Phases of gallium nucleated by small particles

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Abstract. Several structural phases of gallium can be nucleated upon cooling of mixtures of liquid gallium and an excess of particulate material. One such structural phase, which we label the theta phase, was observed in gallium and fullerene mixtures and is efficiently nucleated only by particulate material of small particle size such as soot or the separation products of soot. The θ-phase is possibly a recently discovered phase of gallium.

1. Introduction

Gallium is an obvious candidate to consider for the study of mixtures of metal and small particles of nonmetal. The α-phase, which is the stable phase at atmospheric pressure, melts at approximately 30 °C so one can readily form liquid gallium which can be mixed with another material. The low melting temperature is particularly advantageous for work with the fullerenes since at that temperature the fullerenes will not degrade significantly even in air. Also gallium can be obtained in highly pure form and is not prone to severe oxidation. It will wet a large number of materials and this makes it more likely that mixtures containing gallium will have interesting interactions. Gallium has several superconducting structural phases and, since it is well known that superconducting transitions are sensitive to factors like impurity levels and surface conditions, information about a superconducting transition can be used as a diagnostic to indicate the degree of interaction of the materials comprising a mixture.

Gallium exhibits a large degree of polymorphism. Prior to this work at least ten different solid phases were reported [1, 2]. At atmospheric pressure there are at least five crystalline structural phases of which the α-phase is stable and the β-, γ-, δ- and ε-phases are metastable. This work presents magnetic susceptibility data on mixtures of gallium and various particulate materials which indicate the existence of an unusual phase. For both a mixture of gallium plus fullerenes and a mixture of gallium plus titanium nitride soot, an unexpected superconducting transition was observed to occur at $T = 7.23 \pm 0.02$ K. The titanium nitride result rules out the possibility that the transition is due to some kind of gallium–fullerene compound. Therefore, the material undergoing the unexpected superconducting transition is a structural phase of gallium. It has been labelled the θ-phase.

We briefly list some of the important properties of gallium. Table 1 shows the superconducting transition temperatures of the structural phases of gallium that are stable or metastable at atmospheric pressure, including the θ-phase and except for two phases (ζ and η) reported to exist [2] at intermediate temperatures during cooling. There also exist two high pressure phases [1, 3], Ga(II) and Ga(III), which are not considered in detail here. For the

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Table 1. Superconducting transition temperatures of some phases of Ga which exist at atmospheric pressure.

Phase	T_c (K)
α-Ga	1.0833
β-Ga	6.07 [10]
γ-Ga	7.62
δ-Ga	7.85
ε-Ga	6.9
θ-Ga	7.23
Amorphous Ga	8.5

phases metastable at atmospheric pressure, the method of forming small metal globules by the dispersion of liquid metal in a heated fluid [2, 4] can be used to produce globules that are small enough and separated enough that single phases can form. As the globule size decreases so does the probability that it will contain a potent nucleation site and this is thought to be the condition which allows the metastable phases to form with some reasonable probability. Gallium has a remarkable tendency to supercool [5] and some small globules formed by the method described above can remain liquid down to 130 K [6]. For these reasons, gallium is a particularly interesting material for the study of systems in which multiple phases can be nucleated.

2. Experimental procedure and results

2.1. Sample preparation

Although many different types of powder will nucleate the α- and β-phases of gallium, the formation of the θ-phase required relatively special conditions. In order to nucleate that phase with particulate material, it was necessary to combine gallium with an excess of material of small particle size where small in this case refers to the size of particles found in soot or separation products of soot such as the fullerenes. Since the fullerenes are van der Waals bonded, it is reasonable to assume that this size approaches the 7.1 Å diameter of a single C_{60} molecule. Excess in this case means a volume ratio of particulate material to gallium greater than 3 to 1. Since the particulate material is not a constituent of the structural phase of gallium, but serves as a dispersing medium and as a matrix on which the various phases nucleate, there is obviously considerable freedom in the relative ratio of the two. The practical reason for working with volumes was due to problems with electrostatic forces while attempting to weigh extremely fine powders like soot. Of course, with sufficient care, weighing can be accomplished and a typical sample had a weight ratio of 1 mg of Ga to 2 mg of particulate material.

The mixing can be done with two pieces of plate glass. Glass plates were warmed until they were slightly above 30 °C and then the materials were placed between the plates and mixed with very light pressure and a circular motion of one of the plates. If the material spread to the edges, it was moved back to the centre and mixing was continued. There was no need to keep the temperature above 30 °C because once gallium has melted it will remain liquid to temperatures well below room temperature. The disappearance of the metallic coloured regions gave a good indication of when mixing was sufficiently complete. No attempt was made to exclude oxygen. Excessive pressure on the glass plates opposes mixing because it results in the liquid gallium being pressed out of the particulate material.

