Coherent twin boundaries in high-T_c superconducting oxides

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When subjected to a low-temperature annealing cycle similar to that of Bhargava *et al.*, 1:2:3 superconducting oxides are shown to form fine, 250-Å spaced twins. The symmetry of the crystal is markedly altered. A theoretical calculation shows that twins introduce minigaps into the electronic structure. The implications for high-T_c superconductivity are discussed.

The recent discovery of superconductivity at 40 Kelvin,[1,2] and then at 90 K,[3] in layered copper oxide perovskites has continued to interest a wide spectrum of researchers and laboratories. Coherent twin boundaries form[4] in the 90-K material below the tetragonal-to-orthorhombic transition[5] at 1023 K. The orthorhombic phase has symmetry *Pmmm* and composition $R_1Ba_2Cu_3O_{7-\delta}$ (hereafter called 1:2:3), where R is Y or a rare-earth element. In this paper we focus on two aspects: (1) that by systematically cycling 1:2:3 between 85 K and up to 230 K, we find experimentally that coherent twin boundaries spaced as narrow as 250 Å are nucleated; (2) that their presence modifies both the crystalline symmetry and the ancillary electronic structure. The theoretical microscopic dielectric response of 1:2:3 material with the boundaries has changed qualitatively, suggesting a form of plasmonic coupling of electrons. Our study indicates that twin boundaries may be an important element in the superconductivity of 1:2:3 materials.

Fine coherent twin boundaries seem to be ubiquitous in 1:2:3 materials.[4] We know of no published report where such structures have not been seen with, for example, a transmission electron microscope (TEM) in material which was nominally superconducting at 90 K. We have studied 1-μ-diameter powder samples of R=Y, Gd, or Eu. All samples studied were newly prepared, being small portions from larger batches which were used for other measurements and exhibited substantial fractions ($>40\%$) Meissner behavior at 7 K. The powders were ground from discs which had themselves been repeatedly ground, pressed, and sintered.

A series of TEM experiments at various temperatures and electron beam energies and currents were carried out to determine their effects on the 1:2:3 samples. A wide variety of behaviors was found. Some of these were recorded on video tape using a GATAN TV camera attached to the microscope. Variations in twin structures were seen on several time scales, ranging from 0.1 s to several hours as either beam conditions or sample temperatures was changed. In this paper we address phenomena seen at low temperatures using broadly dispersed beams of low (<20 μA) currents on typical powder 1:2:3 specimens, using tungsten filaments and an accelerating voltage of 120 kV in a Philips 400T microscope.

In Fig. 1 we show two sequential TEM micrographs of a portion of a typical 1:2:3 grain. We select here a sample with (dark) inclusions of Cu-O, and with internal microcracking. When viewed in the TEM at nitrogen temperature, excellent superconducting samples, which showed in other experiments at least 90% shielding effect at 7 K, always exhibited twin boundaries in every grain. Twins are omnipresent in excellent 1:2:3 material. Poor samples with significantly lower shielding effect contained many 1:2:3 grains without twins.

Thermal cyclings of excellent 1:2:3 materials were undertaken after the appearance of the work of Bhargava *et al.*[6] When cooled once from room temperature to liquid-nitrogen temperature, and held there for several hours, a variety of twin spacings in different specimens were seen, with a medium boundary to boundary spacing of about 1100–1200 Å. Figure 1(a) shows a specimen cooled once from room temperature with 800–900-Å twins. When cycled slowly from 85 to 230 K (30 min each warming and cooling), samples develop finer twin structures during the warming part of the third and fourth full cycle. There were no additional structural refinements upon further cyclings. The refined boundaries of the same specimen are shown in Fig. 1(b). The finer structure is developed through the one-sided introduction of pairs of additional twins from the surface of a grain and not from the motion of existing twin boundaries within a grain. Warming to room temperature destroys fine twins; they are fully recovered upon recycling. We had observed twins and twin refinement many times over the last six months. Based on our results and on the recent increase in superconducting temperatures observed by Bhargava *et al.* using a similar thermal cycling treatment, we conclude that coherent twin boundaries are an important feature in the unusual high-T_c superconductivity of 1:2:3 materials.

