

$$\cos\Delta_{ij} = \sin\delta_i\sin\delta_j + \cos\delta_i\cos\delta_j\cos(\alpha_j - \alpha_i) \quad (3)$$

These angular distances may be turned into a source of random integers r_i distributed over the range $(0, 10^k)$ via the transformation

$$r_i = \text{integer}[10^k(1 + \cos(\Delta_{ij}))/2] \quad (4)$$

The relative primality of two such integers (r_i, r_j) can then be determined by the standard euclidean algorithm for finding greatest common divisors², and a value of π derived from the proportion of such pairs having greatest common divisors of unity.

Using the astrometric data for the 100 brightest stars in the sky given in ref. 4, we computed the corresponding 4,950 values of $\cos(\Delta_{ij})$, and from them derived 10^6 pairs of random integers (r_i, r_j) in the range $(0, 10^6)$. We found that

$$P(r_i, r_j) = 0.6133333,$$

so that, by equation (2),

$$\pi_{\text{Stars}} = 3.12772$$

which is within 5 parts per 1,000 of the standard value. Latter-day Pythagoreans may take encouragement from learning that a 99.6% accurate value for π can be found among the stars above their heads.

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Superconductivity of boro-nitrides

STR — The discovery of superconductivity with critical temperatures reaching $T_c=23$ K in a new class of compounds has reinvigorated searches for high-temperature intermetallic superconductors^{1,2}. $\text{LuNi}_2\text{B}_2\text{C}$ is prototypical^{3,4}, consisting of flat nickel layers closely coordinated by boron atoms. These Ni_2B_2 sheets are separated by LuC layers, yielding a layered structure. This structure, combined with the presence of potentially magnetic Ni, is reminiscent of the very high- T_c copper-oxide superconductors and has added to the excitement. However, theoretical studies^{5,6} have shown that, from the point of view of their electronic structure near the Fermi energy, the materials are quite three-dimensional and more closely related to previous families of intermetallic superconductors.

The subsequent discovery⁷ of superconductivity at 12–13 K in the structurally related material $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ is remarkable. This compound may be derived from $\text{LuNi}_2\text{B}_2\text{C}$ by replacing the LuC layers by three LaN rock-salt layers while keeping the Ni_2B_2 sheets intact. The result is much

more widely separated Ni_2B_2 sheets, with nominally insulating LaN trilayers in-between. The natural expectation is of considerably more two-dimensional behaviour, possibly pointing the way to much higher T_c by analogy with the cuprates. The crystal and electronic structures and the phonons are crucial to understanding the superconductivity.

The reported crystal structure determined primarily by electron diffraction⁸ is, however, anomalous. In particular, the B height above the Ni planes is much smaller than in the boro-carbides: 0.60 compared with 1.19 Å in $\text{LuNi}_2\text{B}_2\text{C}$. We have used first-principles methods, as in our earlier studies of $\text{LuNi}_2\text{B}_2\text{C}$, to analyse the properties of $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$. The three internal coordinates not fixed by symmetry have been calculated along with the corresponding Raman optical phonon frequencies. The lattice parameters were fixed at their accurately determined X-ray values⁷. The atomic positions (notation of Zandbergen *et al.*⁸) are 0.131 for La (2), 0.128 for N (2) and 0.199 for B. This corresponds to a B height of 1.05 Å, much more like $\text{LuNi}_2\text{B}_2\text{C}$, and a more reasonable B–N (2) distance of 1.46 Å (compared with 1.81 Å). The calculated energy with the positions of Zandbergen *et al.*⁸ is 2.2 eV per formula unit higher — well outside plausible errors caused by the local-density approximation. We find that the structure of Zandbergen *et al.* is incorrect, perhaps because of reliance on electron diffraction measurements.

The fully symmetric A_{1g} Raman vibrations in the harmonic approximation are an almost pure La mode at 106 cm^{-1} , and two strongly mixed B–N modes at 323 cm^{-1} and 896 cm^{-1} . The upper mode has adjacent B and N atoms moving against each other. The upper, but not the middle, mode is strongly coupled to electronic states near the Fermi energy. This may be important for superconductivity, although the different couplings of these two modes, both of which involve modulation of the NiB_4 tetrahedral bond angles, suggests a more complex mechanism than that proposed by Mattheiss and co-workers⁹. The electronic structure near the Fermi energy is somewhat more anisotropic than that of $\text{LuNi}_2\text{B}_2\text{C}$, but cannot be described as even quasi-two-dimensional. The ratio of the Fermi velocities in the x and z directions is only 2:1.

The similarity to the boro-carbides is the result of unanticipated incomplete ionization of La and therefore metallic LaN layers in this structure.

Thus, $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ is well described as the first member of a subclass of the $\text{LuNi}_2\text{B}_2\text{C}$ class of intermetallic superconductors. These materials appear much more similar in their electronic properties to previous families of intermetallic superconductors than to the high- T_c copper-oxide materials.

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ZANDBERGEN AND CAVA REPLY — Our original reported structure for $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ (ref. 8) did contain some inaccuracies. Since that paper was submitted, three types of structure determination have been used to obtain an improved refinement of the crystal structure of that phase. They are: total-profile neutron powder diffraction¹⁰; through-focus exit-wave reconstruction using a series of high-resolution electron microscope images¹¹; and refinement of the electron-diffraction data in the original paper that now takes into account the effects of dynamical diffraction (J. Jansen *et al.*, manuscript in preparation).

The atomic positions obtained by these three methods are approximately the same, and broadly agree with those calculated by Singh and Pickett. But comparison with the structure reported in ref. 8 shows significant differences in the positions of the B atoms ($z=0.195$, as compared with $z=0.221$ in ref. 8) and N atoms ($z=0.125$, as against $z=0.133$ in ref. 8). As refinement of the original electron-diffraction data including dynamical diffraction gives results similar to those of neutron powder diffraction measurements, the inaccuracies in the positions of B and N in ref. 8 must be due to the neglect of the dynamical diffraction effects. (This was noted as a possible complication in that paper.) At the time our paper⁸ was submitted, only the kinematic refinement could be performed.

On the other hand, the positions of the Ni and La atoms reported in ref. 8 are the same (within the stated errors) as those obtained by the three new methods. We anticipate that within a few years, quantitative electron diffraction (taking into account dynamical diffraction) will provide a quick way to determine crystal structures from small crystallites which does not require the growth of bulk single crystals or high-purity materials.

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