“Entropics”: Science and engineering of caloric phenomena related to itinerant-electron magnetism and spin fluctuations

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Abstract In this paper, the relationship between giant caloric phenomena and itinerant-electron magnetism is examined in order to construct of a newly proposed concept “Entropics”, which is a fusion of science and technology with the objective of solving and controlling entropic phenomena. An anomalous hall resistivity is present in the paramagnetic state of the La(Fe0.88Si0.12)13 magnetocaloric compound. Further, its coefficient exhibits a Curie-Weiss type temperature dependence, indicating the existence of disordered local moment, even though the Rhodes-Wohlfarth (RW) ratio reveals that the magnetic feature in the system is an itinerant-electron type. In addition, the correlation between the magnitude of the transition entropy change of the itinerant-electron metamagnetic transition and the RW ratio was observed. In the Mn3GaN barocaloric compound, the transition entropy of the first-order antiferromagnetic-paramagnetic phase transition marginally depends on the external pressure, in contrast to the data for Gd5Ge2Si2. The origin of this tendency is phase stability against the pressure, as opposed to large volume change at the transition temperature, which results in an enhancement of the barocaloric effect. The influence of topological frustration is also distinguished by comparing it with that of other Mn-based antiperovskite compounds.

1. Introduction
The recent development of thermal management technologies has resulted in many new viewpoints in fundamental and applied solid-state physics, such as spincaloritronics [1] and spin entropy-driven thermoelectricity [2]. Various giant caloric effects owing to latent heat of the solid-state first-order phase transitions are also attracting attention because of the strong prospect of realizing a solid-state heat pump/ refrigeration [3].

With respect to the kind of external field used as a trigger for the phase transition, giant caloric phenomena are classified into categories such as magnetocaloric (MC), baro- (BC) or elast-caloric, and electrocaloric (EC) effects [4-9]. These effects naturally contain common features from a
thermodynamic viewpoint and, sometimes, have common physical issues. To treat these issues, we propose the concept of “Entropics”—a fusion of science and engineering developed with the objective of treating such entropic phenomena. In particular, for the strong social demands on the usage of ubiquitous elements, 3d transition metal-based materials are favorable in application and, as a consequence, analyses and control of spin fluctuations in finite-temperature magnetism [10] have become very important in metallic magnetic substances. In this paper, we introduce various examples with striking features in relation between caloric phenomena, such as MC and EC effects, and itinerant-electron magnetism.

2. Results and Discussions

La(Fe, Si_{1-x})_{13} is a typical itinerant-electron type magnetocaloric material which exhibits an itinerant-electron metamagnetic (IEM) transition above the first-order thermally induced transition at the Curie temperature $T_C$ [7, 11]. The IEM transition appears only at a high Fe concentration range above $x = 0.86$, where the value of $T_C$ lies at approximately 200 K. Further, hydrogen absorption increases in $T_C$ and the value of $T_C$ can be tuned by hydrogen concentration; e.g., the value varies from 195 K for $y = 0$ to 332 K for $y = 1.3$ in La(Fe_{0.88}Si_{0.12})_{13}H_3 [7].

Both theoretically and fundamentally, the paramagnetic state as a zero-field state of the IEM transition tends to appear at a maximum in the temperature dependence of susceptibility [12, 13]. This phenomenon is fundamentally explained by spin fluctuations in a (exchange-enhanced) Pauli paramagnetic state [13]. On the other hand, no maximum susceptibility is observed in La(Fe, Si_{1-x})_{13} except that measurement under the hydrostatic pressures [14], and temperature dependence of paramagnetic susceptibility $\chi$ appears to obey the Curie-Weiss (CW) law [14, 15]. In order to verify the thermal behavior of the paramagnetic state, we conducted Hall resistivity $\rho_{xy}$ measurements above $T_C$. Figure 1 shows the temperature $T$ dependence of the slope of $R_H$ derived from the range close to the zero-magnetic field. As shown in the inset in Fig. 1, the magnetic field dependence of $\rho_{xy}$ is very similar to the magnetization curve, which is featured as a nonlinear increase in magnetization due to the IEM transition. This means that the main part of the observed $\rho_{xy}$ consists of the anomalous Hall effect (AHE) [16]. It is natural for the ferromagnetic state after the IEM transition to induce the AHE, because it contains the spontaneous local moment. Further, the variation of $R_H$ in the paramagnetic state shown in Fig. 1 clearly corresponds to the $T^{-1}$ function denoted by the solid line, indicating that a

![Figure 1](image-url)  

**Figure 1.** Temperature $T$ dependence of anomalous Hall coefficient $R_H$ in the paramagnetic state for La(Fe_{0.88}Si_{0.12})_{13}. Inset shows the magnetic field dependence of the Hall resistivity $\rho_{xy}$ at 205 K.