A number of different particulate materials were tried but the only ones found to efficiently nucleate the θ-phase were C_{60}, C_{70}, fullerene mixtures, carbon soot and titanium nitride soot. For example, graphite powder will nucleate the α- and β-phases but never nucleated any
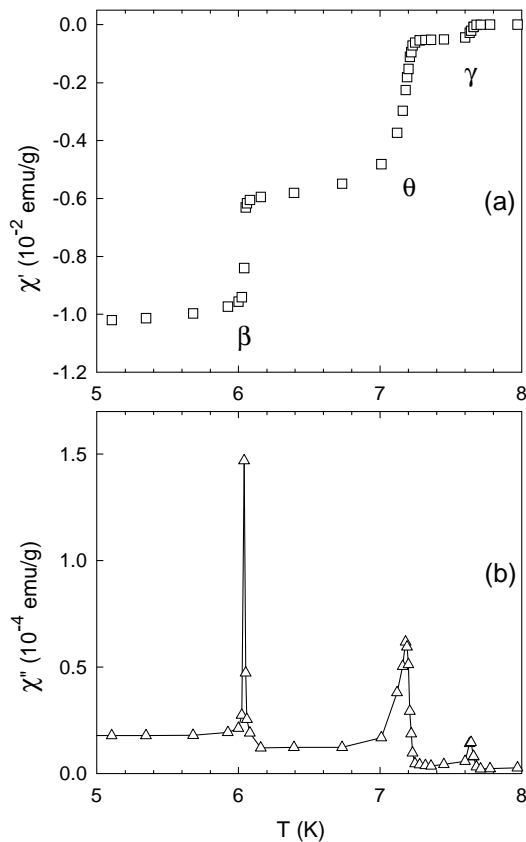
Figure 1. (a) χ' and (b) χ'' versus T from a mixture of gallium and titanium nitride soot in the form of a loosely packed powder (sample 1). The presence of the β-, θ- and γ-phases is indicated by the transitions at 6.07, 7.23 and 7.6 K respectively.

measurable amount of the θ-phase. The two types of soot were produced in a chamber suitable for fullerene production. The titanium nitride soot was produced under conditions of pressure and current that were comparable to those of the arc method of fullerene production but nitrogen was used instead of helium and the electrodes were made of titanium instead of graphite. Clusters of $(TiN)_n^+$ have been produced by a laser-induced plasma reactor source [7]. In analogy with the development of fullerene production from laser-induced to arc methods, an attempt was made to use an arc to produce titanium nitride particles of a size range down to that of clusters.

It should be noted that the surface properties of the particulate material have a strong effect on the resulting mixture. For example, once soot has been exposed to a liquid, it clumps together upon drying and thereafter will only nucleate the α- and β-phases. The fullerenes do not suffer from this problem as long as the solvents are sufficiently pure and the residual solvent can be adequately driven off from the crystals before they are mixed with gallium.

2.2. Magnetic susceptibility versus temperature

The sensitivity of susceptibility measurements provides a powerful method of determining the existence of multiple superconducting structural phases in a polymorphic gallium sample.
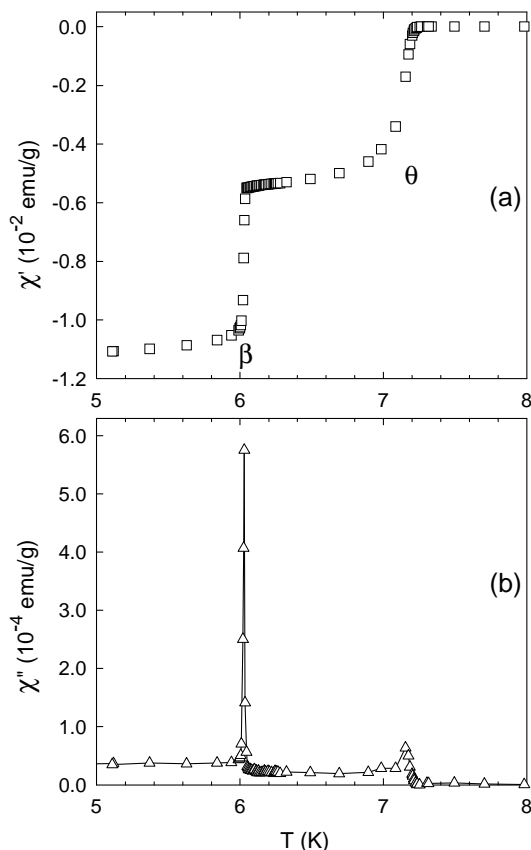
Figure 2. (a) χ' and (b) χ'' versus T from a mixture of gallium and C_{60} in the form of a loosely packed powder. The presence of the β- and θ-phases is indicated by the transitions at 6.07 and 7.23 K respectively.

