Daedalus

Superficial relaxation

The thing engineers have nightmares about is brittle fracture. A component carries its maximum tension at its surface, which is covered in stress concentrations of all kinds. A fatal crack may start from the surface long before the bulk of the material is seriously stressed. 'Toughened' glass has its surface put into compression by thermal or chemical treatment. With luck, even severe deformation will not stretch it enough to load the surface in tension and start a crack. Daedalus now has a scheme to relax extremely high surface stresses in engineering materials such as metals.

His plan is to put the material under its design loading, and then heat the surface only. It will anneal and relax, fully shedding all dangerous tensions. The process should work not only on single components, but on whole assemblies: bridges, turbines, aircraft, and so on. There is no need even to know their distributions of stress. But how to heat their surfaces so briefly that the bulk stays cool? Nanosecond laser pulsing should work for small objects. But for big ones, Daedalus proposes surface explosion. Thus iron and picric acid react on contact to give the sensitive detonator iron picrate — which often caused trouble in the days when picric acid explosives were put in iron shells. Many other metals form sensitive explosive compounds — lead azide, copper acetylide, and so on. DREADCO's chemists are now devising intimate explosive coatings for all the engineering metals.

The turbine, plane, or whatever will have its tensile surfaces painted with the explosive reagent mix, and will then be spun or stressed up to the greatest load it can endure. The explosive then will be fired. The superficial blast will race over the tensed surfaces, annealing them in its fierce but momentary passage. The bulk material will receive a compressive shock (which, acting in opposition to the applied tensile loading, will do no harm), but no significant heating. The assembly can then be relaxed. The resulting discoloured or burnt surface must not be smartened up by polishing; that might remove or damage the crucial annealed layer, now in strong compression. Instead, it must be sealed in by paint or plating. Thereafter, the assembly will bear unprecedented loads.

Components such as girders and wire rope, and assemblies such as cars, aircraft and rockets, all will benefit from explosive de-stressing. Even existing installations might, with one mighty bang, be toughened up for heavier duties.

David Jones

pared with the relaxation period of the local lattice deformation that 'dresses' the carrier. These small polarons move diffusively — that is, thermal energy is needed for them to hop from one site to the next.

De Teresa et al. suggest that the increase in thermal expansion in their sample in the range $T_c < T < 1.8T_c$ indicates that the ferromagnetic clusters are dressed by cooperative lattice deformations, which would make them 'small' magnetic polarons consisting of several cation centres. The growth in size and decrease in the number of ferromagnetic domains on application of a magnetic field above T_c implies that the field stabilizes greater ferromagnetic order, so these polarons may condense into larger ferromagnetic domains containing many delocalized charge carriers. Within a ferromagnetic domain, the conductivity is presumably metallic, so the resistance decreases as the fraction of the metallic volume increases.

Aside from their technological potential, the manganese oxides are important because, like the copper-oxide superconductors, they appear to exemplify a dynamic phase segregation occurring at a transition from localized to itinerant electronic behaviour. Where there is a discontinuous increase in the mean kinetic energy of the electrons, there must be a corresponding decrease in their mean potential energy according to the virial theorem of classical mechanics. A jump in potential energy would be reflected in a discontinuous change in the equilibrium metal–oxygen bond length and hence in the volume at the transition, making this a first-order transition.

First-order transitions may give rise to either a global, homogeneous change of volume or a phase segregation. Phase segregation is normally accomplished by atomic diffusion, which can only occur at higher temperatures. But at a transition from localized to itinerant electronic behaviour, phase segregation may be accomplished at low temperatures by cooperative atomic displacements that create domains of shorter bond lengths containing delocalized electrons, separated by regions where the atoms contain localized electrons. Such cooperative atomic displacements may either be static or remain dynamic down to the lowest temperatures.

In the $La_{1-x}A_xMnO_3$ perovskites, the transition from localized to itinerant (delocalized) behaviour of the conduction electrons occurs in the presence of localized electron configurations having a total localized spin $S = 3/2$, so the phase containing mobile charge carriers is ferromagnetic, whereas the phase with no delocalized charge carriers remains paramagnetic in the range $T_c \lesssim T \lesssim 1.8T_c$ in $La_{0.67}Ca_{0.33}MnO_3$. Where a dynamic phase segregation occurs, as appears to happen in this case, application of a magnetic field above T_c stabilizes the ferromagnetic relative to the paramagnetic phase, which increases the volume fraction of the

more conductive ferromagnetic phase to give a colossal magnetoresistance.

Oxides with perovskite-related structures can accomplish a dynamic phase segregation by moving their oxygen atoms without having to make a large perturbation of the cation positions. If these displacements are dynamic or spatially aperiodic, the heterogeneity introduced by the phase segregation cannot be detected by a diffraction experiment, and so some other technique is required to reveal it. Small-angle neutron scattering can detect a magnetic heterogeneity involving larger ferromagnetic clusters in a paramagnetic background, but not clusters involving only two or three manganese atoms.

The magnetic susceptibility data of De Teresa et al. indicate the presence, at temperatures $>1.8T_c$, of superparamagnetic clusters consisting of ferromagnetically coupled $Mn(III) + Mn(IV)$ pairs. These Zener[3] pairs become segregated below $1.8T_c$ into larger ferromagnetic regions within a paramagnetic matrix. Zener pairs are charge carriers, and their segregation into isolated ferromagnetic regions traps them, but they are released by cooling below T_c or by a magnetic field that makes the ferromagnetic regions grow until they overlap. De Teresa et al. assume that the conduction electrons become itinerant below T_c because they observe long-range magnetic order and a low resistivity. However, the localized-electron phase would also become ferromagnetic below the long-range ordering temperature T_c, so the disappearance of magnetic heterogeneity does not guarantee the disappearance of small mobile clusters. The resistivity below T_c remains high relative to that expected for a conventional metal, and Louca et al.[2] have identified three-atom dynamic clusters at 12 K, well below T_c, which is out of the detection range of SANS. It appears that De Teresa et al. may have identified a trapping out of Zener-pair charge carriers in larger ferromagnetic clusters in the range $T_c < T < 1.8T_c$.

It is now becoming more generally recognized that the copper-oxide superconductors may owe their peculiar transport properties to a similar dynamic phase segregation. Non-adiabatic polarons containing just five or six copper centres[4] in underdoped oxides condense into large 'stripe' domains[5,6] in the more heavily doped, superconducting compositions. The realization that such a dynamic phase segregation can occur in real systems is opening a new chapter in solid-state science, and is providing surprises that may yet prove to have great technical importance. □

John B. Goodenough and J.-S. Zhou are in the Center for Materials Science and Engineering, University of Texas at Austin, Austin, Texas 78712, USA.

1. De Teresa, J. M. et al. Nature **386**, 256–259 (1997).
2. Louca, D., Egami, T., Brosha, E. L., Röder, H. & Bishop, A. R. (personal communication).
3. Zener, C. Phys. Rev. **82**, 403–405 (1951).
4. Goodenough, J. B. et al. J. Mater. Chem. **1**, 715–724 (1991).
5. Bianconi, A. et al. Phys. Rev. Lett. **76**, 3412–3415 (1996).
6. Tranquada, J.-M. et al. Nature **375**, 561–563 (1995); Phys. Rev. **54**, 7489–7499 (1996).