

revised  
10-12-01

IS.M 907

## The fruition of *4f* discovery, the interplay of basic and applied research

K.A. Gschneidner, Jr.

Ames Laboratory\* and  
Department of Materials Science and Engineering  
Iowa State University  
Ames, IA 50011-3020 USA

**Keywords:** magnetic refrigeration, supercooling, superheating, regenerator materials, magnetocaloric effect, erbium, dysprosium,  $Gd_5(Si_xGe_{1-x})_4$ , Pr-doped Er alloys

**CONTACT:** K. A. Gschneidner, Jr.  
Ames Laboratory  
Iowa State University  
Ames, IA 50011-3020  
Telephone: 515-294-7931  
Facsimile: 515-294-9579  
E-mail: cagey@ameslab.gov

**Abstract**

A broad base of knowledge is necessary for the successful solution to applied problems, but on the other hand, developing such practical solutions can open the door to new and exciting adventures in basic research. Several such synergistic events are briefly described. These include the design and development of magnetic refrigerant materials (1) for the liquefaction of  $H_2$  gas, and (2) for near-room temperature cooling and refrigeration; and (3) the design and development of cryocooler regenerator materials. The first led to the discovery of both supercooling and superheating in the same substance (Dy and Er); the second to the discovery of the giant magnetocaloric effect, the colossal magnetostriction, and the giant magnetoresistance in the same substance  $[Gd_5(Si_xGe_{1-x})_4]$ ; and the third the disappearance of three of the four magnetically ordered phases in Er by Pr additions in both high purity Er and commercial grade Er.

## 1. Introduction

Before ~1990 most of my efforts were concerned with basic research involving several different areas: (1) the preparation and purification of the rare earth metals; (2) phase relationships and crystal structures of metallic rare earth alloys; (3) the theory of alloy phase formation; (4) low temperature heat capacity measurements as a function of magnetic field of the pure rare earth metals and intermetallic compounds; (5) electrical and magnetic property measurements on rare earth intermetallics; and (6) intermediate valences in Ce and Ce-based compounds. Although I was focused on the fundamentals and the basic knowledge of chemical, metallurgical and physical phenomena, I have had an appreciation of applied research, technology transfer and the business side of the rare earth field. This awareness was developed and enhanced as the Director of the Rare-earth Information Center (RIC). The merging of these two proclivities, however, did not occur until the late 1980's and early 1990's.

One of the driving forces for this merger was the expectation that long term, continuing funding would shrink or at best remain constant for basic research on the low temperature behaviors of anomalous  $4f$  systems, such as heavy Fermions, mix valent behavior, co-existence of magnetism and superconductivity. Although these fields of research are still popular, new discoveries and other advancements (e.g. quasicrystals, high temperature ceramic superconductors), and the limited availability of funds has led to a continuous redistribution of research dollars. As a result, I began to think about new research areas which have the following characteristics: it is basic in nature, has a lot of pizzazz and is relevant to the United States Department of Energy's (my primary and long time funding agency for which I am thankful) mission. The second driving force was discussions with John Barclay (Los Alamos National

Laboratory and later at Astronautics Corporation of America) about magnetic refrigeration for cooling especially below 77 K (the boiling point of liquid N<sub>2</sub>).

## **2. Liquefaction of H<sub>2</sub> gas**

In late 1989 we helped John Barclay, then at Astronautics Corporation of America (ACA), put together a proposal for the liquefaction of H<sub>2</sub> gas, which condenses at 20 K. The ACA proposal was funded in June 1990. Our contribution was to develop new and cost effective magnetic alloys or intermetallic compounds as "active magnetic regenerator" (AMR) materials used in the low temperature stage of a magnetic refrigerator (MR) for the liquefaction of H<sub>2</sub>. The goal was to replace GdPd, an intermetallic compound, which orders at 40 K and has good magnetocaloric properties for an AMR/MR. Obviously, the high cost of Pd metal (\$2800/kg) limits its usefulness in an economically viable and practical MR. We were successful in designing several new materials which were much less expensive. The best, and also the lowest cost, material was (Dy<sub>0.5</sub>Er<sub>0.5</sub>)Al<sub>2</sub>. Not only was Pd replaced by inexpensive Al, the magnetocaloric properties of the compound were 20% better than that of GdPd [1-3]. This was our first success in which basic knowledge of *4f* electron systems enabled us to provide a solution to a practical problem.

