Growth, characterization and duality of BaZnGa

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BaZnGa has been a widely discussed hypothetical material; existing more as a concept rather than an actual compound. Here we report the growth, structure and characterization of BaZnGa, identifying it as the sole known ternary compound in the Ba-Zn-Ga system. Single crystals of BaZnGa can be grown out of excess Ba-Zn and adopt a tI36 structure type. There are three unique Ba sites and three M = Zn/Ga sites. Using DFT calculations we can argue that whereas one of these three M sites is probably solely occupied by Ga, the other two M sites, most likely, have mixed Zn/Ga occupancy. Temperature dependent resistivity and magnetization measurements suggest that BaZnGa is a poor metal with no electronic or magnetic phase transitions between 2 K and 300 K. In toto, BaZnGa indeed manifests a true duality: it is a ternary compound with the well defined properties of a poor metal and it fulfills its metaphorical role as being a signal or indication of a rather curiously constructed jest or Jape.

I. INTRODUCTION

Humanity is drawing tantalizingly closer to being able to predict new compounds and materials, as well as their functionalities, *ab initio* rather than the more historically common *a posteriori* explanation of their measured properties. To this end, recent experimental work ranging from the confirmation of high-temperature superconductivity in hydrogen rich compounds[1] to the creation of complex, topological electronic states[2] underscores the importance of judiciously trying to test theoretical claims. In condensed matter / new materials physics, predictions, or even announcements, of new materials can take a wide variety of forms ranging from formal publication to a passing reference to a new discovery at a conference.[3] In whatever form predictions or discoveries are announced, it falls on the research scientist to separate the wheat from the chaff. Over the past decade there have been multiple references to an undiscovered, Ba-Zn-Ga ternary compound that we have been able to grow, identify and characterize.

Dr. Sheldon Cooper is, arguably, recognized as one of the more prolific, living theoretical physicists and has certainly captured the attention of the general public. The record of his accomplishments[4] ranges from seminal work in string theory to studies of dark matter and predictions of stable, ultra-heavy elements. Dr. Cooper has also ventured into the realm of condensed matter physics, being on record as having made contributions to the fields of Bose-Einstein condensation, topological insulators and graphene.[4] As such, when Dr. Cooper forays into the realm of materials by design, i.e. predicting a new compound, we feel obliged to treat his prediction with all the gravity and import appropriate to it. Over the past several years Dr. Cooper has publically made reference to a barium, zinc, gallium ternary compound.(BaZnGa or "BAZINGA") These have been fleeting, but repeated, and certainly more widely disseminated than the original announcement of superconductivity in MgB_2.[3]

One of the key stumbling blocks, historically, associated with predictions of unknown compounds has been the sad experimental fact that often predicted compounds are not actually stable. In the case of BaZnGa, stability seems to have been a forgone conclusion; one that we have been able to verify. As such, herein we report the discovery and characterization of the only known Ba-Zn-Ga ternary compound, $BaZn_{1-\delta}Ga_{1+\delta}$ or BaZnGa for short.

II. EXPERIMENT

Single crystals of BaZnGa were grown out of a low temperature Ba-Zn eutectic.[5] In order to check the utility of the eutectic and possible reaction between alumina crucible and Ba, we put $Ba_{0.5}Zn_{0.5}$ into an alumina crucible and sealed in an amorphous silica tube. We heated up to 800 °C over 5 hours, kept it there for 12 hours, cooled down to 400 °C over 12 hours, and then finally decanted using a centrifuge.[6] All of the material was in a liquid state and passed through an alumina frit.[7] In addition, there was no sign of attack on the alumina crucible by Ba or Zn.

As a next step, Ba, Zn and Ga were placed into a new alumina crucible with an initial stoichiometry of $Ba_{0.45}Zn_{0.45}Ga_{0.1}$ (shown on the ternary phase diagram in Fig.1) and sealed in an amorphous silica tube. The ampule was heated up to 800 °C over 5 hours, kept there for 5 hours, cooled down to 400 °C over 60 hours,[8] and then finally decanted using a centrifuge. The obtained crystals are plate-like (Fig. 1) and are broader than they are high, manifesting what Dr. Cooper would call, "a classic Hofstadter morphology, BaZnGa". The crystals

