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Communication

Synthesis of the Candidate Topological Compound Ni_3Pb_2

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ABSTRACT: Spin−orbit coupling enables the realization of topologically nontrivial ground states. As spin−orbit coupling increases with increasing atomic number, compounds featuring heavy elements, such as lead, offer a pathway toward creating new topologically nontrivial materials. By employing a high-pressure flux synthesis method, we synthesized single crystals of Ni_3Pb_2, the first structurally characterized bulk binary phase in the Ni−Pb system. Combining experimental and theoretical techniques, we examined structure and bonding in Ni_3Pb_2, revealing the impact of chemical substitutions on electronic structure features of importance for controlling topological behavior. From these results, we determined that Ni_3Pb_2 completes a series of structurally related transition-metal-heavy main group intermetallic materials that exhibit diverse electronic structures, opening a platform for synthetically tunable topologically nontrivial materials.

Over the past decade, the field of topological materials grew at an explosive pace, fundamentally reshaping our depiction of solid-state systems.[1−5] Topologically nontrivial materials host band structures that enforce transport along specific paths, for example through spin-momentum locking and surface currents.[6−8] This phenomenon offers the potential to protect electron transport from sources of noise[9,10] with spintronic[11,12] and fault-tolerant quantum computing applications.[13−16] Recent computational studies demonstrate that topologically nontrivial classifiers are shared by ∼30% of known materials.[17] However, progressing from the classification of band structures to the application of useful transport properties, dependent on the overall electronic structure of each system, remains a key hurdle in the field. Amelioration of this challenge requires the creation of topologically nontrivial single crystal compounds, where the response of the material's band structure to chemical changes can be predicted, designed, and harnessed.[18]

Topological character is defined by the symmetry of the electronic wave functions of a material, reflecting two chemically intertwined effects: the real space symmetry of the system, as well as the interaction and identity of the atoms that comprise it.[19−21] Together they determine the band dispersions and crossings as well as the position of the Fermi energy relative to features of interest. To uncover the principles underpinning topological behavior, we pursued an approach to maintain physical structure and symmetry while introducing degrees of chemical freedom, allowing for minute adjustments. Targeting binary phases, whereby doping with a third element would be synthetically accessible, promises the requisite combination of precise chemical tunability and structural control.

High-pressure techniques are powerful tools for synthesizing new binary intermetallic materials, as they effectively add another axis to temperature−composition phase space.[22−26] Pressure also changes chemical heuristics,[27] promoting reactivity of high atomic number elements that introduce large amounts of spin−orbit coupling (SOC),[28−31] a key component in creating the targeted topological band structures motifs of interest.[32,33] To search for new topologically nontrivial phases, we explored the Ni−Pb system in which no bulk and thermodynamically stable materials are known, yet a report of bimetallic films accessed via vapor deposition suggests metastable reactivity.[34−36] Since Pb is the heaviest element stable to radioactive decay, we anticipated a strong SOC contribution to the band structure from Pb.[37−39] Employing high-pressure techniques, we synthesized and recovered the new Ni−Pb binary intermetallic phase, Ni_3Pb_2, elucidating its structure. Computational comparison of Ni_3Pb_2 with chemically related systems reveals its flexible topologically nontrivial character.

To synthesize Ni_3Pb_2, we performed high-pressure reactions using a Kawai-type multianvil press (MAP). We pressurized a pellet composed of a mixture of Ni and Pb to 8.4(1) GPa (see Supporting Information (SI) for details, Figure S4),[40] monitoring the reaction progress using synchrotron powder X-ray diffraction (PXRD) (λ = 0.1923 Å, MAXPD Endstation at NSLS-II, 28-ID-2-D). While heating the mixture to ∼1123 K, we observed the formation of new diffraction peaks corresponding to a pseudohexagonal structure[41] (Figure 1 and SI). Notably, decompression experiments revealed that the material persists to ambient conditions (Figure S9).

