Magnetic entropy change in Fe-based compound LaFe$_{10.6}$Si$_{2.4}$

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A large magnetic entropy change has been observed in an intermetallic compound LaFe$_{10.6}$Si$_{2.4}$. The maximum $-\Delta S_M = 3.2$ J/kg K was found at its Curie temperature, $\sim 242$ K, upon a 2 T magnetic field change. Although the entropy change is slightly smaller than that of pure Gd metal, such Fe-rich compounds still appear to be very attractive candidates since (a) the raw materials are much cheaper than pure Gd metal; (b) the Curie temperature can be easily shifted by tuning the composition; (c) the materials are much more chemically stable than pure Gd metal. © 2000 American Institute of Physics. [S0003-6951(00)03345-3]

A temperature change of a magnetic material associated with an external magnetic field change in an adiabatic process is defined as the magnetocaloric effect (MCE), which is an intrinsic property of the magnetic solids. Because of their potential application as magnetic refrigerator materials, substances with large MCE have attracted much attention. Advantages of the magnetic refrigeration include high efficiency, small volume and environmental protection. The search for materials with large MCE has continued since the discovery of MCE in iron by Warburg 100 yrs ago. So far, besides certain paramagnetic salts, which have been used to obtain the very low temperatures, a broad class of rare-earth elements, alloys and compounds has been extensively studied for large MCE in the temperature range from a few Kelvin to room temperature and above.

There are two prerequisites for a material to possess a large MCE. One is a large enough spontaneous magnetization and the other is a sharp drop in magnetization with increasing temperature. Generally the former leads to the use of heavy rare earth elements and the latter is associated with ferromagnetic-paramagnetic transitions at the Curie temperature. As is well known, the Fe-rich rare-earth-iron compounds such as $R_2$Fe$_{17}$, $R$(Fe,M)$_{12}$, and $R$(Fe,M)$_{13}$, where $R$=rare earth element, $M$ is Si, Al, etc. the main group elements, show high magnetizations. Furthermore, due to the direct magnetic exchange interaction between Fe atoms, their magnetizations change relatively sharply in the vicinity of the Curie temperatures compared to rare-earth based compounds. In this letter, we report the entropy change in LaFe$_{10.6}$Si$_{2.4}$, an alloy with a NaZn$_{13}$-type cubic structure.

Samples of LaFe$_{10.6}$Si$_{2.4}$ were prepared by arc melting the raw materials with a purity of 99.9%, then annealing at 1000 °C under vacuum for about one month, followed by quenching in water. X-ray powder diffraction pattern (Fig. 1) shows that the sample crystallizes in the NaZn$_{13}$-type structure with lattice constant $a = 11.47$ Å. A small amount of $\alpha$-Fe is also found in the sample as the secondary phase.

Figure 2 shows the temperature dependence of the magnetization measured in a low field of 10 Oe. A Curie temperature $T_C = 245$ K is obtained, which is roughly in agreement with that reported by Palstra et al. The field-dependent magnetization data obtained at different temperatures show that the coercive field is very small (less than a few oersteds), indicating that the material is magnetically soft enough to be a magnetic refrigerant.

In Fig. 3 the isothermal magnetization is plotted as a function of applied magnetic field up to 2 T. The temperature was varied from 150 to 300 K at intervals of 5 K. The sweep rate of magnetic field in a superconductor magnet is slow enough for the $M$-$H$ curves to be isothermal. The observed nonlinear field dependence of magnetization above the Curie temperature (e.g., not perfect paramagnetic behavior) may result from the $\alpha$-Fe contaminant. However, this has a negligible effect on the calculation of the entropy change.

