A study of freezing temperature and magnetic relaxation for epitaxial $La_{0.67}Sr_{0.33}MnO_{3-\delta}$ films

2002 J. Phys.: Condens. Matter 14 4309

(http://iopscience.iop.org/0953-8984/14/17/304)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 4309–4317 PII: S0953-8984(02)30072-9

A study of freezing temperature and magnetic relaxation for epitaxial $La_{0.67}Sr_{0.33}MnO_{3-\delta}$ films

C S Xiong[1,2], Y H Xiong[1,3], W Yi[2], G N Meng[2], Z C Xia[1], X G Li[4] and S L Yuan[1]

[1] Institute of Materials Physics and Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China
[2] Department of Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China
[3] Department of Astronomy and Applied Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China
[4] Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

Received 15 October 2001, in final form 4 March 2002
Published 18 April 2002
Online at stacks.iop.org/JPhysCM/14/4309

Abstract

The variations of magnetic susceptibility and magnetic relaxation obtained by a superconducting quantum interference device magnetometer are investigated systematically for epitaxial $La_{0.67}Sr_{0.33}MnO_{3-\delta}$ films grown on (001) $LaAlO_3$ single-crystal substrate using a direct-current magnetron sputtering technique. Spin-glass-like behaviour can be observed, which is caused by the competition between ferromagnetism and antiferromagnetism, a direct consequence of the random distribution of Mn^{3+} and Mn^{4+} ions. Using the concept of spin glass and the double-potential-well model, we have calculated the relation between the applied field and the freezing temperature and the relaxation of M versus time. All the calculated results are in good agreement with the experimental values.

1. Introduction

Recently, it was reported that there are special magnetic properties in the manganese oxides, which show the colossal-magnetoresistance (CMR) effect. To explain this phenomenon, it has been suggested that the oxides possess spin-glass-like properties due to the competition between the ferromagnetism and antiferromagnetism below the metal–insulator transition temperature (T_P) [1–5]. For example, von Helmolt *et al* [1] observed spin-glass behaviour in $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ thin film. Zhang *et al* [2] indicated that $La_{0.67}Ca_{0.33}MnO_x$ bulk material is comprised of ferromagnetic and antiferromagnetic clusters, through analysing the magnetization as a function of temperature during different treatments (zero-field cooled (ZFC) and field cooled (FC) with an applied field of 0.01 T). Cai *et al* [3] reported that in

Table 1. Direct-current sputtering conditions for LSMO film.

dc sputtering voltage (kV)	0.22
dc sputtering current (A)	0.3
Sputtering gas	Ar: 21(SCCM)[a]; O_2: 7(SCCM)
Gas pressure (Pa)	4.0
Base pressure (Pa)	8×10^{-5}
Substrate temperature (°C)	600
Sputtering time (h)	2
Thickness of the films (nm)	600

[a] SCCM means 'standard millilitre per minute'.

bulk $La_{0.67}Ca_{0.33}Mn_{0.9}Fe_{0.1}O_3$ (LCMFO) prepared by the conventional solid-state reaction process in air, random substitutions of Fe for Mn lead to the formation of antiferromagnetic and ferromagnetic clusters. The spin-glass behaviour of LCMFO seems to arise from the competition between them. But detailed studies, especially ones concerning the mechanism and comparison between theory and experiment for spin-glass-like behaviour in epitaxial $La_{0.67}Sr_{0.33}MnO_{3-\delta}$ (LSMO) films, have seldom been reported.

In this paper, by investigating the relation between susceptibility (χ) and temperature (T) in different external fields (H), and magnetization relaxation behaviour (M–t curve) at different temperatures with the same applied field, 0.1 T, we are able to conclude that there is also a spin-glass-like behaviour in epitaxial LSMO film. We try to use the concept of the spin glass [7] and the double-potential-well model to explain the experimental phenomena qualitatively and to calculate the relation between the applied field (H) and the freezing temperature (T_f). We were also able to use them to derive the formula for magnetization relaxation.