## **3. Supercooling and superheating**

From this initial work on hydrogen liquefaction AMR materials, it was apparent that our low temperature, high magnetic field calorimeter which for many years had an upper temperature limit of 20 K, but was extended to ~40 K by minor modifications, would seriously limit our research on magnetocaloric materials. Thus, I submitted a proposal (December 1989) for internal Ames Laboratory funds to construct a high magnetic field (0-100 kOe) calorimeter to operate between ~3.5 and 350 K. This would allow us to study the magnetothermal behavior of materials up to, and just above, room temperature. There were several unique things associated with this small sample (~1 gm) adiabatic calorimeter: (1) a very low mass addenda, (2) a drifting, not precisely controlled heat shield, (3) a software program which completely controlled the operating parameters and data collection process without human intervention once the calorimeter was started, and (4) an extremely high sensitivity with an accuracy of 0.5 to 1.0% over the whole temperature range [4]. The apparatus became fully operational in the summer of 1993.

Although the calorimeter was built primarily to work on an applied problem, we also used it for basic research. One such an effort involved determining the heat capacity of some extremely high purity Dy and Er metals as a function of temperature and magnetic field. Much to our surprise, when we measured the heat capacity of Dy during its first order magnetic/crystallographic phase transition at ~90 K, the sample was actually colder after a heat pulse than before the heat pulse; normally a sample heats up when energy is introduced into the sample (heat pulse). This was the first observation of superheating in an unrestrained sample [5]. A similar effect was observed in the first order magnetic transition in Er at ~19 K [6]. Additionally we used the calorimeter to make heating and cooling curves, and we observed both supercooling and superheating in both Dy and Er, another first. But the story does not end here. Dy

undergoes the first order transformation directly from the high temperature antiferromagnetic phase to the low temperature ferromagnetic phase and back with no evidence for an intermediate state, but in Er we observed two intermediate metastable states on cooling and four on heating while undergoing this first order transition [6]. These experimental findings sparked the interest of theoretical physicists and it is becoming clear that the anomalies are probably due to the large magnetostatic effects of the localized  $4f$  electrons [7]. It was the small mass of the addenda (and the high sensitivity) of the calorimeter which was critical in making these discoveries; these effects were not observed in our earlier measurements on exactly the same Er sample [8] using the old 1-20 K calorimeter with an addenda mass about 5 times larger than that of our new 3.5 to 350 K calorimeter.

In this case, the development of a unique apparatus to carry out applied research allowed us to make some exciting discoveries about the fundamental nature of first order transformations in solids, especially the lanthanide metals.

#### **4. Proof-of-principle magnetic refrigerator**

As a result of our work on the liquefaction of  $H_2$  using an AMR/MR we realized that if low temperature magnetic refrigeration is as efficient as it appeared, tremendous amounts of energy could be saved if magnetic cooling replaced today's conventional gas compression technology. A detailed analysis indicated that for large scale cooling (office buildings, food processing plants [frozen and refrigerated food products], supermarket chillers, etc.) magnetic cooling would be about 30% more efficient than gas compressor units, and that it would take

about five years to recover the higher capital costs for the MR units. With this analysis in hand, we submitted a joint Ames Laboratory/Astronautics proposal to the U.S. Department of Energy's Advanced Energy Projects to design, construct and test a near room temperature proof-of-principle apparatus. This three year project was funded in the spring of 1994. In February 1997, we announced the successful operation of the proof-of-principal apparatus, which had been in operation for about two months at that time. By the time the apparatus had been shut down it had been operating for over 1500 hours over an 18 month period (5 days a week, 8 hours a day) without any major problems [9].

The active magnetic regenerator consisted of two 1.5 kg beds of 0.3 mm diameter Gd spheres. The Gd spheres were made by an American company from a commercial grade of Gd (95 at.% pure) purchased from a Chinese vendor. The heat transfer fluid was water. The apparatus achieved a cooling power of 600 watts at a magnetic field of 5 T, a temperature span (the temperature difference between the hot and cold heat exchangers) of 38 K, a maximum COP (coefficient of performance – the heat removed at the cold end divided by the work required to operate the refrigerator) of 16 (most gas compression refrigerators/freezers have COP's of 1 to 3), and a Carnot efficiency of 60% [9]. Since then a Japanese team from Toshiba and Chubu Electrical Co. has essentially duplicated these results [10].