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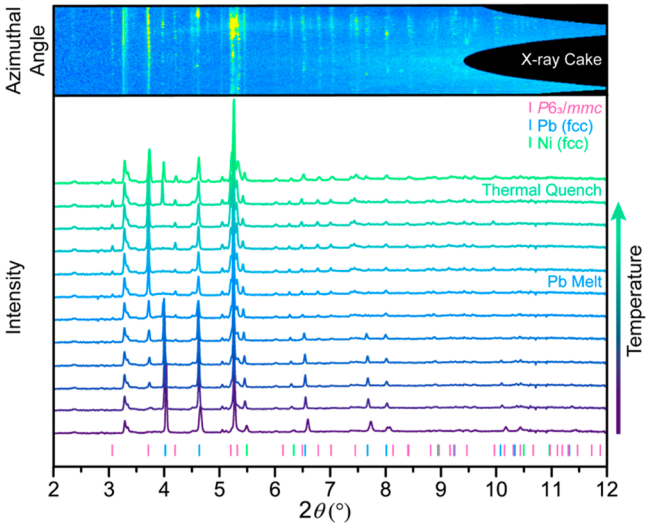

Figure 1. *In situ* PXRD data collected while heating a mixture of elemental nickel and lead at 8.4(1) GPa (λ = 0.1923 Å). The PXRD patterns (bottom) show the structural evolution with increasing temperature up to and beyond the lead melt (~1123 K) as well as the ambient temperature data (green). The $P6_3/mmc$ ticks (pink) correspond to the new phase. The unrolled cake image (top) shows a slice of the 2D PXRD pattern collected at ambient temperature.

Using the conditions established during the *in situ* studies, we scaled up the reaction (Figure S5) (APS, 13-ID-D).[40] As a consequence of the formation of a lead flux at high pressure, we found that the recovered samples consisted of high-quality crystallites amenable to structural characterization. Ambient pressure single crystal X-ray diffraction data revealed that Ni_3Pb_2 crystallizes in the $P2_1(\alpha 0\gamma)0$ superspace group with unit cell constants of a = 4.1705(2) Å, b = 5.2881(3) Å, c = 4.1848(2) Å, and β = 119.881(4)°, $q = 0.5a^* + 0.25c^*$ (Figure 2 center; see SI for details). It is a commensurately modulated member of the B8-type structure family and can be reduced to an orthorhombic cell setting, isostructural to the known *Pnma* superstructures of Ni_3Sn_2 and Co_3Sn_2.[42] Structural modulations exist presumably due to long-range ordering between Ni atoms and vacancies.

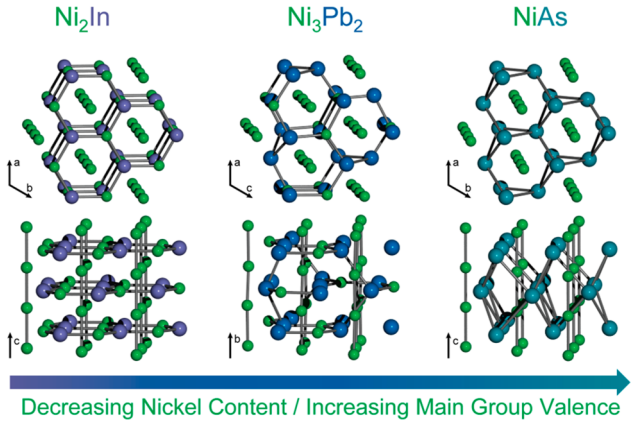

Figure 2. Comparison of the Ni_3Pb_2 crystal structure (generated from a supercell in the *P*1 space group, a = 8.3410(2) Å, b = 5.2881(3) Å, c = 16.7392(2) Å, α = 90, β = 119.881(4), γ = 90) with the NiAs and Ni_2In structures. Ni, In, Pb, and As are represented by green, purple, blue, and teal, respectively. The structures differ by the decrease in the occupancy of the Ni2 site from 1 → 0 across the series.

Many compounds within the B8-type family possess a nontrivial topological $\mathbb{Z}$-valued invariant, recommending this example for further investigation.[43] Structurally, Ni_3Pb_2 can be described as an intermediate between NiAs ($B8_1$) and Ni_2In ($B8_2$) if we consider the occupancy of the Ni atoms (Figure 2). All three structures share several features. They have chains of Ni atoms (Ni1 site) running along the *c*-axis in the $P6_3/mmc$ cell (*b*-axis in the $P2_1(\alpha 0\gamma)0$ cell) and triangular layers of main-group atoms perpendicular to the Ni chains where each layer is shifted by half a unit cell. Beyond the NiAs and isostructural NiSb structure, Ni_2In has a second Ni site (Ni2 site) that sits in the holes within the main group layers creating hexagonal layers of alternating Ni and main group atoms. In the Ni_3Pb_2 structure, this Ni2 site is half occupied. The overall similarities of these structures outside of the occupancy of a single type of site promise chemical tunability while maintaining overall structural motifs.