Published[7] electronic structure calculations of 1:2:3 show a complicated set of narrow bands below the Fermi level, but a few simple sets of bands about 2.5 eV wide in the vicinity of E_f. The bands near E_f arise from covalent antibonded cooper e_g d orbitals and O p orbitals. Two sheets of the Fermi surface are derived from the orbitals of two-dimensional planes, and one sheet arises from the (one-dimensional) chain containing plane. The rest of the planes containing either R or Ba derived orbitals do not have any significant fraction of their structure in the bands near E_f. These results were derived for the *Pmmm* orthorhombic phase.[5] What is the effect of the

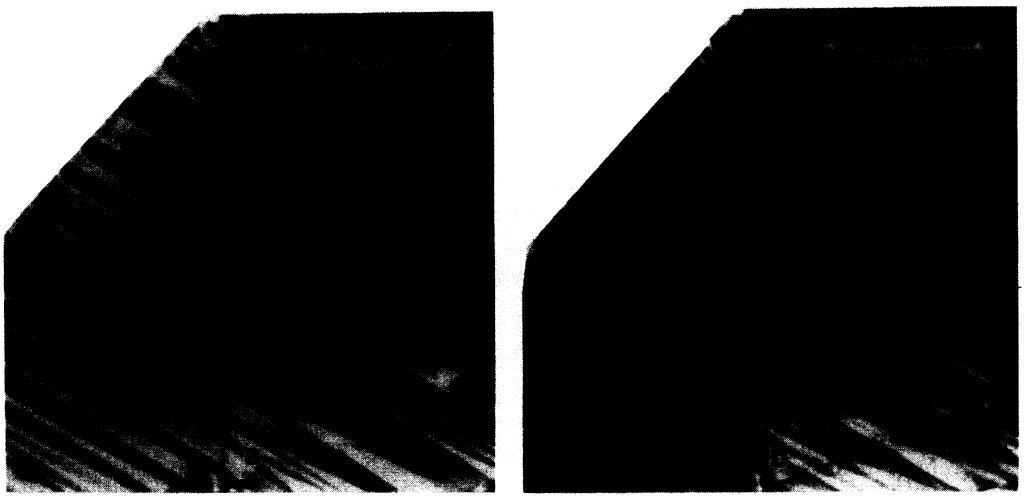

FIG. 1. TEM micrographs of a portion of a grain of 1:2:3 superconducting oxide. The different contrast bands are from regions of the material in which the a and b axes are mirror interchanged forming twins. (a) Twins formed by cooling once from room temperature; (b) refined twins formed by thermal cycling.

introduction of the 250-Å spaced twins? By examining our own results and the TEM micrographs of other groups,[4] we view twinned 1:2:3 materials as similar to superlattice materials produced by artificial layering.[8] The superlattices of 1:2:3 materials are formed naturally by the twins. Atoms in most layers or planes of 1:2:3 material are hardly affected by the existence of the twins. We focus here on the plane containing the chain atoms. The tetragonal to orthorhombic transition leads to a difference between the a and b axis lengths which is important for developing twins.[4] By examining a series of total energies using pair potential models, we have concluded that the microstructure of a single (110) boundary plane must pass through copper atoms. A model boundary is shown in Fig. 2, containing three chain units per twin. Cycled material contains about ~ 100 chain units and some boundary relaxations.

Coherent twin boundaries affect the symmetry of crystals.[9] Looking at the model boundary of the plane of Cu-O chains depicted in Fig. 2, we see that the σ_z mirror operation of the a-b plane has been preserved, that the orthorhombic-based mirror perpendicular to a and b has been destroyed, but that a new mirror parallel to the twin boundaries has been introduced. These new boundary and antiboundary mirrors are shown in Fig. 2 as cyan and magenta rods. More subtle is that a new space-group operation has been introduced by the twins: A glide operation of a twofold rotation parallel to c about Cu followed by a half-lattice translations. (Clearly these operations hold for all the layers of twinned 1:2:3, not just those depicted in Fig. 2.) This is shown as the white vertical twofold axis and the white half-lattice translational arrow. Coherent twin boundaries have destroyed inversion symmetry, introduced boundary mirror and glide symmetry operations, and formed polarized boundaries. (Breaking of inversion of oxide perovskites like $BaTiO_3$ is a prerequisite for forming a ferroelectrically active material.) The important effect of the breaking of inversion by the introduction of coherent twin boundaries hold for twins of every separation thickness or number of chain units.