2. Experimental procedure

The target, with nominal composition of $La_{0.67}Sr_{0.33}MnO_3$, was made by the conventional solid-state reaction method. The LSMO films were grown on (001) $LaAlO_3$ single-crystal substrate using direct-current magnetron sputtering techniques. The sputtering conditions are listed in table 1. Using a Rigaku D/Max-γA rotating-anode powder diffractometer with Cu Kα radiation and a B-7-type pole-figure diffractometer, we obtained x-ray diffraction (XRD) patterns and reflecting pole figures. From these results, we believe that all the samples presented here are high-quality epitaxial films [6]. The commercial superconducting quantum interference device (SQUID) magnetometer was used to study the magnetic properties of our LSMO film sample.

3. Results and discussion

3.1. The relation between H and the freezing temperature (T_f)

The dependence on temperature (T) of the susceptibility (χ) is shown in the inset of figure 1. These data were measured as the films were cooled down from room temperature to 4.2 K in zero field (ZFC) and in a field (FC) respectively. From the inset, it is seen that there are two transition temperatures. One is called the Curie temperature (T_C), the temperature of the transition from the ferromagnetic phase to the paramagnetic phase. With increase of the applied field (H), T_C does not change, because the structure of LSMO film does not change. The other transition temperature is defined as T_f (the freezing temperature). When H increases, T_f shifts to lower temperatures, and it disappears when $\mu_0 H$ is almost equal to 1 T.

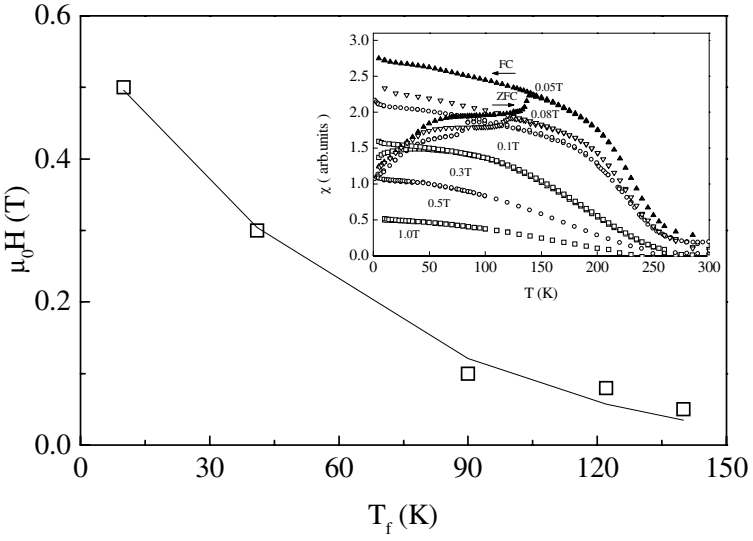

Figure 1. The curve for H versus T_f. The inset shows the temperature dependence of the susceptibility.

It is well known that there are two typical characteristics for a spin-glass system: one is the freezing temperature where a sharp cusp appears in the curves of magnetization or susceptibility versus temperature at low external magnetic field; and the other is the magnetization relaxation effect. In our experiment, the above two characteristics can be observed, so we therefore believe that there is spin-glass-like behaviour in the epitaxial LSMO films.

To form the spin-glass state, there must be two factors: disorder of sites or bonds and competition between different magnetic interactions. For example, disorder arises from the random substitution of Fe for Mn in the bulk LCMFO [3]. But in our samples, there are no such substitutions between two different elements, so there may be another mechanism for producing spin-glass-like behaviour.