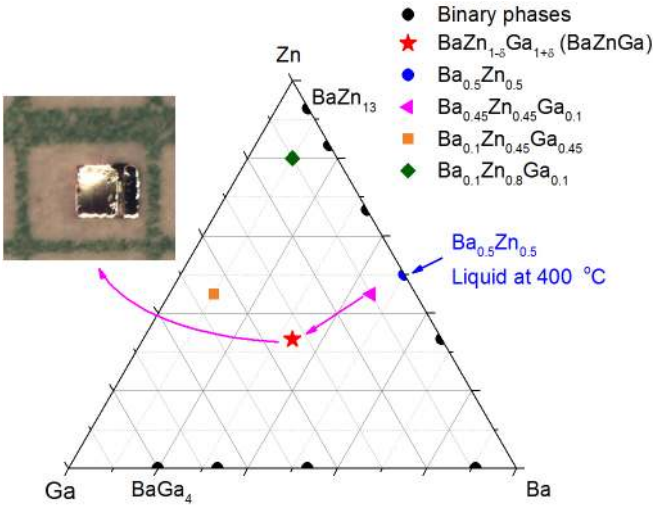

FIG. 1. (color online) Ternary phase diagram of Ba-Zn-Ga. Photograph of a single crystal of BaZnGa on a mm grid.

are sensitive to air, so all the sample preparations and handling were done inside a glove-box filled with Argon or Nitrogen. We also tried two other initial compositions, $Ba_{0.1}Zn_{0.45}Ga_{0.45}$ and $Ba_{0.1}Zn_{0.8}Ga_{0.1}$. These are also shown on Fig.1, but neither resulted in any ternary phase growth. Instead they resulted primarily in binary phases of $BaGa_4$, and $BaZn_{13}$, respectively.

Single crystal X-ray diffraction intensity data for BaZnGa were collected at room temperature (293 K) using a Bruker SMART APEX II diffractometer (Mo K_α radiation, $\lambda = 0.71073$ Å). (BaZnGa single crystals were examined under microscopy and sealed into capillaries in a glove box.) Data reduction, integration, unit cell refinements, and absorption corrections were done with the aid of programs integrated into the APEX2 software package.[9,10] Space group determination, Fourier Synthesis, and full-matrix least-squares refinements on F^2 were carried out with SHELXTL 6.1.[11] The program Superflip[12] was used to yield the initial structural model, in which three independent sites could be assigned to Ba and the remaining three to Ga (or Zn) based on peak intensity and interatomic distances. The occupancy parameter for each site was found to be close to full occupancy ($< 1\ \sigma$) when separate refinements with unfixed occupancy parameter were tried. However, attempts to refine the Zn/Ga mixture on these three Ga (or Zn) sites were not successful, which is common for systems containing elements with similar scattering powers. Table I gives the crystal data and structure refinement for BaZnGa and Table II lists the refined atomic positions and equivalent isotropic displacement parameters.

Magnetization measurements were performed in a Quantum Design, Magnetic Property Measurement System (MPMS), SQUID magnetometer for $H = 10$ kOe and $1.8\,\mathrm{K} \leq T \leq 300\,\mathrm{K}$. The samples for the magnetization were put into a gel capsule without a well defined orientation. The magnetization data of BaZnGa were obtained

TABLE I. Crystal data and structure refinement for BaZnGa.

Empirical formula	BaZnGa
Space group	$I4/mmm$ (tI36)
Unit cell dimensions	$a = 6.3652(2)$ Å
	$c = 25.593(1)$ Å
Volume (Å^3)	1036.91(8) Å^3
Z	12
Reflections collected	8645 [$R_{int} = 0.0557$]
Data / restraints / parameters	557 / 0 / 21
Goodness-of-fit on F^2	1.163
Final R indices [I> $2\sigma(I)$]	R1 = 0.0462, wR2 = 0.1036
R indices (all data)	R1 = 0.0480, wR2 = 0.1043
Largest diff. peak and hole	3.933 and -2.128 e.Å^{-3}

TABLE II. The refined atomic positions and equivalent isotropic displacement parameters for BaZnGa.

Atom	Wyck.	Site Symm.	X	y	z	U_{eq} (Å^2)
Ba1	4d	-4m2	1/2	0	1/4	0.015(1)
Ba2	4e	4mm	1/2	1/2	0.1322(1)	0.041(1)
Ba3	4c	mmm	1/2	0	0	0.046(1)
M1	4e	4mm	0	0	0.0508(1)	0.015(1)
M2	4e	4mm	0	0	0.1987(1)	0.015(1)
M3	16n	.m.	0.2955(2)	0	0.1236(1)	0.015(1)

by subtracting the background signal of the empty gel capsule from the sample plus gel capule data set. Samples for *ac* resistivity measurement were prepared in a standard 4-probe geometry. Au wires (12.7 µm diameter) were attached to the crystal using DuPont 4929N silver paint inside the glove box as shown in the inset to Fig. 3 below. The temperature dependent electrical transport measurements were carried out in a Quantum Design Physical Property Measurement System (PPMS) for $1.8\,\mathrm{K} \leq T \leq 300\,\mathrm{K}$.

Elemental analysis was done via Oxford Aztec energy dispersive spectroscopy(EDS) using FEI quanta 250 FEG scanning electron microscope.