However, precise symmetry descriptions are crucial for evaluating topological character. Single crystal X-ray diffraction experiments revealed that the void space introduced by the Ni2 half-occupancy results in a distortion away from hexagonal symmetry shared by the NiAs and Ni_2In examples. This distortion to lower symmetry is observed in the isostructural Ni_3Sn_2 phase,[37] suggesting that the malleability of the hexagonal symmetry is generalizable for this stoichiometry of B8 compounds. The precise atomic positions revealed by our structure solution allows for visualization of the atom-specific interactions that drive the symmetry lowering, seen as undulations in the chains of Ni1. We posit these interactions serve to optimize Ni−Pb bond distances and stabilize Ni−Ni bonding interactions, differentiating the crystal symmetry in this series of materials based on local interactions. Further, many of the Ni−Pb distances (2.504(5)−2.9(1) Å) fall within the sum of the metallic radii (Ni, 1.244 Å; Pb, 1.746 Å).[44] The persistence of these interactions, despite ~3% changes in radius ratios of these elements over the pressure range explored,[45,46] suggest a sufficient energy barrier to decomposition enabling its persistence at ambient pressure (see SI for details). Together, these observations indicate the power of high-pressure synthesis to expand chemical control over structure in this class of materials.

To interrogate the potential topological properties of Ni_3Pb_2, we performed electronic structure calculations on the relaxed Ni_3Pb_2 structure at ambient pressure (Figure 3 and SI for details).[47] Examination of the band structure showed that the Ni *d* orbitals comprise the majority of bands near the Fermi level, as is expected for intermetallic phases with *sd*- and *p*-band metals. Below the Fermi energy, Pb *p* orbitals also contribute to the structure, suggesting orbital overlap that enables Ni-*d*−Pb-*p* bonding. Two-band crossings are observed at the Fermi energy, one at the S-point and one along the Γ−X trajectory with potential topological importance. By combining band structure calculations with elementary band representations and compatibility relations,[17,48] we determined that the topological classification describing the highest energy occupied bands in Ni_3Pb_2 is $\mathbb{Z}_4$ = 3, confirming that Ni_3Pb_2 is a candidate topologically nontrivial material. This topological index points to the presence of Dirac or Weyl nodes depending on the inversion and time reversal symmetry of the system.[49−53] Specifically, Ni_3Pb_2 exhibits avoided crossing that may engender Dirac nodes at interfaces that support unusual charge and spin transport properties.

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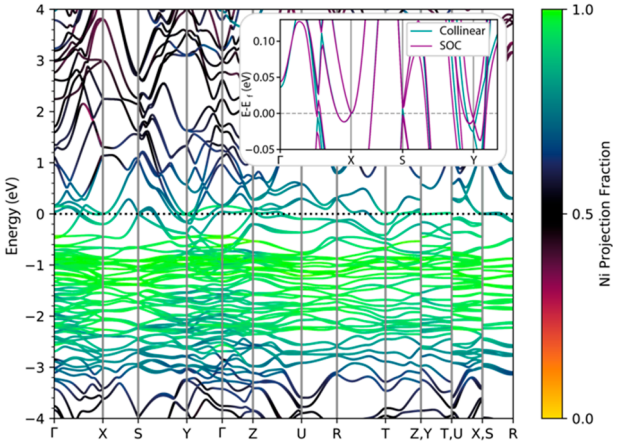

Figure 3. Band structure of Ni_3Pb_2 at ambient pressure where the bands are color coded to indicate the contribution of Ni electrons to each band. The inset highlights the band crossings near the Fermi level with (purple) and without (blue) SOC.