As is well known, the manganese oxides $Re_{1-x}T_xMnO_3$ have the natural perovskite crystal structure [8]. Their magnetoresistance effect can be well explained using the double-exchange (DE) model [9]. Wollan and Koehler [10] have studied several magnetic structures in the $La_{1-x}Ca_xMnO_3$ system and found that it shows a ferromagnetic phase for $x \sim 0.35$, an antiferromagnetic phase for $x = 0$ and $x > 0.5$ and simultaneous occurrence of ferromagnetic and antiferromagnetic phases for $0 < x < 0.25$ and $0.4 < x < 0.5$. It can be concluded that the magnetic properties strongly depend on the relative content, distribution and interaction between Mn^{3+} and Mn^{4+} ions in the LCMO system. In our case, we suggest that there may exist disordered distributions of Mn^{3+} and Mn^{4+} ions in our LSMO epitaxial film system; also the changes for the Mn^{4+} ions arise from the minor deviation of oxygen from the nominal composition during the preparation process. With the random distribution of Mn^{3+} and Mn^{4+} ions, ferromagnetic and antiferromagnetic clusters will form in our film material, and hence ferromagnetic and antiferromagnetic interactions may coexist. The spin-glass behaviour caused by the randomness of the distributions of Fe and Mn ions was also observed in the $Fe_{0.5}Mn_{0.5}TiO_3$ mixed compound [11], to which our LSMO system is similar.

Then, we would like to explain the phenomenon that with increase of the applied field, T_f decreases and finally disappears. We suggest that in the same applied field, because of the increase of temperature, the energy of the thermal movement makes these magnetic moments

Table 2. The parameters fitted by equation (8).

T (K)	α (10^{-4} au)	β (10^{-4}au)	γ	$\alpha-\beta$ (calculation) (10^{-4} au)	M_0 (experiment) (10^{-4} au)	M_H (experiment) (10^{-4} au)
2	2.273	1.091	0.001	1.182	1.185	2.262
5	2.185	0.974	0.004	1.211	1.21	2.173
10	2.125	0.849	0.008	1.276	1.27	2.120
30	2.079	0.523	0.012	1.556	1.56	2.058
50	1.991	0.276	0.018	1.715	1.72	1.99
100	1.920	0.090	0.021	1.830	1.84	1.918

rotate further and, in the end, they turn to the same direction as that of H. At this time, the magnetization reaches a maximum for these conditions. With the increase of H, more and more magnetic moments of spin clusters are turned to the direction of H, and the energy of thermal movement needed to change the direction of the magnetic moments into the direction of H becomes less and less. So, T_f moves to lower temperatures. When $\mu_0 H \geqslant 1.0$ T, there is no transition from weak magnetism to ferromagnetism. This suggests that in this case, the external magnetic field is so strong that it can make the large majority of magnetic moments which are not in the direction of H turn to the direction of H. As a result, the energy of the thermal movement does not affect them any longer.

We can quantitatively scale the relation between H and T_f by means of the following equation, according to our experimental data:

$$H = H_0\left(1 - \frac{T_f}{T_C}\right)^b \tag{1}$$

where H_0 is a definite field, under which the freezing temperature (T_f) disappears; b is a scale parameter; T_C is the Curie temperature. Using equation (1), we can calculate the two parameters, which are: $\mu_0 H_0 = 0.574$ (T), $b = 3.929$. The corresponding curve is shown in figure 1, in which the line shows the calculated data and the squares show the experimental data. From figure 1, it is seen that there is a good match to the relation between H and T_f.

In short, by introducing the concept of spin glass, we can explain well the relation between the freezing temperature (T_f) and the applied field (H) in our LSMO films.

3.2. The relaxation phenomenon

Another typical property of spin glass is that there is a long relaxation time, which represents the irreversible magnetization process of the spin-glass system. This property can be seen in figure 2.

Figure 2 shows the relaxation relations between magnetization and time when the external field $\mu_0 H = 0.1$ T, and the temperature $T = 2$, 5, 10, 30, 50 and 100 K. This is a typical relaxation phenomenon. It suggests that the magnetization, which is in a metastable state that has deviated from the equilibrium state, under the effect of the external factors, is restored to the original state. Relaxation is a common phenomenon, which always accompanies the change of a lot of physical properties. From figure 2, it is seen that with increase of the temperature, the initial magnetization M_0 increases gradually (see table 2).

This non-equilibrium dynamical relaxation, in general, can be described using several theoretical models, but we would like to use the double-potential-well model to derive relaxation relations, because the calculated results are more accurate in this case.