##### **5. The extremum material – $Gd_5(Si_xGe_{1-x})_4$**

As part of the Advanced Energy Project on demonstrating the feasibility of magnetic refrigeration, the Ames Laboratory team was to furnish the magnetic refrigerant for the proof-of-

principle apparatus (see § 4) and to evaluate known magnetic materials with magnetic ordering temperatures near room temperature for their magnetocaloric properties. To improve the efficiency of a magnetic refrigerator it may be necessary to use a material which has a magnetic ordering (Curie) temperature higher than that of Gd (293 K). Only a few Gd-based compounds have Curie temperature ( $T_C$ ) greater than 293 K; these include  $Gd_4Bi_3$  ( $T_C = 333$  K) and  $Gd_5Si_4$  ( $T_C = 336$  K). Our initial choice was to study  $Gd_5Si_4$ , which in hindsight was a good one since recent research [11] shows that the magnetocaloric effect in  $Gd_4Bi_3$  is not nearly as large as in  $Gd_5Si_4$ .

Research in the late-1960's by Holtzberg *et al.* [12] reported that the substitution of Ge for Si would lower the  $T_C$  of  $Gd_5Si_4$ , but at about a 50% replacement of the Si atoms, a new crystal structure was formed, and that at even higher Ge contents the magnetic structure changed from ferromagnetic (at  $Gd_5Si_4$ ) to antiferromagnetic (at  $Gd_5Ge_4$ ). Since more detailed information would be needed for the utilization of  $Gd_5Si_4$ -based materials in magnetic refrigerators, we began a thorough crystallographic, magnetic and thermal study of the  $Gd_5(Si_xGe_{1-x})_4$  pseudo-binary system. The substitution of Si by Ge slowly lowers  $T_C$  from 336 K at  $x = 1$ , the  $Gd_5Si_4$  composition, to  $\sim 300$  K at about  $x = 0.5$ , the  $Gd_5(Si_2Ge_2)$  composition, see Fig. 1. At the  $Gd_5(Si_2Ge_2)$  composition there is a sudden change in the properties and behavior of the  $Gd_5(Si_xGe_{1-x})_4$  alloys: the room temperature crystal structure changes from orthorhombic for  $x > 0.5$  to monoclinic for  $x \leq 0.5$  and  $T_C$  drops from  $\sim 300$  K to  $\sim 275$  K, see Fig. 1. The effect of this crystal structure change on the physical properties are discussed in the next five paragraphs. Further Ge additions rapidly lowers  $T_C$  from  $\sim 275$  K to  $\sim 140$  K at  $x = 0.24$ , and a new phase forms for  $x < 0.24$  which has the  $Sm_5Ge_4$ -type orthorhombic structure at room temperature. It exists over a solid solution region from  $x = 0.20$  to  $x = 0$  ( $Gd_5Ge_4$ ). The

magnetic ordering process for the latter alloys, however, is more complicated in that the paramagnetic phase first changes to an antiferromagnetic phase between  $\sim 140$  K at  $x = 0.20$  to  $\sim 125$  K at  $x = 0$ , and the antiferromagnetic phase in turn undergoes a first order transition to a ferromagnet with  $T_C$  falling rapidly from 130 K at  $x = 0.20$  to  $\sim 15$  K at  $x \sim 0$  (see Fig. 1) [13-18]. There is also a crystal structure change associated with the magnetic transformations for the Ge-rich alloys with  $x \leq 0.5$ : the monoclinic phase [ $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ -type structure] transforms on cooling to the orthorhombic  $\text{Gd}_5\text{Si}_4$ -type structure for  $0.24 \leq x \leq 0.5$ ; and the orthorhombic  $\text{Sm}_5\text{Ge}_4$ -type structure transforms on cooling to the orthorhombic  $\text{Gd}_5\text{Si}_4$ -type structure for  $0 \leq x \leq 0.2$ . In both cases these are first order simultaneous magnetic/structural transformations. The paramagnetic to ferromagnetic transformation for  $0.5 \leq x \leq 1.0$  and the paramagnetic to antiferromagnetic transformation (at  $\sim 140$  K) for  $0 \leq x \leq 0.2$  are both second order transformations and are strictly magnetic phase changes.