CW variation also appears in the $\rho_{xy}$ - $T$ curve, as with the $\chi$ - $T$ curve. Although the details of the AHE have not yet been fully developed, the spin-orbit interaction (SOI) is the inevitable factor for appearance of the AHE. This result means that the CW behavior in $\chi$ originates not only from the
pure spin term but also from the unquenched orbital term. An effective moment value of 3.2 \( \mu_B \) obtained from the \( \chi - T \) curve has been reported, corresponding to a Rhodes-Wohlfarth (RW) ratio [17] of approximately 1.2. The RW ratio larger than unity in the La(Fe\(_{x}\)Si\(_{1-x}\))\(_{13}\) system signifies the itinerant-electron character of magnetism, while its closeness to unity, in addition to the trace of the SOI, proves the local moment character in the PM state. Such a feature is categorized into the so-called “interpolation” region [18], which is located between the weakly itinerant-electron limit in which the dominant magnetic fluctuations are the long wavelength and small frequency types, and the localized moment limit in which dominant fluctuations are characterized by the directionally randomized single-site polarizations. A disordered local moment (DLM) picture has been proposed to treat the paramagnetic local moment in the interpolation region [19, 20]. From first-principle calculations based on the local density approximation (LDA) together with the coherent potential approximation (CPA) [21], the amplitude of the DLM for La(Fe\(_{0.88}\)Si\(_{0.12}\))\(_{13}\) has been evaluated to be approximately 1.9 \( \mu_B \). This value is slightly smaller than the magnetic carrier \( p_c = 2.3 \mu_B \), which is determined by the relation \( p_c(p_c + 2) = p_{\text{eff}}^2 \). The discrepancy is attributable to an additional contribution from the longitudinal spin fluctuations characteristic of itinerant-electron magnetism.

One of the measures used to evaluate the MC performance is isothermal entropy change, \( \Delta S_M \). In general, the value of \( \Delta S_M \) tends to become maximum at just above \( T_C \) and subsequently, a plateau is formed at higher temperature ranges. Because the first-order transition occurs at the point where low-temperature and high-temperature phases balance their free energies, \( F, F_{\text{high}} - F_{\text{low}} = 0 \). Then, the relation \( S_{\text{high}} - S_{\text{low}} = \Delta S = U_{\text{high}} - U_{\text{low}} \) is derived, where \( U \) is the internal energy, because \( F = U - TS \). This means that the phase transition occurs in order to gain internal energy and the internal energy gain is compensated by releasing the entropy difference of two phases. Among them, the internal energy in the FM state is determined a priori when constituent elements and crystal structure are fixed. Further, the contribution of thermal fluctuations to \( S \) in the FM state is relatively smaller than that in the PM (DLM) state. Consequently, the nature of spin fluctuations in the DLM state is one of the key factors governing the magnitude of \( \Delta S_M \). Figure 2 shows the maximum value of the isothermal entropy change \( \Delta S_M^{\text{max}} \) plotted against the RW ratio for La(Fe\(_{0.88}\)Si\(_{0.12}\))\(_{13}\), together with the result of La(Fe\(_{0.89}\)Si\(_{0.12}\))\(_{13}\). An increase in the RW ratio was observed after partial substitution of Al, indicating that the nature of the spin fluctuations shifts towards a long-wavelength type. Meanwhile, the value of \( \Delta S_M^{\text{max}} \) gradually decreases with increasing RW ratio. The results shown in Fig. 2 do not instantly signify a causal relationship between these

![Figure 2](attachment:image.png)

**Figure 2.** Maximum value of isothermal entropy change \( \Delta S_M \) plotted against the Rhodes-Wohlfarth ratio for La(Fe\(_{x}\)Si\(_{1-x}\))\(_{13}\) (\( x = 0.88 \) and 0.89) and La(Fe\(_{0.88}\)Si\(_{0.12-y}\)Al\(_y\))\(_{13}\) (\( y = 0.01, 0.02 \) and 0.03)
two quantities, as the CW behavior means that some kind of interaction between DLMs also influences the fluctuating motions of the DLMs. Note that similar studies into the relationship between transition entropy and the RW ratio for various ferroelectric systems have resulted in data with a tendency very similar to that of the present results [22]. The PM state in the localized moment state has a larger entropy in the magnitude of \( R \ln(2J+1) \), where \( R \) is the gas constant and \( J \) is the total angular moment of the localized moment. On the other hand, in general, the energy difference between the FM and PM states in the itinerant-electron system is large [23], resulting in an enlarged difference in \( U \) between the FM and PM states. Accordingly, the DLM character in the itinerant-electron magnetism has a certain merit for obtaining a large magnetocaloric effect. Further precise observations for the DLM may result in further advantages in usage of the paramagnetic state of the itinerant-electron magnetism.