Crucially, this nontrivial topological classifier differs from the NiAs and Ni_2In systems, which are predicted to have enforced semimetal character.[54−57] In comparison, at the S point of the band structure for Ni_3Pb_2 we observe a gap that introduces topological insulating character. To explore the origin of this gap, we made a series of comparisons. First, we observed that when SOC is not included in our calculation, this gap of ∼10 meV disappears (Figure S47). Similarly, examining the previously determined topological character of Ni_3Sn_2 reveals a similar phenomenon, although the gap at the S point is significantly smaller (<1 meV), further reflecting the importance of SOC in tuning topological character.[58] Complementarily, we computationally enforced a hexagonal primitive cell in Ni_3Pb_2 equivalent to having ordered half-occupied Ni2 sites in the $P6_3/mmc$ primitive cell of Ni_2In, resulting in a $P\bar{6}m2$ structure in which topological semimetal character is recovered (Figures S49 and S50). Thus, the nature of the topologically protected crossing at the S point reflects both the overall symmetry of the Ni2 site occupations as well as the amount of SOC engendered by the main group atom.

Controlling the extent of site occupancy in a material can pose a synthetic challenge. However, in B8-type Ni−main group phases, the main group element identity is known to determine the amount of Ni incorporated, which, in turn, determines the symmetry of the structure.[59] Namely, the amount of Ni incorporated decreases as the valence electron count on the main group element increases, such that main group elements requiring more electrons to achieve full orbital configurations incorporate more Ni into their structure. Indeed, Ni_3Pb_2 falls within this trend. One physical manifestation of this model is the expected charge transfer from the Ni center to the Pb, compensating for unfilled p-band electronic states. Examination of the electron density around each metal using X-ray absorption spectroscopy (XAS) revealed a shift of the Pb L_3-edge (13030(2) eV) to lower energy than the reference (13035 eV), and the Ni K-edge (8339(2) eV) to higher energy than the reference (8333 eV).[60] These data are consistent with XAS spectra for known Ni−main group B8-type compounds[61−65] as well as calculated projected charges (Table S32), confirming that there is a partial negative charge transfer from the Ni to the main group element. Thus, the role of the main group metal is twofold: its atomic number directly determines the amount of band mixing in the avoided crossings and its electron count indirectly influences the overall symmetry of the material based on the amount of Ni incorporated into the structure, creating a tractable synthetic handle to control topology.

In parallel, we also explored computationally the electronic structure of the hypothetical Co_3Pb_2 material inspired by the known isostructural Co_3Sn_2 phase (Figure S51). Although we were not able to synthesize any phase in this system under analogous conditions in a diamond anvil cell (up to 16 GPa, ∼1123 K), this is consistent with calculations that show its enthalpy of formation only becomes negative under higher pressure conditions (Figures S52−S56). Notably, electronic structure calculations revealed that a magnetic ground state is predicted, suggesting an additional handle for expanding topological behavior in systems without time-reversal symmetry. However, by enforcing nonmagnetic ordering in the predicted Co_3Pb_2 phase to allow for direct comparison with Ni_3Pb_2, we found that its hypothetical density of states is well-described within a rigid-band approximation. The Fermi level is shifted by ∼+0.75 eV relative to that in Ni_3Pb_2. This result combined with the analogous chemistry of Co_3Sn_2 suggests that transition metal identity provides another parameter for tuning topological properties, determining the energy of the Fermi level relative to topological electronic states while maintaining the overall symmetry. Explorations of chemical substitution through alloying at both the Ni and the main group metal site are of interest for future studies.

Our high-pressure discovery of Ni_3Pb_2 completes a series of B8-type compounds to reveal a chemical phase space in which overall structural motifs are maintained while electronic structure factors relevant for topology are tuned. This approach is promising for the creation of new families of flexible topologically nontrivial materials. Future studies will focus on doping this material to tune its Fermi energy and extending this conceptual approach to create new topologically nontrivial materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c03485.

Additional synthesis and data analysis details, crystallographic refinements and structure solutions, and details for electronic structure calculations. (PDF)

Accession Codes

CCDC 2163166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

MAP, multianvil press; MAXPD, Multi-Anvil X-ray Powder Diffraction; PXRD, powder X-ray diffraction; SOC, spin−orbit coupling; XAS, X-ray absorption spectroscopy

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