The measurements were taken using a Lake Shore 7225 susceptometer/magnetometer. The temperature was calibrated and estimated to be accurate to ± 0.02 K. A gallium rod of 5 N purity was purchased from Electronic Space Products International. Pieces of approximately 100 mg mass were broken off and magnetic susceptibility measurements taken near 4.2 K showed a signal characteristic of eddy currents with no superconducting transition evident. Various mixtures were then examined. Figure 1 shows susceptibility data from sample 1 consisting of a mixture of titanium nitride soot and gallium with transitions at 6.07, 7.23 and 7.6 K corresponding to the β-, θ- and γ-phases respectively. Figure 2 shows susceptibility data from a gallium plus C_{60} mixture with transitions at 6.07 and 7.23 K corresponding to the β- and θ-phases respectively. The transition for α-Ga at 1.08 K is below the temperature range of the susceptometer. The transition at 7.23 K does not correspond to any well established superconducting transition temperature for a previously reported phase of gallium. It is the same as the superconducting transition temperature of Pb but significant contamination has been ruled out.

An attempt to corroborate the susceptibility data with powder x-ray diffraction data taken at 80 K proved to be inconclusive. The susceptibility data from sample 1 (figure 1) in the temperature range of 4.2 to 8 K indicate the presence of phases in addition to the α- and β-phases, but the x-ray data at 80 K show only the α- and β-phases. Yet the sizes of the
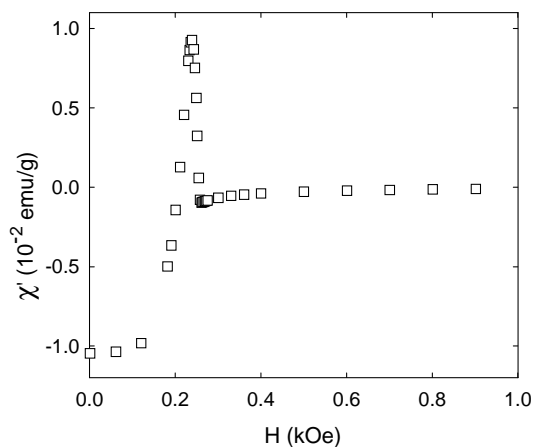
Figure 3. χ' versus H at 4.2 K from a mixture of gallium and carbon soot showing the differential paramagnetic effect.

transition steps in the susceptibility data indicate that, at least at 4.2 K, there should be comparable amounts of β- and θ-gallium.

2.3. Magnetic susceptibility versus applied field H

These mixtures also exhibit the differential paramagnetic effect [8]. Figure 3 shows χ' versus H data at 4.2 K for a newly made mixture of gallium plus carbon soot. The effect decreases to zero after the sample is kept at room temperature for several days. These results are not surprising since differential paramagnetism is related to the surface properties of a superconductor and these mixtures contain small particles of gallium; therefore the surface to volume ratio is large. The decrease of the effect over a period of days is most likely due to oxidation.

3. Discussion

The crystallization processes occurring between room temperature and 4.2 K are remarkably reversible with respect to thermal cycling. Upon returning from 4.2 K to room temperature, some if not all of the gallium becomes liquid again as was evident from the fact that moderate pressure on the mixtures caused liquid gallium to be pressed out. The cooling to 4.2 K was not done in a systematic way since it simply involved inserting the sample into the cryostat. In fact, the rate of sample insertion was varied in order to determine whether that would change the relative ratio of β- to θ-Ga as evidenced by changes in the two transition step heights. Unexpectedly, the step heights were very insensitive to variations in the cooling process.

There are consistent differences in the shapes of the β- and θ-Ga superconducting transitions. Although the χ' step heights are comparable in size, the superconducting transition due to the θ-phase is always more rounded than that of the β-phase. There are also differences in χ'' as shown in figures 1(b) and 2(b). The β-phase generally has a sharper and higher change in χ''.

Attempts to separate the phases contained in the mixtures proved to be unsuccessful in spite of the fact that for the gallium plus fullerene mixtures, the excess fullerenes could be removed with any of a number of suitable solvents. The metal rich gallium–fullerene composite that remained after washing contained a combination of the phases for all individual globules on

which susceptibility measurements were performed and it is not known whether the θ-phase can exist without the presence of the particulate material.

It is possible that strong surface interactions between the particulate material and one of the previously reported (α, β, γ, δ, ε, amorphous) structural phases of gallium could cause a shift in the superconducting transition temperature of that phase. However, such a shift due to surface interactions would be expected to be strongly sample dependent. More than ten distinct samples exhibited a transition at 7.23 ± 0.02 K and the 0.02 K error bar is meant to take into account a possible systematic error in calibration and is greater than one standard deviation. In particular, it is unlikely that both C_{60} and titanium nitride soot would cause the same shift in transition temperature. Even for a single type of particulate material such as C_{60}, it is unlikely that all C_{60} plus gallium mixtures would exhibit the same shift.

The θ-phase may have been observed during work on gallium in porous glass for which a phase with a superconducting transition near 7.0 K was reported [9]. This phase was conjectured to be either γ-Ga or a new structural phase and the x-ray data supported the possibility of a newly discovered phase. If the constrained geometry of porous glass can result in the formation of a new structural phase of gallium, then a similar geometrical or surface effect could be occurring due to gallium interacting with small particles.

Acknowledgments

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