The antiferromagnetic \( \text{Mn}_3\text{GaN} \) compound is another example of an itinerant-electron caloric material. The ground state of this compound is the antiferromagnetic (AF) phase with \( \Gamma^5_{\text{g}} \) spin structure [24], owing to a geometric frustration [24, 25]. At the Neel temperature \( T_N \) of about 290 K, the first-order phase transition appears and the paramagnetic (PM) state appears above \( T_N \) [26]. A notable feature is volume shrinkage of about 1% accompanied by the AF-PM first-order transition at \( T_N \) [26, 27]. Attempts have been made to utilize this large volume change as new negative thermal-expansion materials, which alternate with conventional Invar alloys [28]. Recently, a giant entropy change \( \Delta S \) was observed when an external pressure \( p \) was applied and the value of \( \Delta S \) became approximately 22 J/kg K under an external pressure of 0.14 MPa [8]. Because a magnetic field-induced caloric change, i.e., the magnetocaloric effect, is not expected in antiferromagnetic systems, the barocaloric effect is a suitable way to assess the phase transition entropy change. From the differential scanning calorimeter (DSC) measurement, the heat absorption (latent heat) across \( T_N \) was evaluated at approximately 22 J/kg K; thus, it is apparent that the magnitude of the latent heat governs that of the BC effect.

Figure 3 shows the pressure dependence of the latent heat \( L \) for \( \text{Mn}_3\text{GaN} \), together with that for \( \text{Gd}_5\text{Ge}_2\text{Si}_2 \). For both materials, the technique for caloric measurements under external pressure is the same as that in our previous paper [8]. \( \text{Gd}_5\text{Ge}_2\text{Si}_2 \) is known as a typical giant MC material [29] and its magnetic behavior is characterized by Gd 4f localized moment. Its first-order phase transition is fundamentally driven by structural transition, and the FM-PM magnetic transition is induced as a subsidiary. In other words, the magnetic characteristics of these two compounds are completely different. As shown in Fig. 3, the amount of latent heat for the first-order \( \text{Gd}_5\text{Ge}_2\text{Si}_2 \) apparently decreases with increasing external pressure. A similar decline of the BC effect with
increasing pressure has been observed, and the result has been attributed to a decrease in phonon entropy involved in the total transition entropy [30]. Meanwhile, the value of $L$ scarcely depends on the pressure in these pressure ranges for Mn$_3$GaN. Such a feature is plausibly explained by the pressure stability of the magnetic state in Mn$_3$GaN. The appearance of the giant BC effect owing to the pressure stability, or smaller pressure effect on $T_N$, in contrast to the large volume change at $T_N$ has also been pointed out in this compound [8].

The large volume shrinkage at $T_N$ is caused by a reduction in amplitude due to a change from the ordered local moment (OLM) to the DLM. Meanwhile, the relatively smaller pressure effect of $T_N$ is derived from the small pressure shift of the free-energy balance point. The 3d band contribution to the pressure effect of $T_N$ is relatively smaller than the contribution of spin fluctuations [31]. Accordingly, the difference between the pressure effect on the OLM and DLM is one of the measures used for the pressure effect on the first-order transition temperature. A contrastive example to the present compounds is Mn$_3$SnC, which exhibits first-order transition from a non-collinear ferrimagnetic to the PM state [26, 32]. In the pressure effect on this transition temperature, $T_t$ is approximately -16 K/GPa [32], whereas the volume change at $T_t$ is approximately 0.2 % [26]. This means that the difference between the OLM and DLM is not very large, resulting in both the small pressure effect and volume change. The transition entropy change estimated from an extrapolation of $\Delta S_M$ to zero-magnetic field becomes a relatively small value of approximately -5 J/kg K [33]. On the other hand, the shrinkage in amplitude from the OLM to DLM is attributable to the influence of topological frustration in Mn$_3$GaN [8]. In other words, the origin of the shrinkage in the local moment amplitude is different from the band energy gain [23], which is directly correlated with a change in volume, or in Mn-Mn atomic distances. A precise determination of both the OLM and DLM amplitudes and their pressure dependence is inevitable for further detailed discussion. From the viewpoint of engineering, usage of frustration in the AF materials is a notable advantage in the BC effect, and such a case can be a rare example of a positive application of the AF materials to practical applications.

3. Conclusion

In this paper, two examples were presented that helped to clarify the relationship between giant caloric phenomena and itinerant-electron magnetism. Compared to localized moment systems, the controllability of magnetic entropy is more significant in itinerant-electron systems, because of their various characteristics, such as amplitude of local moment, magnetovolume effects, and spin fluctuations. Accordingly, itinerant-electron magnets are very important materials for the concept of “Entropics,” which is a fusion of science and technology with the objective of solving and controlling giant entropic phenomena in terms of physics and applications. However, the details of its physics, such as finite-temperature magnetism and the spin-fluctuation model in the “interpolation” region, are still debatable. It is expected that significant progress will be made in these issues in the future.

Acknowledgement

We would like to extend our sincere appreciation to Prof. Yoshinori Takahashi at University of Hyogo, for enlightening us about theoretical visions of spin fluctuations, and for imparting essential advice.

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