The three crystal structures in the  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  pseudo-binary are closely related and consist of layers (slabs) that are infinite in the  $a$  and  $c$  directions and the slabs are connected in the  $b$  direction by (Si,Ge) atoms which in the case of the  $\text{Gd}_5\text{Si}_4$ -type structure form covalent pairs. However, in the intermediate phase, the  $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ -type structure, only half of the possible covalent pairs are formed, while in the  $\text{Sm}_5\text{Ge}_4$ -type structure all of the inter-slab Ge-Ge bonds are broken (i.e. no covalent pairs are formed) [15 and 17]. It is interesting to note that only the  $\text{Gd}_5\text{Si}_4$ -type structure which has all possible covalent pairs of (Si,Ge) atoms is ferromagnetic. The intermediate monoclinic form is only paramagnetic, while the  $\text{Sm}_5\text{Ge}_4$  orthorhombic type phase is either paramagnetic or antiferromagnetic.

We will now focus our attention on the physical properties associated with the first order magnetic transitions. As is the case with all first order transitions, they are hysteretic in nature

with a temperature difference on cooling from that on heating of 5 to 8 K while holding the magnetic field constant. When the temperature is held constant, the field hysteresis is 5 to 10 kOe for the increasing field value vs. the decreasing field value. Initial property measurements on the  $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$  phase revealed the unique nature of these materials [13]. Both the zero magnetic field heat capacity and the magnetization measurements near  $T_C$  showed that the magnetic transition was of first order, e.g. the heat capacity showed a narrow peak at  $T_C$  rather than the typical lambda-type peak for a typical second order magnetic transition. Furthermore, when calculating the magnetocaloric effect (MCE) from both the magnetization data and the magnetic field dependence of the heat capacity, extremely large values were obtained for  $\Delta S_M$  (the MCE in terms of the isothermal entropy change) and  $\Delta T_{ad}$  (the adiabatic temperature change), about twice as large as that of Gd metal for  $\Delta S_M$  and ~30% larger for  $\Delta T_{ad}$ . This effect was known as the “giant MCE” [13]. For compositions richer in Ge the giant MCE was up to 600% larger than those measured in the previously best known materials [14].

Later measurements [15-18] showed that this crystallographic/magnetic transformation is accompanied by large shear movements of the slabs relative to one another, leading to changes of ~0.8 to ~1.3 Å in the inter-slab distances along the  $a$  axis. This translates into a colossal magnetostriction of 9,000 to 16,000 parts per million, i.e. approximately ten times larger than that observed in Terfenol D  $[(\text{Tb}_{0.3}\text{Dy}_{0.7})\text{Fe}_2]$ , which is one of the best performing commercially available magnetostrictive materials [19].

Also in the same time frame, resistance measurements as a function of magnetic field revealed that there is also a giant magnetoresistance change of about 25% associated with this crystallographic/magnetic transition [20-22]. This effect is about the same as found in artificial multilayered thin films used as read heads in the magnetic recording devices. The sign of the

giant magnetoresistance has been found to be both negative (for  $x = 0.45$  [20] and  $0.5$  [21]) and positive for  $x = 0.375$  [22]) in the  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  pseudo-binary system. The reason for the change in sign is not understood.

More recently, a resistivity study of  $\text{Gd}_5\text{Ge}_4$  revealed another surprise, the occurrence of a metal/semiconductor transition at the paramagnetic to antiferromagnetic transition ( $T_N = 130$  K) [23]). At high temperature the magnetically disordered phase exhibits semiconducting behavior, and at low temperature the magnetically ordered phases have a metallic resistivity. Theoretical calculations (tight-binding linear muffin-tin orbital method) suggest that the high temperature phase behaves as a Mott-Hubbard semiconductor.

