

have sampled the lava terrain to determine the scale of along- and cross-axis variations in magma composition. The goal is to decipher the magmatic plumbing that feeds the ridge segments and the heterogeneity of the parent material.

The new sonar images hold out the prospect of deducing some key aspects of the spreading cells' magmatic plumbing directly from the cross-sectional shape of the ridge-crest topographic bulge. They hint that where the axial magma chamber is best developed, the high is broad and there is a summit graben. A shrinking of

the chamber along the axis away from the injection centre and towards the discontinuities seems to be mimicked by a tapering of the high into a more peaked ridge and the transformation of the graben into a swarm of fissures. Because the differences in morphology also appear off-axis on older crust, it is likely that sonar imagery will become useful for the study of changes in the magmatic budget and source locations back through time. □

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Oxide superconductors

Clues from copper-free samples

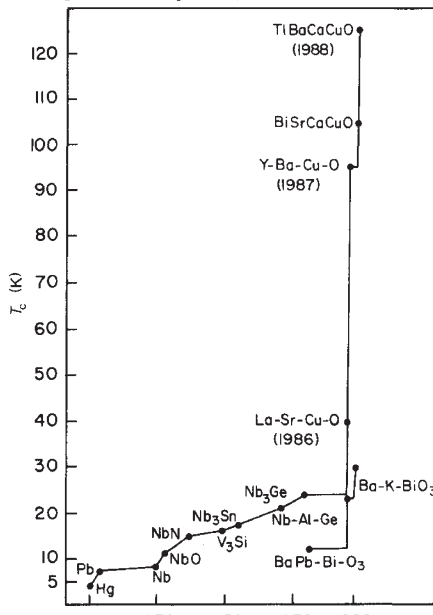
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ALTHOUGH the superconducting transition temperature (T_c) of the compound $Ba_{1-x}K_xBiO_3$ reported by Cava *et al.* on page 814 of this issue¹ is, at 30 K, much less than others reported over the past year (see figure), it is substantially higher than the highest value (23 K) obtained previously in conventional intermetallic compounds. The new system is closely related to one of the earliest superconducting oxides, $BaPb_{1-x}Bi_xO_3$ discovered by Sleight *et al.*² in 1975, for which the maximum T_c of 13 K occurs at $x \approx 0.75$. The discovery of this new family of copper-free oxide superconductors will help elucidate the characteristics necessary to achieve high transition temperatures.

After Bednorz and Müller's breakthrough³ in high-temperature superconductivity with the $La_{2-x}Ba_xCuO_4$ system in 1986, several groups attempted to make the analogous doping for the $BaBiO_3$ system. Instead of introducing carriers in the parent insulating compound by substituting on the active site (bismuth or copper) as was done with $BaPb_{1-x}Bi_xO_3$, they are introduced on the other site as in Bednorz and Müller's technique, thus keeping the bismuth (or copper) network intact.

The chemistry of substitution, however, is more difficult for the $BaBiO_3$ system. The first report of success came from Mattheiss *et al.*⁴ at AT&T Bell Laboratories who achieved a $T_c \approx 22$ K in a multiphase sample of $Ba_{1-x}K_xBiO_3$ but with a superconducting fraction of only 4 per cent. Cava, Batlogg and co-workers¹, also at AT&T, using a sealed-tube technique to contain the volatile potassium oxides, obtain single-phase material with $x \approx 0.4$ and a higher T_c (about 30 K). The superconducting fraction, measured as the volume from which magnetic flux is expelled (the Meissner effect), is greatly improved at 30 per cent. This new work establishes the bismuth oxides as the clear runner-up to the copper oxides in the high- T_c race.

It is naturally very interesting to compare and contrast the two oxides. There are several similarities. First, both are based on perovskite-type oxide structures. Second, both parent compounds are effectively single-valence insulators: for example, in La_2CuO_4 , each Cu^{2+} is one



Progress in superconducting transition temperatures (T_c) since Kamerlingh Onnes' initial discovery of superconductivity in 1910.

electron short of a 'filled' d^{10} -shell, giving one 'hole' per copper, and each Bi^{3+} in $BaBiO_3$ has an electron outside a filled shell. Third, superconductivity in both is achieved by introducing a few charge carriers by substituting ions, Sr^{2+} or Ba^{2+} for La^{3+} and K^+ or Rb^+ for Ba^{2+} , and superconductivity occurs in samples with stoichiometry close to the transition from insulating to metallic behaviour.

There are, however, noteworthy differences. The bismuth oxides are truly three-dimensional compounds in contrast to the two-dimensional or layered structure

of all the superconducting copper oxides. Also, the parent compounds are different types of insulators. The cuprate materials, La_2CuO_4 and $YBa_2Cu_3O_6$, are antiferromagnetically ordered 'Mott' insulators, the magnetic moment of neighbouring ions cancelling. But $BaBiO_3$ is diamagnetic, the bismuth ions having zero magnetic moment, and has a doubled unit cell corresponding⁵ to a formal charge ordering $Ba_2Bi^{3+}Bi^{5+}O_6$. Thus, in the cuprate materials, the superconductivity occurs as the antiferromagnetism is suppressed, whereas in the bismuth oxides, because Cava *et al.* report¹ a cubic perovskite structure for $Ba_{0.6}K_{0.4}BiO_3$, it seems that the unit-cell doubling associated with the charge ordering is suppressed.

This raises the question of whether the mechanism of superconductivity is similar in both systems. If the superconductivity in the Cu-O planes of the cuprates arises from an essentially magnetically induced interaction, then this mechanism is not simply transferable to the bismuth oxides. On the other hand, $Ba_{1-x}K_xBiO_3$ seems a natural candidate for a 'bipolaronic' mechanism. In simple terms, the charge-ordered parent compound $Ba_2Bi^{3+}Bi^{5+}O_6$ can be regarded as a lattice ordering of bipolarons (or two-electron pairs) on alternate Bi^{5+} sites stabilized by the strong relaxation of the surrounding oxygen octahedra.

The effect of potassium-doping is to make these pairs mobile by changing the number of bipolarons per bismuth-site from the commensurate value of a half. This new system is the best candidate so far for the long-sought bipolaronic limit of superconductivity^{6,7}. Alternatively a common mechanism for the bismuth and copper oxides could be postulated if the superconductivity is a property mainly of the oxygen network. This can only be decided after detailed experiments on the normal and superconducting states.

A related set of questions concerns the possibility of raising T_c further in the bismuth oxides. Of possible dopant atoms, potassium seems optimal, because the similarity of the ionic radius of K^+ (1.33 Å) to that of Ba^{2+} (1.35 Å) should make it the least disruptive dopant. In the copper oxides, the really high transition temperatures (above 40 K) were achieved by more complex methods of doping by using quaternary compounds (see figure). Can something similar be achieved in the bismuth oxides? At present one can only speculate. □

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