Due to the antiferromagnetic interactions between ions, antiferromagnetic clusters are formed below the Curie temperature (T_C). And because of the random distribution of Mn^{3+} and Mn^{4+} ions, magnetic moments are organized into ferromagnetic clusters with different sizes

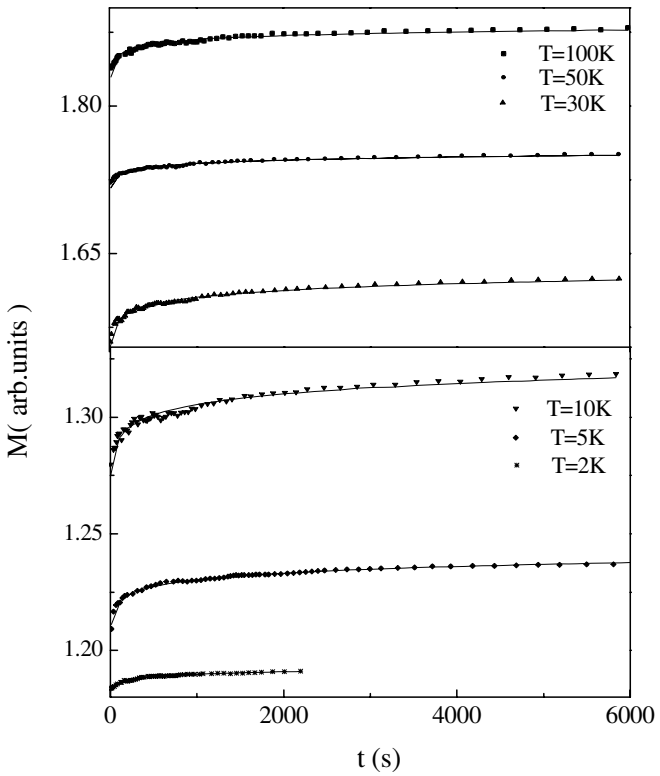

Figure 2. The relaxation relations between M and time ($\mu_0 H = 0.1$ T).

and directions. Thus we can reasonably focus our attention on the contribution of ferromagnetic clusters to the magnetization process of the spin-glass system. In the following paragraphs, a microcosmic picture of the magnetization of one such cluster will be discussed using the model of the double potential well. Then by summing up the contributions of all the clusters, the overall relation will be arrived at.

Let us consider a single magnetic cluster with index i. The process of relaxation can be described as transitions of particles from a higher-energy state to another state with lower energy. During the transition a certain potential barrier must be overcome first. A schematic diagram of the double-potential-well model appears as figure 3.

In the model above, the higher energy level can be regarded as the state of spontaneous magnetization, or the spin-glass state, while the lower energy level represents the state of ferromagnetism, an equilibrium state. Note that the disparity between the minima of the wells (W_m) is brought about by the external field.

Let ε_i represent the barrier energy that a single magnetic moment has to overcome in the transition, P_i represent the probability of any single moment of the cluster being resident in the higher-energy state and τ_i represent the lifetime of that state. According to the formal theory of relaxation [12], we have

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = \frac{P_\infty - P_i}{\tau_i} \tag{2}$$

$$\tau = \tau_0 \exp\left(\frac{\varepsilon_i}{k_B T}\right) \tag{3}$$

where τ_0 is a constant.

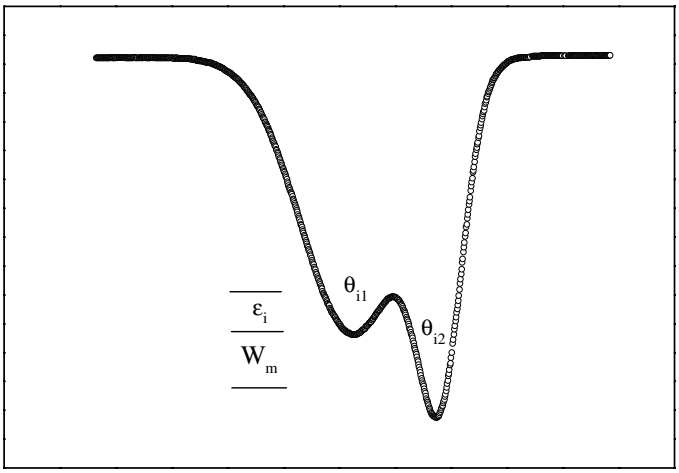

Figure 3. The schematic diagram of the double-potential-well model.