In order to test the effect of the coherent twin boundaries on the electronic structure, we have employed a tight-binding model in which we have included the dominant first-neighbor interactions between both x^2-y^2 and $2x^2-x^2-y^2$ e_g orbitals on the copper sites and an x or y p orbital on those oxygen sites which point toward their nearest copper atom in the plane of the chains. We fit a Slater-Koster–like scheme to the results[7] of Yu *et al.* to obtain the transfer integral parameters. Further neighbor interactions were derived, but changed results only slightly. We focus in this work on the interactions occurring within the plane of the chains and those in the intermediate vicinity of the Fermi level. In the upper part of Fig. 3 we show the electronic energy band structure for twins with 1, 2, and 3 chain units. The panel labeled 3-1 corresponds to the structure depicted in Fig. 2. Because of the glide symmetry, the two dimensional zig-zag chain of Fig. 2 maps onto the one-dimensional gapped structure seen in Fig. 3. The presence of the glide operation is signaled by the band degeneracy at the X zone edge. Most linear chain electronic structures show a gap at X. The coloring in Fig. 3 is based on the fractional parentage of the bands. The middle green flat bands are pure Cu d based orbitals. The yellow-white bands are of mixed 50% Cu d orbitals and 50% O p orbitals. The gap regions in the upper panel have been colored gray and the band regions have been colored yellow for clarity. There are no pure oxygen bands. The constancy of the color of the yellow bands shows that the mixing is independent of k. This holds for all cases considered.

The sizes of the real space unit cells vary as the separation of the twins. Brillouin zones vary in Fig. 3 inversely with unit cell size. By intercomparing the upper cases shown in Fig. 3, we see that new gaps are developed as boundaries with more chain units are considered. The process is similar to, but more subtle than just repeated zone foldings because of the presence of the glides. Note

FIG. 2. The modification of the *a-b* chain plane of 1:2:3 oxides developed by the presence of coherent twins. Pictured is a twin with three chain units. The blue box marks a unit cell. The twin boundaries are indicated by the cyan and magenta rods. The important glide symmetry operation is pictured as the white twofold rotation followed by the white half-lattice translational arrow in the *a-b* plane. As discussed in the text, the twins break inversion symmetry making the boundaries polarizable.

