

Giant magnetocaloric effect and soft-mode magneto-structural phase transition in MnAs

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Abstract – Maxwell relation and mean-field approximation are chosen to estimate the total entropy change and the magnetic entropy change, respectively. The experimental results are exactly consonant with the theoretical results. Consequently, the magnetic entropy changes make up the majority of the total entropy change, and the lattice entropy changes are small. The giant magnetocaloric effect in MnAs is clarified. According to thermodynamics discussion, the modulus of compression and the stress at T_C decrease dramatically. Therefore, the magneto-structural phase transition in MnAs is a kind of soft mode.

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The magnetocaloric effect (MCE) discovered by Warburg [1] means isothermal magnetic entropy change or adiabatic temperature change through magnetizing or demagnetizing of magnetic solids which are similar to the compression or expansion of gases. The hotspots of the MCE research are focused on materials which undergo a first-order magnetic phase transition nowadays [2–10]. Obviously, the entropy change would be prominent in the vicinity of phase transition. However, first-order magnetic phase transitions are always accompanying with the discontinuous volume deformation even the structural phase transition. Imaginably, the magnetic degrees of freedom couple with that of the lattice intensely. The total entropy change can be estimated by the experimental method according to the thermodynamics Maxwell relations. But the magnetic, the lattice, and the electronic parts of entropy changes are difficult to distinguish. Therefore, the meanings of this kind of MCE have gone beyond the original conceptual category.

MnAs, a ferromagnet with saturation magnetization of $3.4 \mu_B/\text{Mn}$, is a good candidate for studying the coupling between the magnetic and the lattice degrees of freedom.

MnAs undergoes a first-order phase transition from α -MnAs (ferromagnetic hexagonal NiAs-type structure) to β -MnAs (paramagnetic orthorhombic MnP-type structure) at approximately 313 K; at higher temperatures, ~ 393 K, the structure reverts back to γ -MnAs (paramagnetic hexagonal structure) in a second-order phase transition [11]. The study will focus on the first-order magneto-structural phase transition. The large volume contraction due to structural transformation (α -MnAs to β -MnAs) couples with a first-order magnetic phase transition, and approaches 2% [12,13]. The magnetic field can drive T_C to a higher temperature which is a result of metamagnetic transition.

Some interesting phenomena of MnAs and its Sb-doped compounds are associated with the first-order metamagnetic transition, such as giant MCE [7], large magneto-elastic response [12], “colossal-like” magneto-resistance [14]. The peak value of the entropy change can reach 30 J/kgK and the adiabatic temperature change can reach 13 K for $\Delta H = 5$ T [7]. MnAs and its Sb-doped compounds are regarded as attractive candidates to be used as magnetic refrigerants. The MCE of MnAs under static pressure may be quite surprising since the entropy change achieves 267 J/kgK ($T = 281$ K,

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$P = 2.23$ kbar, $\Delta H = 5$ T) and it is referred to as colossal MCE [9]. Subsequently, an entropy change of 300 J/kgK is observed in $\text{Mn}_{0.997}\text{Fe}_{0.003}\text{As}$ at ambient pressure [10]. It is believed that the lattice plays a key role in the colossal-MCE problem. The giant and colossal MCE of MnAs and $\text{MnAs}_{1-x}\text{Sb}_x$ compounds have been investigated theoretically by von Ranke *et al.* [15,16] by using the Bean-Rodbell model [17]. The results show that lattice deformation may enhance the MCE. According to the results of heat capacity measurement on the $\text{La}_{1-x}\text{Pr}_x\text{Fe}_{11.5}\text{Si}_{1.5}$ compound, Liu *et al.* [18] give a different explanation of giant MCE which uncovers the importance of phase coexistence in MCE problems. In fact, the detail of phase transition is still unclear due to strong magneto-elastic coupling. From both the experimental and the theoretical point of view, the true course of a first-order magneto-structural phase transition is valuable and important, but this kind of work is deficient. Subsequently, the MCE of MnAs will be discussed deeply, and the relationship between the giant MCE and soft modes will be uncovered.