III. RESULTS AND ANALYSIS

A. Crystal structure and composition

Based on our growth and identification, BaZnGa is the only, currently known, ternary phase in the Ba-Zn-Ga system. It crystallizes in a new structural type, with Pearson symbol of $tI36$. This is distinct from both $BaZn_2$ (KHg_2 type, oI12) and $BaGa_2$ (AlB_2 type, hP3) binary compounds. The structure features a packing of double octahedral layers of Zn and Ga at $z = 0$ and 1/2. These layers are identical but shifted by half unit cell in both the a and b directions and separated by a layer

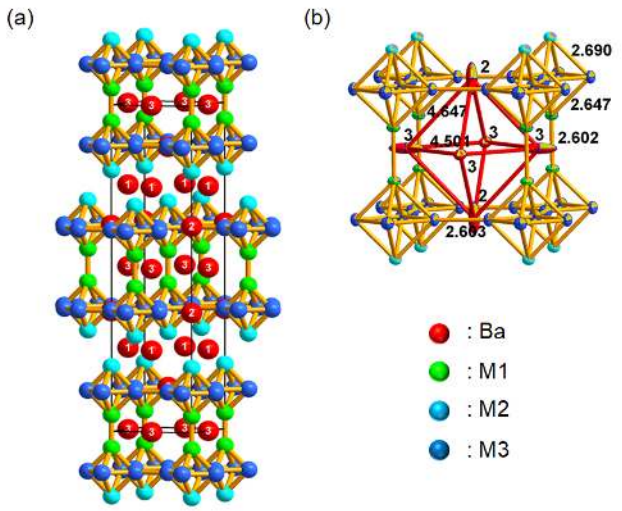

FIG. 2. (color online) (a) The structure of BaZnGa at a unit cell level, containing two identical double octahedral layers. Red spheres denote Ba atoms, with numbers showing independent atoms. Green, cyan, and blue spheres denote atoms on the M1, M2, and M3 sites, respectively. (b) The repeating structural unit in one double octahedral layer. Important Ba-Ba and (Zn/Ga)-(Zn/Ga) bond distances are marked.

of Ba1 atoms (Fig. 2 (a)). The Ba2 and Ba3 atoms are located at vacancy centers of four neighboring octahedra, and they form octahedra slightly elongated along the c axis, as indicated by the interatomic distance of Ba3 - Ba3 (4.501 Å) and Ba2 - Ba3 (4.647 Å). In each double octahedral layer, neighboring (Zn/Ga) octahedra are connected by M3 - M3 inter-cluster bonds in the ab plane and M1 - M1 bonds along c; both are $\sim$2.60 Å. In contrast, the intra-cluster bond distances of the octahedra are longer (2.65 Å - 2.69 Å), suggesting more delocalized bonding interactions. Crystal orbital Hamilton Population (COHP) analyses reveal that the inter-cluster bonding interactions are about 2.23 - 2.28 eV/bond.mol, i.e. $\sim$30 % larger than those of intra-cluster bonds (1.65 - 1.75 eV/bond.mol). The arrangement between the Ba_6 octahedron and its neighboring octahedra (Fig. 2 (b)) can be viewed as an inversed Perovskite structure with a general formula of ABX_3, in which the large size cation A is now replaced by the Zn/Ga octahedra and the anion X by Ba, whereas the small size cation B is missing.

Although analysis of the X-ray data cannot shed light onto the Zn/Ga ratio, we were able to perform semi-quantitative composition analysis via EDS. The Ba:Zn:Ga ratio was consistent with 1 : 1 : 1, although it did suggest that there may be more Ga than Zn, i.e. $BaZn_{1-\delta}Ga_{1+\delta}$.