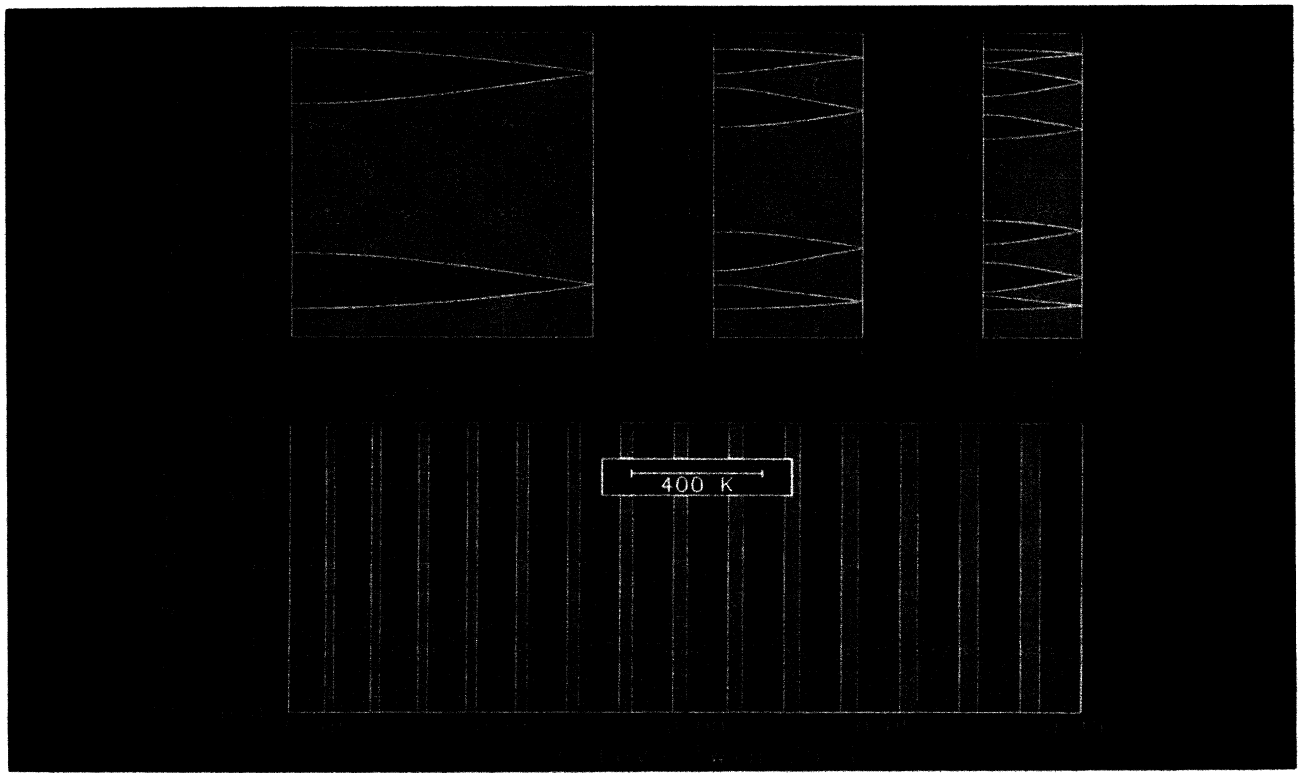

FIG. 3. The electronic structure of twinned 1:2:3 superconducting oxides. The bands shown in the upper part are for twins containing 1, 2, and 3 chain units respectively. Case 3 is the twin structure shown in Fig. 2. The density of states, shown in the lower part, is for the case of a twin with 75 chain units. As discussed in the text, twins in 1:2:3 oxides promote the development of mini-energy-gaps, break inversion symmetry in the boundaries, and enhance plasmonic superconductive mechanisms.

also that all gaps occur at Γ. Such gaps cannot be understood on the basis of Peirels-like distortions. Adding further-neighbor interactions slightly changes the shape and hybridization behavior of the bands forming three-dimensional rather than one-dimensional structures. But the physics we have considered here will be preserved. Gaps develop because of the breaking of the linear chains by the twins as depicted in Fig. 2. They arise as and accommodation of the electronic structure to the presence of the complex structure factors in the twin boundaries and the nature of the Cu d to O $P\ \pi$ bonding in those boundaries.

Impossible to show as bands in Fig. 3 is the electronic structure of a realistic case involving 75 chain units. We have calculated this case explicitly, solving a large (rank $6\times75=450$) complex secular matrix repeatedly. Most of our matrix is in tridiagonal form, similar to the case of disordered one-dimensional phonons considered[10] by Schmidt. Our case differs from his in that every off-diagonal matrix element is k dependent due to the varying phase of structure factors. The electronic structure for the 75 chain case is similar to the cases shown in the upper panel of Fig. 3, but with many more bands and gaps. The main features of the 75 case may be gleaned from the density of states near the Fermi level shown in Fig. 3. (The Fermi level is at zero energy, dictated by our fit[7] to Yu *et al.*). Gaps are shown as gray and bands as yellow, matching the upper panel. Relative gap spacings change systematically as a function of energy, as do the values of the density of states minima. The maxima at the gaps diverge, but are parts of integrable singularities. The material of the density of states depicted in Fig. 3 is a semimetal or semiconductor in the plane of the chains. Twin boundaries have introduced an altered energy scale from 2 eV to of order 200 K into the electronic structure of 1:2:3 material that contains 75 chain units. Some consequences of the existence of minigaps have been considered[11] by Wohlleben.

We apply the Penn dielectric function[12] formula

$$\epsilon=1+(\omega_p/\text{gap})^2\ , \tag{1}$$

and expect that plasmons will be screened as

$$\omega_p^2=4\pi ne^2/\epsilon m^*\ . \tag{2}$$

These screening processes interact or affect each other. Using the gaps near E_f in Fig. 3 and an unscreened plasma energy of 2 eV, we find[13] an ϵ of about 3600 and a screened plasma energy of about 0.1 eV or 1200 K. It is an easy argument that a density of states structure filled with minigaps as in Fig. 3 leads to an oscillatory dielectric frequency response containing positive and negative regions. Electrons can be condensed into superconducting pairs in such regions as described[14] by Ginzburg and Kirzhnits. If we examine the recent[15] plasmon ideas of Ruvalds and use his relation of coupling strength to plasmon energy, we find a predicted T_c of about 240 K for the electronic structure of Fig. 3. This value is higher than any of the reported stable and reproducible enhanced T_c values found[6] by Bhargava *et al.* We conclude that it is likely that the broken inversion symmetry, electronic minigaps, and screened plasmons induced by refined twins play an important role in the unusual superconductivity of 1:2:3 materials.[16]