The details of sample preparation and measurement have been described previously [7]. The paramagnetic scattering of MnAs measured by spin-polarised neutron scatter indicates that the magnetic moment is stable, and the magnetic correlation is strongly ferromagnetic and temperature independent [11,19]. Therefore, the mean-field approximation (MFA) is a reasonable method used to calculate the magnetic entropy change in MnAs. In the MFA, the magnetic entropy of the system can be written as

$$S_m = Nk_B \left[\ln \frac{\sinh \frac{2J+1}{2J} x}{\sinh \frac{x}{2J}} - x B_J(x) \right], \quad (1)$$

here N is the number of magnetic spins, $B_J(x)$ is the Brillouin function with $x = gJ\mu_B(H + H_m)/k_B T$, $g = 2.27$ is the Landé g factor, μ_B is the Bohr magneton, $J = 3/2$ is the total angular momentum, k_B is the Boltzmann constant, H and H_m are the external magnetic field and the molecular field, respectively. It can be assumed that the magnetic entropy $S(x)$ connects with the Brillouin function $B_J(x)$ one-to-one through the same independent variable x , since both of them can scale the order degree of the magnetic subsystem. Therefore, S changed with temperature, can be codetermined by eq. (1) and temperature-dependent normalized magnetization [20]. According to thermodynamics, the physical quantities mentioned above, can be investigated in another way. Owing to the existence of strong magneto-elastic coupling, Maxwell relations are written as

$$\left(\frac{\partial V}{\partial H} \right)_{P,T} = - \left(\frac{\partial M}{\partial P} \right)_{H,T}, \quad (2)$$

$$\left(\frac{\partial V}{\partial T} \right)_{P,H} = - \left(\frac{\partial S}{\partial P} \right)_{T,H}, \quad (3)$$

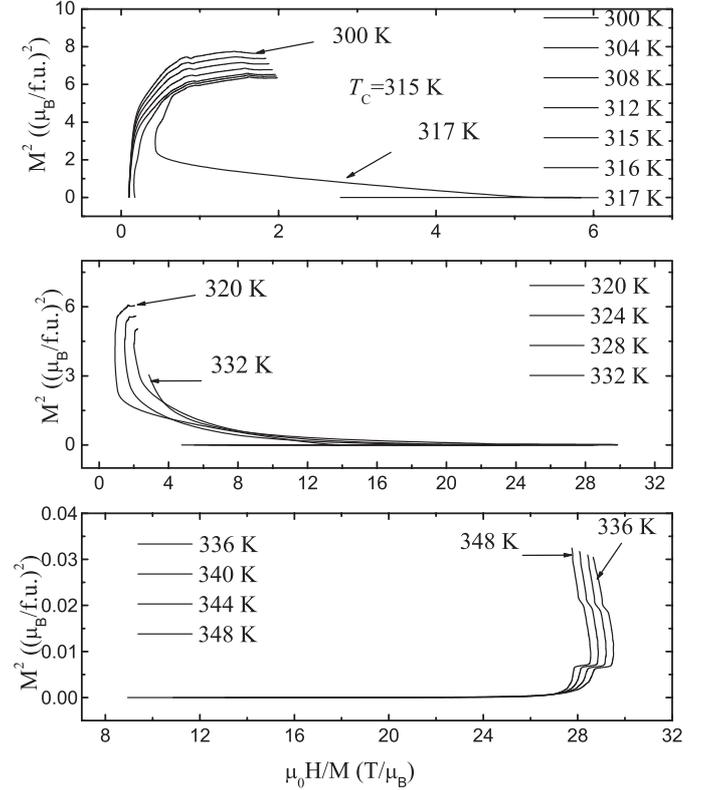


Fig. 1: The Arrott plot of MnAs between 300 K and 348 K. The “S” shape characteristic of the Arrott plot above T_C is the sign of metamagnetic transition.