A more complete description of the crystallographic symmetry and magnetic order of the three phases of the  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  system was recently published [24]. To date only a few compositions in this and other  $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$  systems have been examined, and as often is the case in basic research, many more questions than answers were uncovered. What is clear, however, is that the  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  system bridges the gap between bulk  $4f$  electron based magnetic systems and artificial magnetic multilayers due to the unique nano-layered crystallography and the intimate relationship between the chemical composition, bonding, atomic structure and magnetism. Unlike with artificial nano-layered materials, the control over the crystal structures and thus the properties of the  $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$  materials is straightforward and repeatable, and with time, they should find their place in many applications based on new findings.

## 6. Cryocooler regenerator materials

Cryocoolers are refrigerators which are used in small to medium size systems to reach low temperatures between 4 and 100 K without the use of liquid cryogens, such as liquid He, or liquid H<sub>2</sub>, or liquid N<sub>2</sub>. One of the crucial components of the cryocooler is the regenerative heat exchanger containing a high heat capacity solid (regenerator material) which is used to absorb heat from a gas (thus cooling the gas) on one side of the cycle, and then on the reverse side of the cycle the heat from the regenerator is transferred to the gas which carries the heat to the hot heat exchanger where it is exhausted to the ambient atmosphere. Stainless steel or bronze is used as the regenerator material to cool down to about 50 K. In order to cool below 50 K a second stage regenerator, which is made up of Pb, is added to the cryocooler. Lead is used because it has a high heat capacity below 50 K, while that of stainless steel or bronze drops off and becomes too small to serve as a suitable regenerator material. Lead has the same problem when temperatures lower than 10 K are required. To reach 4 K a magnetic lanthanide material as the lower stage regenerator is required. This compound regenerator consists of either Er<sub>3</sub>Ni or HoCu<sub>2</sub> at the low temperature end of the regenerator and Pb at the high temperature side of the regenerator.

The regenerator bed generally consists of fine spherical powders, but occasionally may be parallel plates, or jelly rolls, or wire mesh, or screens instead of the spheres to improve the efficiency of the cryocooler. But since Er<sub>3</sub>Ni or HoCu<sub>2</sub> are brittle intermetallics the only useful form is spheres. Furthermore, since the high heat capacity of the two lanthanide compounds comes from the magnetic ordering of the lanthanide metal, the heat capacity is high only over a fairly narrow temperature range near the compound's ordering temperature. Because of these limitations the cryogenic engineers would like to have a series of magnetic solids with (1) a large

magnetic heat capacity with ordering temperatures below 20 K, and (2) which are ductile and thus can be fabricated into a variety of shapes.

Because of our successful research on magnetic solids for magnetic refrigeration, Ben Helvensteijn of Atlas Scientific asked us at the 1997 Cryogenic Engineering Conference in Portland, Oregon if we could find or develop materials which might meet these requirements. Working with Ben Helvensteijn and his colleague Ali Kashani we were able to get some funding from NASA to see what we could accomplish to provide a solution(s) to these two limitations.

Since Er metal orders at 19, 25, 52 and 88 K and has a heat capacity which is ~25% larger than that of Pb from ~15 to ~90 K, and essentially the same from 5 to 15 and 90 to 300 K it looked like an attractive candidate material, especially if the 19 and 25 K magnetic ordering temperatures could be lowered by alloying. A number of non-rare earth and rare earth metals were added to Er to see what affect they would have on the magnetic ordering temperature. Most alloying agents tended to destroy or hinder the magnetic ordering processes at 19, 25 and 52 K, and lower the 88 K heat capacity peak. The heavy lanthanide metals additions were not particularly effective since they either raised the magnetic transitions or wiped them out. Praseodymium was found to be particularly useful in changing the Er transition temperatures: the combined 19 and 25 K transitions, which had merged into one transition at 22 K in the commercial grade of Er used in this study, rose slowly up to 10 at.% Pr, and then dropped to ~10 K at 20 at.% Pr where it appears to end at a critical point. The 52 K transition was initially lowered, but then remained constant at 35 K for 5 to 35 at.% Pr additions, and eventually merged with the 88 K transition, which dropped rapidly with increasing Pr concentration, at ~25 at.% Pr. Heat capacity measurements revealed the 27 at.% Pr-Er alloy would be an excellent replacement for Pb for cooling down to ~10 K. But if it were combined with a 50 at.% Pr-Er alloy in a

compound low temperature stage regenerator (where the 50:50 alloy is at the cold end and the 27:73 alloy at the hot end) the efficiency and the cooling power would be increased even more [25]. Indeed to date we have demonstrated that commercial grade Er is as good or slightly better as a regenerator material than Pb in a two stage Gifford-McMahon cryocooler [26].

