Comment on “Superconducting phases of Bi and Ga induced by deposition on a Ni sublayer”

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In a recent publication Moodera and Meservey concluded from their diffraction data that thin Bi films deposited on a Ni buffer layer have the fcc structure. We point out that the observed diffraction pattern can also be assigned to the common rhombohedral phase with a (102) orientation with respect to the surface.

In a recent paper Moodera and Meservey reported on a superconducting phase of bismuth, induced by vacuum evaporation of a Bi film onto a thin Ni sublayer. From x-ray-diffraction (XRD) data the authors deduced a fcc-centered-cubic structure. Tunneling measurements showed little change in the superconducting properties after thermal cycling to room temperature, in contrast to the well-known superconducting phase of amorphous Bi, which is stable only at cryogenic temperatures. The formation of superconducting alloys such as Bi$_x$Ni or BiNi was ruled out because films coevaporated from Bi and Ni sources did not show any sign of superconductivity down to 1 K, while this phase exhibited a transition temperature $T_c$ in the range 1–4 K. No superconductivity resulted also if first the Bi was evaporated and then the thin Ni layer was deposited on top. Moodera and Meservey concluded that the observed (bulk) superconductivity was to be attributed to the fcc structure of their Bi films and that the thin Ni sublayer was required to mediate this structure. The fcc structure was assumed to have a lattice parameter $a$ of 5.71 Å and a preferred (111) orientation. The measured diffraction peaks are then the 111 and 222 peaks with corresponding plane spacings of 3.29 and 1.65 Å. We believe that, for the given set of diffraction peaks, the occurrence of the fcc structure is improbable because the volume per Bi atom in this structure (46.5 Å$^3$) is significantly larger than in the rhombohedral case (35.4 Å$^3$).

In this paper, we offer an alternative interpretation of the XRD data. In Table I, we compare the $d$ values of “Bi” and “Bi on Ni” of Ref. 1 with those of the common rhombohedral phase of Bi from the Powder Diffraction File Data Base. The “cubic hkl” indices refer to the assumed cubic structure. The “hex. hkl” indices refer to a description with the hexagonal axes of the rhombohedral structure. We see from this table that the diffraction data of Ref. 1 for “Bi” can be assigned to the (001) oriented rhombohedral phase. The diffraction data of Ref. 1 for “Bi on Ni” can also be understood as due to the common rhombohedral phase of Bi, with the (102) axis oriented along the surface normal. Since the two diagrams can be interpreted as two different textures of Bi, it is unnecessary to propose a fcc structure with an atomic volume which is 31% expanded.

As bulk rhombohedral Bi does not become superconducting at hydrostatic pressures less than 25 kbars, the superconductivity with a $T_c$ of about 4 K reported by the authors of Ref. 1 still remains to be explained. The possibility of a surface or grain boundary effect, or an even more exotic mechanism involving the nickel layer, can probably be ruled out, as the observed superconductivity appears to be rather robust. Another possibility is a change in the charge carrier density and/or one or more components of the anisotropic mass due to uniaxial strain. Although it appears to be difficult to pinpoint a specific mechanism in this case, the fact that superconductivity occurs in the common rhombohedral structure of Bi, rather than a new (fcc) phase, offers very exciting perspectives for further experiments and forms a theoretical challenge to explain this beautiful and rather puzzling

<table>
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<th>$d$ values of Bi/Ni and Bi.</th>
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<tr>
<td><strong>“Bi”</strong></td>
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<tr>
<td>$d$ (Å)</td>
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<tr>
<td>3.96</td>
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<td>1.98</td>
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<td>1.323</td>
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result.

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205-0519 of the Powder Diffraction File, compiled by the Joint Committee of Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD), 1601 Park Lane, Swarthmore, PA 19081.