$$\left(\frac{\partial M}{\partial T} \right)_{H,P} = \left(\frac{\partial S}{\partial H} \right)_{T,P}; \quad (4)$$

here V is the volume and P the pressure. Based on eq. (4) and at constant pressure, the total entropy change under different magnetic field is expressed as

$$S(H_2, T) - S(H_1, T) = \int_{H_1}^{H_2} \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH. \quad (5)$$

The Arrott plot is shown in fig. 1. The negative slope and inflexion in the Arrott plot are the signs of metamagnetic transition. The metamagnetic transition led to giant MCE in MnAs. The total entropy changes, estimated using eq. (5), are shown in fig. 2. Spontaneous magnetization is extracted from the Arrott plot by data above 2 T. Magnetic entropy changes are calculated by using eq. (1) and are also shown in fig. 2. The theoretical calculations are perfectly consonant with the experimental results (maximum error within 5 J/kgK), which indicates that magnetic entropy changes are dominant. The calculation also shows that the magnetic entropy jump at T_C in zero field is 32.9 J/kgK which is consistent with the heat capacity measurement results very well performed by Wada (28.5 J/kgK) [21] and Schünemann *et al.* (31.6 J/kgK) [22]. From fig. 2 it is easy to draw the conclusion that the total entropy change is approximately

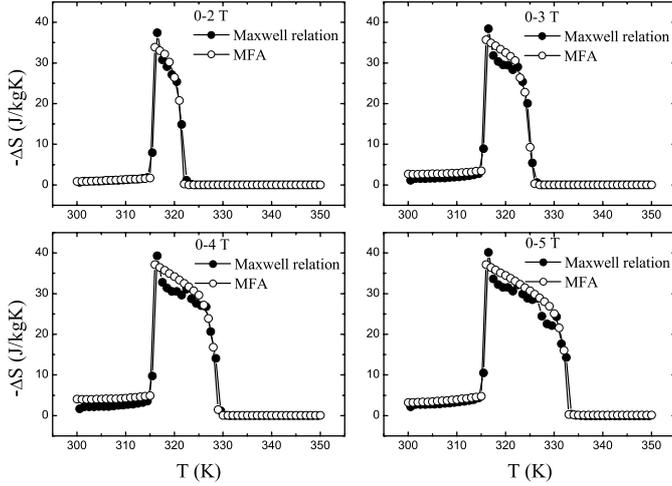


Fig. 2: The total entropy change calculated by using Maxwell relation shown in solid symbols, and the magnetic entropy change calculated by using the MFA shown in hollow symbols under different magnetic field changes. The temperature changes from 300 to 350 K and the temperature interval is 1 K. Solid lines are guides for the eye.

equal to the magnetic entropy change in MnAs. As this is a complex magnetic solid, the total entropy is approximately composed of the electronic part, the magnetic part, and the lattice part, etc. A question emerges as to where the lattice and electronic entropy change go. In fact the electronic entropy change is so small that it is negligible [23]. Therefore, the answer is that the lattice entropy change is small, though its deformation is as large as 2% [12,13]. It is anomalous that such large lattice negative deformation has such small contribution to the latent heat (the product of entropy change multiplies T_C for a first-order phase transition). It should be noted that this is a criterion of soft-mode displacive structural phase transition, which is often observed in ferroelectric materials [24]. The concept of soft mode proposed by Cochran means that the instability of lattice against a particular mode of vibration is approached as the corresponding frequency approaches zero which may be the reason of ferroelectric transition [25].

The case of MnAs can be discussed phenomenologically in the frame of thermodynamics. In the vicinity of phase transition, the stress should possess *nonlinear* form [20]:

$$F = -(1 + B\omega)K\omega, \quad (6)$$

$\omega = (V - V_0)/V_0$ is the volume deformation; V and V_0 are the volume with and without exchange interactions, respectively. Here V_0 is volume of the paramagnetic state in zero external fields and pressure. K is the modulus of compression which is always positive, B is a positive coefficient. The elastic energy per unit volume can be written as