Furthermore, in the United States since Pb is a federally regulated material that is classified as a poison, and since Er and Pr are non-toxic, there are environmental reasons for replacing Pb in cryocooler regenerators.

## 7. The Er-rich, Er-Pr magnetic phase diagram

The development of Pr-Er alloys for cryocooler applications lead to some interesting observations concerning the affect of Pr doping on the magnetic properties of Er, as noted above in § 6. But since a low purity commercial grade of Er (96.8 at.% pure) was used in the development of the cryocooler materials [25], the high level of O, N and C impurities (2.7, 0.3 and 0.2 at.%, respectively) in the Er may have had a significant influence on the observed magnetic behaviors. Thus, in order to determine the effect of Pr on the magnetic Er structures, high purity Er and Pr prepared at the Ames Laboratory (both 99.8 at.% pure) were used in this study.

Even in the preliminary stages of this study we find that there are significant differences between the magnetic ordering temperatures of commercial grade Er and the Ames Laboratory prepared Er metals, and naturally the  $\text{Er}_{1-x}\text{Pr}_x$  magnetic phase diagram ( $x \leq 0.5$ ). In the commercial grade Er the 19 K Curie temperature ( $T_C$ ) and the 25 K spin-slip transition have

merged into one magnetic transition at about 22 K, the 52 K transition remains unchanged; and the 88 K Néel temperature ( $T_N$ ) is lowered by about 4 K to 84 K. Pr additions lower  $T_N$  rather rapidly for both grades of Er metal and at about the same rate. In the high purity Er, 10 at.% Pr is sufficient to destroy both the 52 and 25 K transitions. Unfortunately, this is the lowest Pr concentration alloy we have studied to date and additional alloys with smaller Pr contents are needed to delineate the influence of Pr on these two Er transitions. In the Ames Laboratory Er, the 19 K  $T_C$  is raised by Pr additions and appears to be merging with the 88 K  $T_N$  at ~35 at.% Pr (at 30 at.% Pr the two ordering temperatures are about 4 K apart). Thus we see that for both Er samples two magnetic transitions merge (but not the same ones) to give only one ordered ferro or ferri-magnetic phase at a Pr concentration greater than ~30 at.%. At this point in time we are not able to describe the magnetic ordering in the various phases in the Pr-Er system, but magnetization measurements and neutron scattering studies, which are underway, should help us to determine the magnetic structures of these magnetic phases and to see if some additional surprises are in store for us.

## 8. Conclusions

As described above, over the last twelve years an effective synergism has developed between basic and applied research on  $4f$  electron materials, which has helped on one hand to advance the development of magnetic refrigeration to a point where it may soon be commercialized, and to improve the cooling power and low temperature limit of commercially available cryocoolers. The applied research on the other hand has stimulated and advanced basic research which has led to several new discoveries, such as the demonstration of superheating and

supercooling in the same material, and the co-existence of the giant magnetocaloric effect, the colossal magnetostriction and the giant magnetoresistance in the same material.

### **Acknowledgement**

The author wishes to acknowledge the useful discussions with his colleagues Prof. V. K. Pecharsky and Drs. A. O. Pecharsky and E. M. Levin. This research was carried out in the Ames Laboratory which is operated for the U.S. Department of Energy (DOE) by Iowa State University under contract No. W-7405-ENG-82. Different aspects of this work were supported in part by the DOE's Office of Basic Energy Science, Division of Materials Science; DOE's Office of Science, Advanced Scientific Computing Research, Technology Research Division; Astronautics Corporation of America, Madison, Wisconsin; and Atlas Scientific, San Jose, California.

### **References**

- [1] K.A. Gschneidner, Jr., H. Takeya, J.O. Moorman and V.K. Pecharsky, Appl. Phys. Lett. 64 (1994) 253.
- [2] H. Takeya, V.K. Pecharsky, K.A. Gschneidner, Jr. and J.O. Moorman, Appl. Phys. Lett. 64 (1994) 2739.

