Transition-Metal Substitution in Semiconducting Ba₈Ga₁₆Ge₃₀ Clathrates

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Abstract. We report magnetization, transport, and ⁷¹Ga NMR properties of Ni- and Fe-substituted type-I Ba₈Ge₃₀Ga₁₆ clathrates. While Fe substitutes partially into the lattice, Ni substitutes readily for Ga, and we prepared samples with composition up to Ba₈GeₓₙGa₁₆Niₘ. Results indicate low-density metallic behavior for all samples, with little change in electronic structure caused by Fe or Ni substitution. NMR relaxation behavior (T₁) and Knight shifts in all samples exhibited a constant Korringa product (K²T, T) characteristic of metallic behavior with small exchange enhancement.

INTRODUCTION

Group-IV clathrates form extended fullerene-type frameworks, commonly as the type-I structure (Fig. 1). These are of interest for thermoelectric applications, particularly Ba₈Ga₁₆Ge₃₀ and its Sr- and Eu-centered analogs. The latter exhibit high thermoelectric efficiencies, attributed to loosely held cage-center atoms [1,2]. The Zintl mechanism [3] can provide an explanation for the semiconducting behavior of these materials; valence-3 Ga in the tetrahedral-bonded framework balances the electrons donated by Ba. Several transition-metal-substituted clathrates have been reported [4], with a variety of associated electronic behaviors, including magnetic clathrates [5]. Here we report the properties of new Ni- and Fe-substituted clathrates based on type-I Ba₈Ga₁₆Ge₃₀.

EXPERIMENTAL

Materials were prepared by arc-melting elemental constituents, with subsequent solid-state reaction [5]. Powder x-ray diffraction (XRD) utilized GSAS for refinement [6]. Samples included Ba₈Ge₃₀Ga₁₆ₓNiₘ, x = 0, 1, 2, 4 and 6, and Fe, with 0.5≤x≤6. Magnetization was measured using a Quantum Design SQUID system, transport using a home-built spectrometer with 9T superconducting magnet.

RESULTS AND DISCUSSION

All XRD patterns were fit to the type-I structure, with small amounts of unreacted Ge in some cases (Fig. 2). Electron microprobe measurements showed that formation of FeGe₂ yields a clathrate with Fe content reduced relative to the starting materials [5]. By contrast, Ni has fewer competing phases, and substitutes more readily. The decrease of Ni-clathrate lattice constant with increasing x is comparable to the change reported for Ba₈Ge₃₀Niₘ relative to Ba₈Ge₄₄ [4], while the x = 0 endpoint (1.0784 nm) is equal to the reported value for Ba₈Ga₁₆Ge₃₀ [2]. In the refinement we assumed Ni to be located on the 6c site (Fig. 1), though this fit was not highly sensitive to Ni location. The continuous range of Ni substitution contrasts the discrete substitution behavior of Cu in Ba₈Ge₃₀₄ₓCuₘ.
suggested that stabilization of the Ni material may depart from the bond-filling Zintl mechanism.

The characteristic NMR shifts (described below).

We find Ni-Ga clathrates to be non-magnetic, in contrast to the Fe-substituted materials [5]. Figure 3 shows the weak paramagnetism of Ba$_9$Ge$_{30}$Ga$_{12}$Ni$_4$ (with a low-temperature Curie tail). Ba$_9$Ge$_{30}$Ga$_{16}$ exhibits similar behavior, which is distinct from the large diamagnetism of Cu-clathrate [7]. Ni clathrates also exhibit metallic-like electrical resistivity (Fig. 3), with a magnitude and temperature dependence very close to those of as-prepared Ba$_9$Ge$_{30}$Ga$_{16}$, which is an $n$-type semiconductor doped into the low-density metallic range [2]. Thus, though the continuous substitution behavior of the Ni clathrate signals non-Zintl behavior, and stronger metallic response might be expected for this material, little change is observed in transport, nor do we observe significant changes in NMR shifts (described below).

Static-sample $^{71}$Ga NMR yields Knight shifts ($K$) in the range 0.063% to 0.085% for all samples, considerably smaller than that of Ga metal, $K = 0.43%$. The $T_1^{-1}$ relaxation time was found to be linear in $T$, characteristic of metallic relaxation [8], for Ni and Fe substituted samples as well as Ba$_9$Ga$_{16}$Ge$_{30}$. An analysis assuming a single electron pocket with $m^* = 3$ and $n = 1.5 \times 10^{20} \text{ cm}^{-3}$, values typical of (unsubstituted) Ba$_9$Ga$_{16}$Ge$_{30}$ [2] gives $K = 0.20%$. In this analysis, the conduction band $s$-orbital fraction was assumed to be 1/4, corresponding to $sp^3$ hybridization. The reduced values observed may indicate a smaller $s$-fraction in these materials.

The NMR shifts scale so that $K^2T_1T = (6.5 \pm 0.3) \times 10^{-6} \text{ s}$ for all samples, except the more heavily-doped Fe samples, for which $K^2T_1T$ decreases to $4.4 \times 10^{-6} \text{ s}$.

Except for these samples, $K^2T_1T$ is enhanced by a factor 2.3±0.1, typical of ordinary metallic behavior [8]. From the small change in NMR and resistivity upon substitution, we infer that there is little change in electron density and scattering rate except in more highly Fe-substituted samples.

![FIGURE 2. Ba$_9$Ge$_{30}$Ga$_{12}$Ni$_4$ Cu K$_\alpha$ x-ray pattern, and fit to type-I structure. Inset: Ba$_9$Ge$_{30}$Ga$_{16}$Ni$_4$ lattice parameter vs. $x$. Dashed line is guide to the eye.](image)

![FIGURE 3. Magnetic susceptibility and electrical resistivity for Ba$_9$Ge$_{30}$Ga$_{12}$Ni$_4$.](image)

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REFERENCES