$$U = \frac{1}{2}K\omega^2 \left(1 + \frac{2}{3}B\omega\right). \quad (7)$$

The Gibbs free energy per unit volume can be written as

$$G = -HN\mu_s\sigma - \frac{3}{2} \left(\frac{J}{J+1} \right) Nk_B T_C \sigma^2 + \frac{1}{2}K\omega^2 + \frac{1}{3}BK\omega^3 + P\omega - TS, \quad (8)$$

where the first term on the right is the field; the second is the exchange; the third and fourth stand for the distortion; the fifth is the pressure; and the last is the entropy. The normalized magnetization is $\sigma = M/N\mu_s$ with $\mu_s = gJ\mu_B$. The electronic entropy changes are neglected [23]. For a first-order phase transition, the Gibbs free energy of the low temperature phase (l) equals to that of high temperature (h) at the critical point. In the conditions of zero field and high vacuum, $H \cong 0$, $\sigma_h \cong 0$, $P \cong 0$, and $\omega_h \cong 0$. Then eq. (8) can be simplified as

$$T_C(S_h - S_l) = \frac{3}{2} \left(\frac{J}{J+1} \right) Nk_B T_C \sigma_l^2 - \frac{1}{2}K\omega_l^2 - \frac{1}{3}BK\omega_l^3. \quad (9)$$

According to the above discussion, the magnetic entropy changes are dominant, then the lattice parts are small. Therefore, the sum of the last two terms in eq. (9) should be small. As a result, the modulus of compression K should decrease dramatically in the vicinity of the phase transition. Calculation based on eq. (9) shows $K < 26.7$ GPa at T_C , which is far smaller than the result of first-principle band calculation ~ 200 GPa of MnAs [26]. Consequentially, the stress should decrease dramatically too. The modulus of compression K and stress F will not conclude with zero, they will arrive at a finite value for a first-order phase transition. These phenomena are the typical characteristics of soft-mode structural phase transition [24], which are in accord with the prediction of Palumbo [27] that the anomalous change in the lattice dynamics of MnAs at T_C is strictly related to a critical lowering in the phonon frequencies.

The lattice negative expansion is always an obstacle to achieving large MCE if the modulus of compression K does not obviously decrease [20]. MnAs, however, is a unique compound though large negative lattice deformation occurs. Its modulus of compression K and stress F at T_C decrease dramatically because of the soft-mode magneto-structural phase transition. As a result, the lattice entropy is almost unchanged, and the structural phase transition makes a small contribution to latent heat.

The total entropy changes and magnetic entropy changes are calculated by using Maxwell relation and MFA, respectively. It is shown that the theoretical calculation is very well consistent with the experimental estimation. The magnetic entropy change is undoubtedly prominent; moreover the magnetic entropy changes are dominant. It is easy to conclude that the lattice entropy changes and its contribution to the latent heat at T_C are small. As a result, the modulus of compression K

and the stress F at T_C should decrease dramatically ($K < 26.7$ GPa). Therefore, the magneto-structural phase transition (hexagonal phase α -MnAs change to orthorhombic phase β -MnAs) is a soft-mode one. The giant MCE, soft-mode magneto-structural phase transition and their relationship are firstly clarified in MnAs. It should be pointed out that MnAs is the only compound which has “pure” (derived from magnetic degrees of freedom) giant MCE and the lattice effect is so small that it is negligible at present. The work gains a new insight into the problems of MCE and soft-mode structural phase transition which can be extended to other ferromagnetic transitions, ferroelectric transitions and so on.