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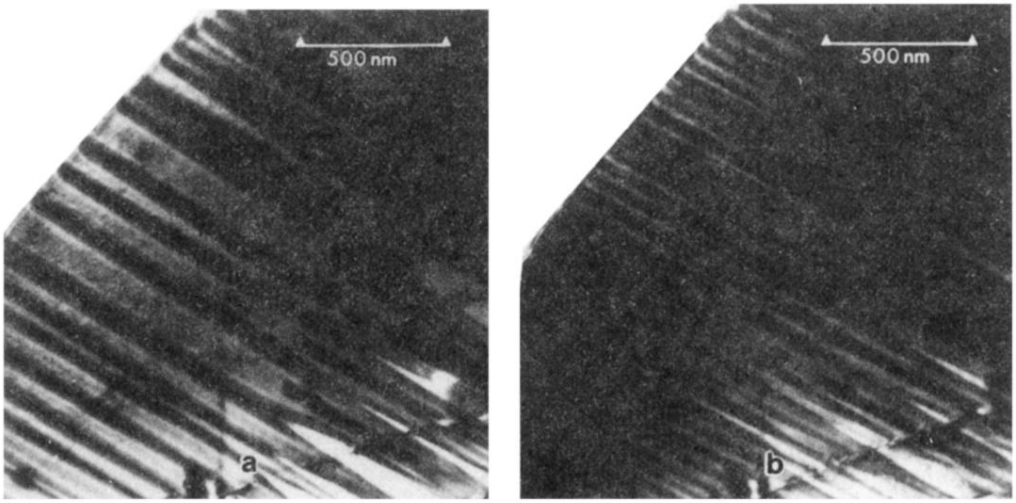

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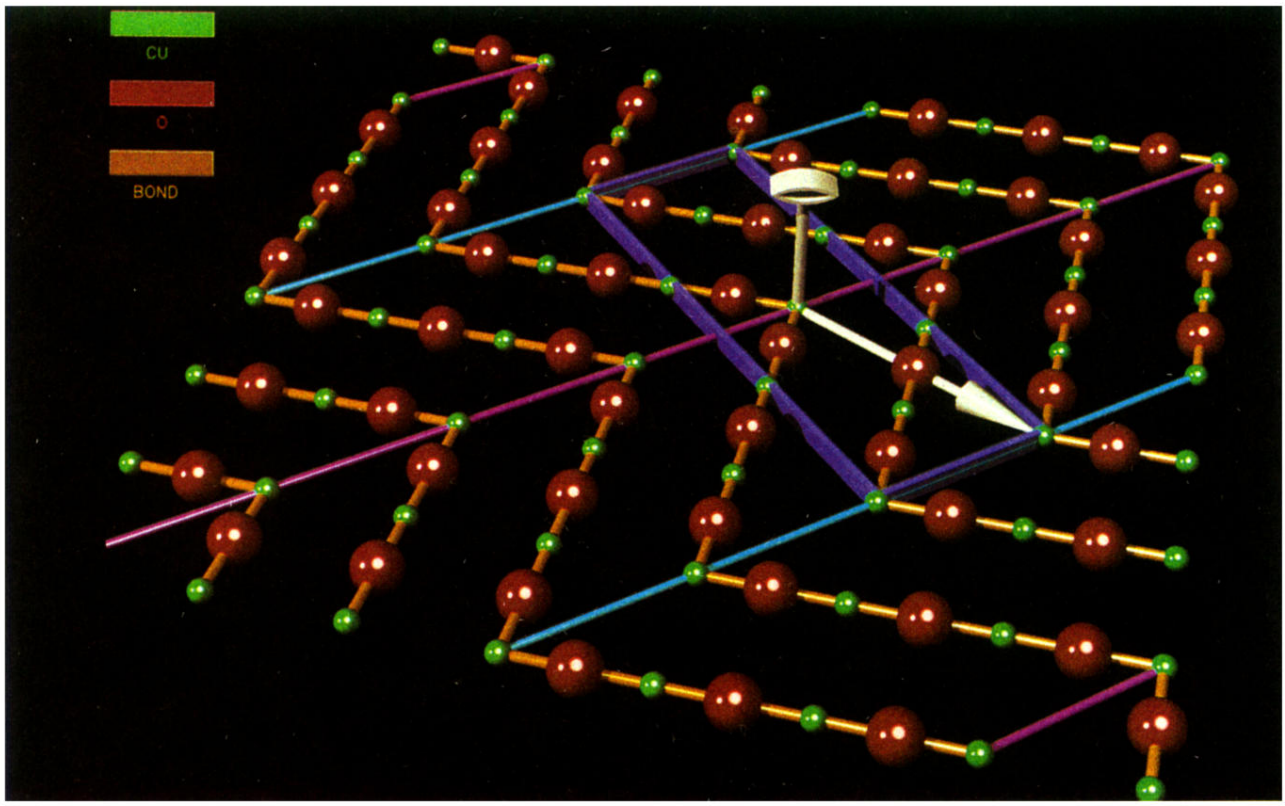

