

electronic structure and electron–phonon coupling from first principles. However, superconductors in the recently discovered high-temperature class (mostly ceramic materials based on copper oxide layers) defy our understanding on the basis of the traditional model. So far there is no consensus on the superconducting mechanism, and many competing theories are available. Not surprisingly, for each new superconducting material we have first to establish if it can be understood by conventional electron–phonon coupling or not.

The present work by Yokoya *et al.* tries to settle this issue in the case of boron-doped diamond by a direct measurement of the electronic structure using angle-resolved photoemission spectroscopy (ARPES). ARPES measures the properties of occupied electronic bands along selected lines of crystal momentum (Fig. 1). The results show very good agreement with calculated valence bands of diamond, strongly suggesting that it is these bands that play an important role for the metallic state, and thus supporting previous theories based on electron–phonon coupling^{4–7}. Such good agreement of the electronic bands for a single boron-doped sample is already an interesting result, but the authors walked the extra mile to carry out the experiment for a set of samples with different doping concentrations. Increased doping should shift the

electron occupation in these bands, and this is precisely what Yokoya *et al.* observe. Interestingly, their results further support the basic theoretical assumption that leads to the intriguing prediction of superconductivity in related materials such as silicon and germanium — although, given the high doping concentrations required, actual observation of superconductivity in those cases seems unlikely⁴.

Although Yokoya *et al.* present clear evidence for the importance of the valence bands in boron-doped superconducting diamond, the impurity band must be better studied for a proper understanding of heavily doped diamond. The interaction of the valence band with the impurity band will certainly be of further interest, because it may help us to understand the metal–insulator transition more deeply. This ultimately holds the key to understanding not only this particular material, but the high-temperature superconductors more generally.

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MATERIAL WITNESS

Birth of the blues

Painters wanted a cheap source of ultramarine blue ever since the natural pigment, made from the semiprecious stone lapis lazuli, was first exported east and west from the famous mines of Badakshan in Afghanistan — a process that seems to have been under way at least by the 6th century, when the pigment appears in Byzantine manuscripts.

So when the French chemist Jean-Baptiste Guimet found a way to synthesize ultramarine in 1826, it should have been cause for rejoicing among artists. Indeed, it appears Dominique Ingres was pleased enough: Guimet attested the following year that “M. Ingres who is an excellent judge in these matters has repeatedly assured me that my ultramarine leaves nothing to be desired.”

But other painters were less easily persuaded that their finest pigment could be reproduced by a chemist. In England, J. M. W. Turner seems to have resisted using the artificial pigment in his oil paintings, and it is said he was deterred from helping himself to a blob of blue on the palette of another artist, during the ‘varnishing days’ at the British

Royal Academy when works hung for display were given the final touches, by the cry that it was ‘French’.

No one was quite as dismayed as Christian Gottlob Gmelin, professor of chemistry at Tübingen. If he’d had his way, synthetic ultramarine would have been known not as French but as German. Gmelin devised a synthesis independently, probably in 1827, and was incensed when Guimet was awarded the prize of 6,000 francs offered by the Société d’Encouragement pour l’Industrie Nationale in 1824 for an industrial route to ultramarine. The story of controversy and industrial secrecy is recounted by Joost Mertens of the University of Maastricht (*Ambix* **51**, 219–244; 2004).

The remarkable thing about ultramarine, which 19th-century chemists were reluctant to accept, is that the rich blue colour is not produced by a metal ion. Rather, it is the result of electronic transitions of polysulphur ions encaged in the sodalite framework of a sodium aluminosilicate. So sulphur is an essential ingredient: Guimet’s and Gmelin’s syntheses are similar, involving baking a mixture of china

clay (the aluminosilicate kaolin), soda, charcoal, quartz and sulphur.

But the 19th-century arguments might be in some sense moot, judging from a recent analysis of ancient Chinese glazed beads (H. Berke *et al.* *Proc. 2nd Int. Conf. Conservation of Grotto Sites Getty Conserv. Inst.*; in the press). This reveals ultramarine in artefacts from the late Western Zhou dynasty, around the 8th century BC: about a thousand years before the first known reports of ultramarine in Chinese art, which is assumed to have been imported along the Silk Road from Afghanistan. The pigment was mixed with other blues in a glaze formed from calcium and barium copper silicates, which are evidently synthetic materials related to Egyptian blue. It seems likely that sulphate impurities in the raw materials and charcoal in the kilns may have led to the inadvertent synthesis of ultramarine — yet another technological ‘first’ for China.



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