Based on general thermodynamics principles, the magnetic entropy change for an isobaric-isothermal process can be described with one of the Maxwell relations, as

![Figure 1](http://apl.aip.org/about/rights_and_permissions)

**FIG. 1.** X-ray diffraction pattern of LaFe$_{10.6}$Si$_{2.4}$. The diffraction peak for the secondary phase $\alpha$-Fe is indicated by the arrow.
Using the magnetization data measured at discrete values of field and temperature, the magnetic entropy change can be calculated approximately using the numerical formula,

$$\left( \frac{\partial S}{\partial H} \right)_{T,p} \approx \left( \frac{\partial M}{\partial T} \right)_{H,p}. \quad (1)$$

Using the magnetization data measured at discrete values of field and temperature, the magnetic entropy change can be calculated approximately using the numerical formula,

$$-\Delta S_M = \sum_i \frac{1}{T_i+1-T_i} (M_i - M_{i+1}) \Delta H_i, \quad (2)$$

where \(M_i\) and \(M_{i+1}\) are the magnetization values obtained at temperatures \(T_i\) and \(T_{i+1}\) in a field \(H\), respectively. In Fig. 4 the calculated \(-\Delta S_M\) is plotted as a function of temperature for different applied magnetic fields. The maximum \(-\Delta S_M\) appears exactly at the Curie temperature \(T_C = 245\) K, and reaches a value of 3.2 J/kg K for a field change of 2 T.

For a magnetic alloy, the total specific heat is composed of three parts: lattice, electronic and magnetic contributions. The magnetic contribution includes the zero-field anomaly near the transition point due to the magnetic order–disorder transition, and that associated with the magnetization change induced by the applied field. Actually the magnetic contribution to the specific heat can be extracted from the isothermal magnetization data as described below.

As we have shown previously, the transition temperature \(\theta\) and the zero field specific heat anomaly near the transition can be obtained from values of \(\alpha\) and \(\beta\). The transition temperature \(\theta (=245\) K, the same as \(T_C\)) is obtained by fitting the data of \(\alpha\) to

$$\alpha = \alpha_c'(T - T_C),$$

where the \(\alpha_c\) is a material constant. The zero field specific heat anomaly near the transition can be calculated by

$$\Delta C_p = \frac{T_c (\alpha_c')^2}{\beta_c},$$

where \(\beta_c\) is the value of \(\beta\) at the Curie temperature. The change in the specific heat associated with the magnetization (or magnetic entropy) can be calculated from \(-\Delta S_M\) data shown in Fig. 4

$$\Delta C_{p,H} = T \frac{\partial (\Delta S_M)}{\partial T}. \quad (6)$$

Once the lattice and electron contribution and the specific heat are known, the \(\Delta T_{ad}\) can be easily obtained.

By using the above equations the following values are obtained: \(\alpha_c' = 0.002155\), \(\beta_c = 8.20 \times 10^{-6}\) and \(\Delta C_p = 69.4\) J/kg K. In Fig. 5 \(\Delta C_{p,H}\) is plotted as a function of temperature. It is clearly seen that \(\Delta C_{p,H}\) changes sharply from the negative to the positive at the Curie temperature. The sum of the two parts is the magnetic contribution to the total specific heat which affects the cooling or heating power of the magnetic refrigerator (or the adiabatic temperature change \(\Delta T_{ad}\)).

The magnitude of the magnetic entropy change of \(\text{LaFe}_{10.6}\text{Si}_{2.4}\) is quite attractive for the Fe-rich rare-earth transition-metal intermetallic compounds, although it is
smaller than 5.0 J/kg K in Gd metal at $T_C=292$ K, which was measured for the comparison purpose. Based on previous investigation, the cubic La(Fe,M)$_{13}$ compounds with $M=$Si, Al, etc., as the stabilization elements have a large magnetization and a sharp temperature dependence at the Curie temperature. On the grounds of the crystal structure, they should be good soft magnets due to the high symmetry and nonanisotropic rare-earth La ions. All the facts indicate that they are attractive candidates as magnetic refrigerant materials. Their Curie temperatures can be easily shifted from $\approx 200$ K to room temperature or above by tuning the concentration of stabilizing elements or adding the other transition metal such Co, Ni, etc. This temperature range is of commercial importance for food storage and air conditioning. Since the mictomagnetic, antiferromagnetic, and ferromagnetic transitions in the La(Fe$_{1-x}$M$_x$)$_{13}$ compounds can be caused by changing composition and applied magnetic field, the mechanism(s) for such a large MCE is not understood yet. Detailed investigations are being carried out. The ability to control giant MCE in the La(Fe,M)$_{13}$ system should lead to great progress in room temperature magnetic refrigeration, due to the very low cost, high chemical stability and easy synthesis and processing of these materials.

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