B. Density Functional Theory

Given that the x-ray scattering strength of Zn and Ga are very close, the occupations of Zn and Ga on 3 Wyckoff sites (two 4e-sites, namely M1 and M2, and 16n-site, namely M3) cannot be resolved by single crystal analysis. To try to gain some insight to potential occupancies, and in deference to Dr. Cooper's theoretical predisposition, first-principles density functional theory (DFT)[13] calculations were performed to investigate the occupancy of Zn and Ga on these 3 sites. In order to allow for an unequal amount of Zn and Ga, one thousand different structures with 8 Zn and 16 Ga atoms scattered randomly on those 3 sites were generated and their corresponding energies were calculated by DFT. The DFT calculations were performed using Vienna $Ab-Initio$ Simulation Package (VASP)[14] with projector-augmented wave pseudopotential method[15,16] and plane wave basis. The generalized-gradient approximation parameterized by Perdew, Burke, and Ernzerhof[17] was used for the exchange correlation energy functional. The energy cutoff was 360 eV and the Monkhorst-Pack's scheme[18] was used for Brillouin zone sampling with a k-point mesh of $6\times6\times2$. An attempt to apply a Koothrappali-Wolowitz energy minimization was unsuccessful. All low energy structures, with energy window of 0.25 eV/unit cell, which is corresponding to thermal energy of liquid Nitrogen (77 K), were collected for site occupation analysis. We find that the M2 site is fully occupied by Ga in all low-energy structures. The M1 site and M3 site are occupied by both Zn and Ga with average occupations $Zn_{1.85}Ga_{2.15}$ and $Zn_{6.15}Ga_{9.85}$, respectively, which are very close to the totally random occupation of Zn and Ga on these 2 sites: $Zn_{1.60}Ga_{2.40}$ and $Zn_{6.40}Ga_{9.60}$. Therefore, we conclude that the M2 site is likely occupied by Ga only, whereas and M1 and M3 sites are occupied by Ga and Zn randomly. We would like to note here that, amongst the M1, M2 and M3 sites, M2 site has a coordination number of 4, whereas both M1 and M3 have coordination numbers of 5. This distinction of coordination number could be the driving force for the distinct occupation of the M2 site. The very strong predisposition of Ga to occupy the M2 site shown above implies that the M2 site is primarily or fully occupied by Ga in the BaZnGa ternary.

C. Physical properties

Figure 3 presents temperature dependent electrical resistivity, $\rho(T)$, and magnetic susceptibility, $M(T)/H$. Not surprisingly, given that the M1 and M3, Zn/Ga sites are likely disordered, the electrical resistivity decreases only slightly from its $2.5\times10^{-4}\,\Omega$ cm room temperature value upon cooling. The overall behavior of the temperature dependent resistivity is comparable to that of $BaFe_2As_2$ above the structural/magnetic transition temperature, which shares the same space group for

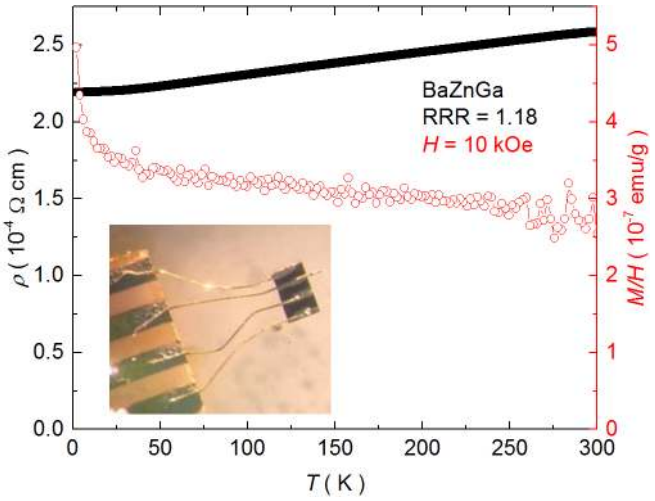

FIG. 3. (color online) Temperature dependent resistivity.(left axis, black filled circles) Temperature dependent magnetic susceptibility of BaZnGa measured at $H = 10\,\mathrm{kOe}$.(right axis, red open circle) The inset shows a picture of BaZnGa with standard 4-probe contacts.

$T > 134\,\mathrm{K}$.[19] $BaFe_2As_2$ is a member of the well known 1-2-2 family of iron-based superconductors that provide a playground for the study of the interaction between superconductivity, magnetism, crystal structure and electronic structure.[19] However, BaZnGa apparently does not have any of these interesting properties and being hard to draw, can't even be used as a heater wire, thus making it similar to non-magnetic quasicrystals.[20]

The magnetic susceptibility also manifests only a modest temperature dependence that can be described as weak Pauli paramagnetism with a low temperature impurity tail. This is similar in size and temperature dependence to YCo_2Zn_{20}[21] or non-magnetic quasicrystals.[20] Neither resistivity nor susceptibility data give any indication of phase transitions between 1.8 and 300 K.

IV. CONCLUSION

Our discovery of BaZnGa, combined with our structural, magnetic and resistivity data provide a clear validation of what we refer to as the BaZnGa dualism. Whereas we have shown that BaZnGa is a well-defined ternary compound, it also manifests the gestalt of its original meaning, to be an *a posteriori* signaling of a (often poorly constructed) jest or jape. As such we checked to see if this new compound was quasicrystalline, BaZnGa; we searched for high temperature superconductivity: BaZnGa; we tested for Stoner and near-Stoner magnetism: BaZnGa; we searched for spin-, charge-, and spin-orbit-density waves: BaZnGa. Given that we have not yet measured either the thermal conductivity or the thermoelectric power, it is possible that new record values may well be found: BaZnGa (i.e. probably not).

In conclusion, Dr. Sheldon Cooper continues to be both a motivation and an enigma. We admire the accuracy of the prediction of BaZnGa, but regret having fallen prey to his legendary wit; BaZnGa!.

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