It is obvious that for different i, τ_i and ε_i are also different. Therefore, the overall properties of the system will be distributed over ε, i.e. will be dependent on the distribution function of ε. As stated by Primak [13], for processes distributed in activation energy, those which contribute to the changing rate of the whole system's particular property lie in a narrow band of activation energies: several times k_BT. In our case, $\mathrm{d}P/\mathrm{d}t$ follows the same rules. It was also stated that the centre of the band is determined by

$$\varepsilon_0 = k_BT\ln(At). \tag{4}$$

As we are concerned with a process of relaxation that lasts for a considerably long time, the following approximation can be accepted:

$$\tau_i = \tau_0 \exp\left(\frac{\varepsilon_0}{k_BT}\right). \tag{5}$$

With equations (2)–(4), it can be derived that

$$P_i = P_\infty - \left(\frac{t}{t_0}\right)^{-\gamma} \tag{6}$$

where t_0 is an constant, and $\gamma = 1/\tau_0 A$.

Let μ_i be the overall magnetic moment of the ith cluster; then with the equations above, the total magnetic moment of the ith cluster can be expressed as

$$M_i = \mu_i\cos\theta_{i1}(1-P_i) + \mu_i\cos\theta_{i2}P_i = \alpha_i - \beta_i\left(\frac{t}{t_0}\right)^{-\gamma}. \tag{7}$$

Here θ_{i1} represents the angle between the direction of the spontaneous magnetic moments in the high-energy state and the direction of H, while θ_{i2} represents the angle between the direction of the magnetic moments in the lower-energy state and the direction of H.

We can now sum over all the clusters. And on doing so, the following relation is derived:

$$M = \sum_i M_i = \alpha - \beta\left(\frac{t}{t_0}\right)^{-\gamma}. \tag{8}$$

Here α, β and γ are time-independent parameters, but γ is dependent on temperature. And t_0 is the time at which the measurements were started.

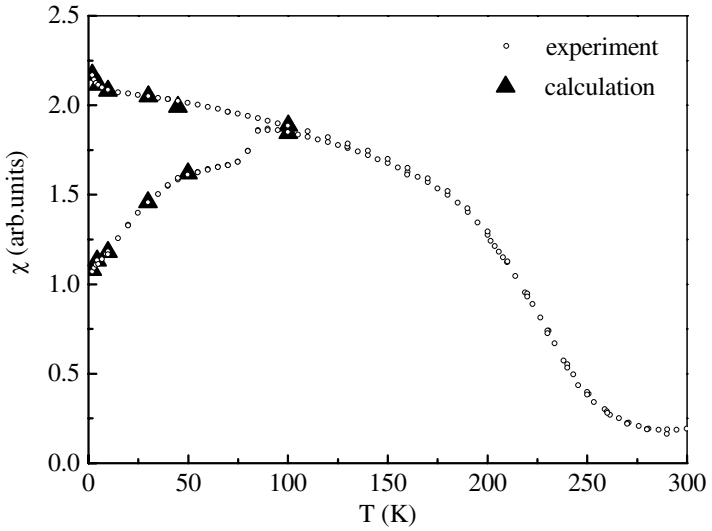

Figure 4. The comparison between the experimental data and the calculated data ($\mu_0 H = 0.1$ T).

From equation (8), we can calculate the relaxation relations between M and time at different temperatures when $\mu_0 H = 0.1$ T. The experimental data in figure 2 can be well fitted by equation (8). The dots and solid curves in figure 2 represent experimental data and calculated data, respectively.

We can also see that when $t = t_0$, M goes to $\alpha - \beta$, which is an initial magnetization of the system and equals M_0, as mentioned above. If $t \to \infty$, we get $M = \alpha$, which stands for magnetization of the system in the equilibrium state. The fitted parameters are listed in table 2.

