizing the Peierls instability — remains BCS in 'functional form' (Gezel (1987); Sulewski (1987)). Additional support includes in that the isotrope effect is anomalously small.

The 3D-behaviour is controlled by the specific-heat measurements (Inderhees et al. (1988)), and trivially shown in the copper-free new perovskite superconductors (Cava et al. (1988); Rice (1988)).

Lastly, we note that the new high-T_c materials generally have highly distorted extended grain-boundary structures which are amorphous in many cases (Hendry et al. (1981)). In these the disorder is localized to the grain boundary, where we believe that icosahedral short range co-ordination even more readily occurs. Observations of twinning in the new high-T_c perovskite-type superconductors (Eaglesham (1987); Vieira (1988)) are indicative of *intra*granular distortion of the basic 'perovskite' cube giving a structure that will inevitably be closer to icosahedral. One of the highly distorted perovskite structure and its icosahedral-like Frank—Kasper coordination is shown as an example in Figure 6.

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A. SZÁSZ Eötvös University H-1088, Budapest
D. J. FABIAN, I. JÁNOSI } Univ. of Strathclyde, Glasgow