- [3] K.A. Gschneidner, Jr., H. Takeya, J.O. Moorman, V.K. Pecharsky, S.K. Malik and C.B. Zimm, *Adv. Cryog. Eng.* 39B (1994) 1457.
- [4] V.K. Pecharsky, J.O. Moorman and K.A. Gschneidner, Jr., *Rev. Sci. Instrum.* 68 (1997) 4196.
- [5] V.K. Pecharsky, K.A. Gschneidner, Jr. and D. Fort, *Scripta Mater.* 35 (1996) 843.
- [6] K.A. Gschneidner, Jr., V.K. Pecharsky and D. Fort, *Phys. Rev. Lett.* 78 (1997) 4281.
- [7] C.S. Durfee and C.P. Flynn, *Phys. Rev. Lett.* 87 (2001) 057202.
- [8] V.K. Pecharsky and K.A. Gschneidner, Jr., *Phys. Rev. B* 47 (1993) 5063.
- [9] C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, K. Gschneidner, Jr., M. Osborne and I. Anderson, *Adv. Cryog. Eng.* 43 (1998) 1759.
- [10] N. Hirano, S. Nagaya, M. Takahashi, K. Ito, T. Kuriyama and S. Nomura, Paper presented at the Cryogenic Engineering Conference, Paper No. C-11E-05, July 16-20, 2001, Madison, Wisconsin.
- [11] X.J. Niu, K.A. Gschneidner, Jr., A.O. Pecharsky and V.K. Pecharsky, *J. Magn. Magn. Mater.*, to be published (2001).
- [12] F. Holtzberg, R.J. Gambino, and T.R. McGuire, *J. Phys. Chem. Solids* 28 (1967) 2283.
- [13] V.K. Pecharsky, K.A. Gschneidner, Jr., *Phys. Rev. Lett.* 78 (1997) 4494.
- [14] V.K. Pecharsky, K.A. Gschneidner, Jr., *Appl. Phys. Lett.* 70 (1997) 3299.
- [15] V.K. Pecharsky, K.A. Gschneidner, Jr., *J. Alloys Compd.* 260 (1997) 98.
- [16] L. Morellon, P.A. Algarabel, M.R. Ibarra, J. Blasco, B. Garcia-Landa, Z. Arnold, F. Albertini, *Phys. Rev. B* 58 (1998) R14721.
- [17] W. Choe, V.K. Pecharsky, A.O. Pecharsky, K.A. Gschneidner, Jr., V.G. Young, Jr., G.J. Miller, *Phys. Rev. Lett.* 84 (2000) 4617.

- [18] L. Morellon, J. Blasco, P.A. Algarabel, M.R. Ibarra, *Phys. Rev. B* 62 (2000) 1022.
- [19] A.E. Clark, in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 2, (K.A. Gschneidner, Jr. and L.R. Eyring eds.), North-Holland Publishing Co., Amsterdam, 1979, p. 231.
- [20] L. Morellon, J. Stankiewicz, B. Garcia-Landa, P.A. Algarabel, M.R. Ibarra, *Appl. Phys. Lett.* 73 (1998) 3462.
- [21] E.M. Levin, V.K. Pecharsky, K.A. Gschneidner, Jr., *Phys. Rev. B* 60 (1999) 7993.
- [22] E.M. Levin, V.K. Pecharsky, K.A. Gschneidner, Jr., P. Tomlinson, *J. Magn. Magn. Mater.* 210 (2000) 181.
- [23] E.M. Levin, V.K. Pecharsky, K.A. Gschneidner, Jr. and G.J. Miller, to be published.
- [24] V.K. Pecharsky and K.A. Gschneidner, Jr., *Advanced Mater.* 13 (2001) 683.
- [25] K.A. Gschneidner, Jr., A.O. Pecharsky and V.K. Pecharsky, in *Cryocoolers 11*, R.G. Ross, Jr., ed., Kluwer Academic/Plenum Publishers, New York, NY), 2001, p. 433.
- [26] T. W. Wysokinski, J.A. Barclay, K.A. Gschneidner, Jr., V.K. Pecharsky and A.O. Pecharsky, to be published.

**Figure Captions**

Fig. 1 The magnetic transition temperatures, and the magnetic and crystallographic phases in the  $\text{Gd}_5\text{Ge}_4$ - $\text{Gd}_5\text{Si}_4$  pseudo-binary system. P = paramagnetic, F = ferromagnetic and A = antiferromagnetic.