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REFERENCES

- [1] WARBURG E., *Ann. Phys. Chem.* (Leipzig), **13** (1881) 141.
- [2] HU F. X., SHEN B. G., SUN J. R., CHENG Z. H., RAO G. H. and ZHANG X. X., *Appl. Phys. Lett.*, **78** (2001) 3675.
- [3] HU F. X., SHEN B. G., SUN J. R., WANG G. J. and CHENG Z. H., *Appl. Phys. Lett.*, **80** (2002) 826.
- [4] FUJITA A., FUJIEDA S., HASEGAWA Y. and FUKAMICHI K., *Phys. Rev. B*, **67** (2003) 104416.
- [5] PECHARSKY V. K. and GSCHNEIDNER K. A. jr., *Phys. Rev. Lett.*, **78** (1997) 4494.
- [6] PECHARSKY V. K. and GSCHNEIDNER K. A. jr., *Appl. Phys. Lett.*, **70** (1997) 3299.
- [7] WADA H. and TANABE Y., *Appl. Phys. Lett.*, **79** (2001) 3302.
- [8] TEGUS O., BRUCK E., BUSCHOW K. H. J. and DE BOER F. R., *Nature*, **415** (2002) 150.
- [9] GAMA S., COELHO A. A., DE CAMPOS A., CARVALHO A., MAGNU G. and GANDRA F. C. G., *Phys. Rev. Lett.*, **93** (2004) 237202.
- [10] DE CAMPOS A., ROCCO D. L., CARVALHO A., MAGNUS G., CARON L., COELHO A. A., GAMA S., SILVA L. M. D., GANDRA F. C. G., SANTOS A. O. D., CARDOSO L. P., VON RANKE P. J. and DE OLIVEIRA N. A., *Nat. Mater.*, **5** (2006) 802.
- [11] DONATH MARKUS and NOLTING WOLFGANG, *Local-Moment Ferromagnets* (Springer, Berlin, Heidelberg) 2005.
- [12] CHERNENKO V. A., WEE L., MCCORMICK P. G. and STREET R., *J. Appl. Phys.*, **85** (1999) 7833.
- [13] ISHIKAWA F., KOYAMA K., WATANABE K., ASANO T. and WADA H., *J. Phys. Soc. Jpn.*, **75** (2006) 084604.
- [14] MIRA J., RIVADULLA F., RIVAS J., FONDADO A., GUIDI T., CACIUFFO R., CARSUGHI F., RADAELLI P. G. and GOODENOUGH J. B., *Phys. Rev. Lett.*, **90** (2003) 097203.
- [15] VON RANKE P. J., DE OLIVEIRA N. A. and GAMA S., *Phys. Lett. A*, **320** (2004) 302.
- [16] VON RANKE P. J., GAMA S., COELHO A. A., DE CAMPOS A., CARVALHO A., MAGNUS G., GANDRA F. C. G. and DE OLIVEIRA N. A., *Phys. Rev. B*, **73** (2006) 014415.
- [17] BEAN C. P. and ROBBELL D. S., *Phys. Rev.*, **126** (1962) 104.
- [18] LIU G. J., SUN J. R., SHEN J., GAO B., ZHANG H. W., HU F. X. and SHEN B. G., *Appl. Phys. Lett.*, **90** (2007) 032507.
- [19] NEUMANN K.-U., ZIEBECK K. R. A., JEWISS F., DÄWERITZ L., PLOOG K. H. and MURANI A., *Physica B*, **335** (2003) 34.
- [20] ZOU J. D., SHEN B. G. and SUN J. R., *J. Phys.: Condens. Matter*, **19** (2007) 196220.
- [21] WADA H., lecture on “Magnetocaloric Effect of $MnAs_{1-x}Sb_x$ and $Co(S_{1-x}Se_x)$ ” (2006) Beijing.
- [22] SCHÜNEMANN J. W., LANGE A., GOVOR G. A., BÄRNER K. and GMELIN E., *J. Alloys Compd.*, **178** (1992) 237.
- [23] JIA L., LIU G. J., SUN J. R., ZHANG H. W., HU F. X., DONG C., RAO G. H. and SHEN B. G., *J. Appl. Phys.*, **100** (2006) 123904.
- [24] BLING R. and ŽEKŠ B., *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland) 1974, translated in Chinese.
- [25] COCHRAN W., *Phys. Rev. Lett.*, **3** (1959) 412; *Adv. Phys.*, **9** (1960) 387; **10** (1961) 401.
- [26] YAMADA H., TERAOKA K., KONDO K. and GOTO T., *J. Phys.: Condens. Matter*, **14** (2002) 11785.
- [27] PALUMBO O., CASTELLANO C., PAOLONE A. and CANTELLI R., *J. Phys.: Condens. Matter*, **17** (2005) 1537.