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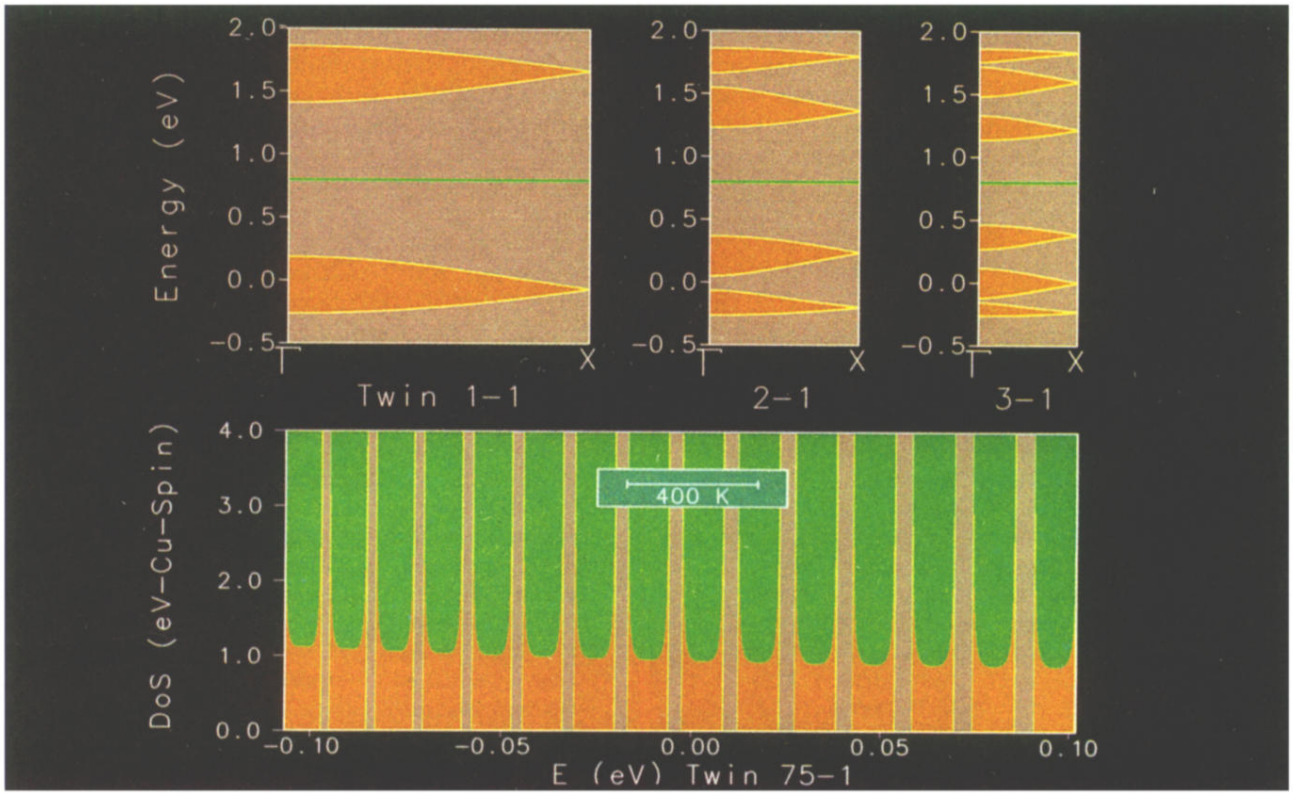

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