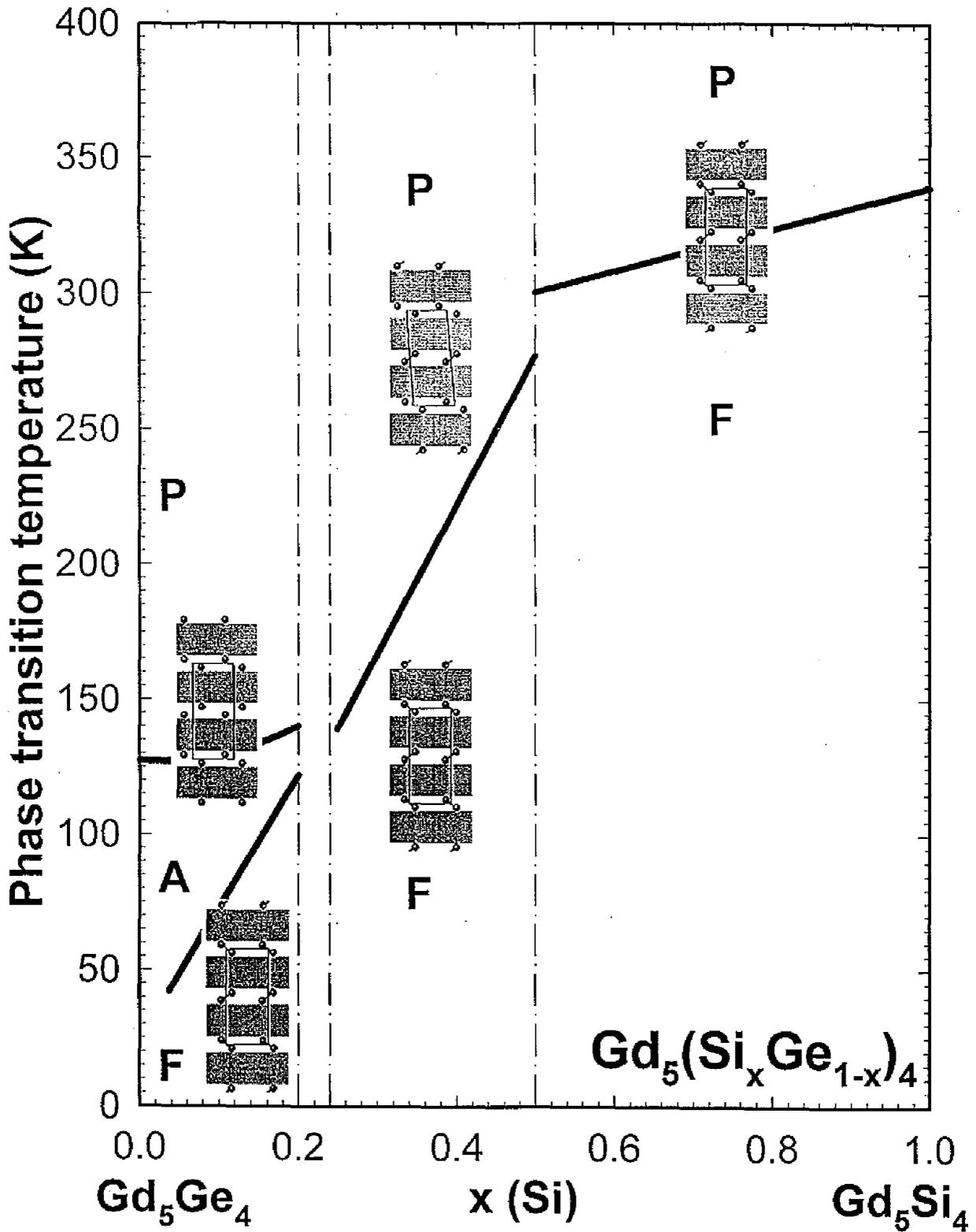


Fig. 1. The magnetic transition temperatures, magnetic and crystallographic phases in the  $Gd_5Ge_4 - Gd_5Si_4$  pseudo-binary system. P = paramagnetic, F = ferromagnetic, and A = antiferromagnetic.