Analysing these data further, we can see that the parameters α and $\alpha - \beta$ stand for the magnetization when the sample was cooled down in the field and in zero field, respectively. The comparison between the experimental data and the calculated data is shown in figure 4, in which the circles and triangles stand for the experimental data and the calculated data, respectively.

If $\gamma \ll 1$, equation (8) can be transformed into a logarithmic form via the first-order approximation of the Taylor expansion, as indicated by equation (9), which accords with the well-known empirical formula given by Guy [14]:

$$M = \alpha - \beta + \beta\gamma \ln\left(\frac{t}{t_0}\right). \tag{9}$$

From the analysis above, it can be concluded that the experimental results are well explained by the double-potential-well model.

Moreover, we would like to apply the double-potential-well model to the relation between H and the freezing temperature T_f. In the macroscopic range, by summing the contributions of all the magnetic clusters, we can still find two macroscopic states. One is the state of spontaneous magnetization, or the spin-glass state; the other is the state of ferromagnetism. And the situation here is similar to that of our model, in which transition between the two states is essential. The macroscopic picture can also be applied to explain the relation between the freezing temperature and the external field. When H is applied, the latter state will have lower energy than the former one. Thus transitions occur between the two states by overcoming an

energy barrier whose height is determined by the external field and temperature. It is obvious that the bigger the applied field is, the lower the energy barrier will be, which means that the probability of transition from the higher-energy state to the lower-energy one will increase. Then less thermal fluctuation energy will be needed to bring the system into the ferromagnetic state. That is, with the increase of H, T_f becomes smaller. We can observe this in the inset of figure 1, in which every curve can be divided into three parts when $\mu_0 H < 0.5$ T. For example, when $\mu_0 H = 0.05$ T, the first part in the range from 4.2 to 50 K shows that there is a linear relation between χ and T, which represents the turning of the magnetic moments within small clusters or with small angle relative to the direction of H. The second part in the range from 50 to 130 K shows a shoulder-like relation between χ and T, which represents saturation of these clusters. The third part in the range from 130 to 150 K shows yet another linear relation between χ and T, which represents the turning of the magnetic moments within bigger clusters or with greater angle relative to the direction of H. When the applied field increases, the three parts can still be observed, but T_f shifts to lower temperatures and the temperature ranges decrease. Finally, when the applied field is big enough, there is no energy barrier between the states; the 'double potential well' simply transforms into a single potential well and there is no freezing temperature.

From this, we can conclude again that, because the experimental data agree well with the calculated ones, the double-potential-well model has demonstrated practicability.

4. Conclusions

We have investigated systematically the magnetic properties obtained by a SQUID magnetometer and observed the behaviour of a spin-glass-like state, which is caused by the competition between ferromagnetism and antiferromagnetism in epitaxial LSMO films. This competition, together with disorder brought about by the random distribution of Mn^{3+} and Mn^{4+} ions, might result in frustration, an important prerequisite of a spin-glass state, which will lead to many characteristics of spin glass—for instance, magnetic relaxation. The concept of spin glass and the double-potential-well model are introduced to explain: the curves for susceptibility versus temperature; the relation between H and T_f; and the critical magnetic field H_0. They are also applied to calculate the relaxation of M over time. All calculated results are in good agreement with the experimental data.

Acknowledgments

The authors would like to thank Dr L Pi, J F Zhang and Y F Deng. This work was partly supported by the National Science Foundation of China (Grant No 10174022) and the Trans-Century Training Programme Foundation for Talents administered by the Ministry of Education of the People's Republic of China.

References

[1] von Helmolt R, Wecker J, Lorenz T and Samwer K 1995 *Appl. Phys. Lett.* **67** 2093
[2] Zhang X X, Yu R H, Tejada J, Sun G F, Xin Y and Wong K W 1996 *Appl. Phys. Lett.* **68** 3191
[3] Cai J W, Wang C, Shen B G, Zhao J G and Zhan W S 1996 *Appl. Phys. Lett.* **71** 1727
[4] Sundaresan A, Maignan A and Raveau B 1997 *Phys. Rev.* B **55** 5596
[5] Moritomo Y, Higashi K, Matsuda K and Nakamura A 1977 *Phys. Rev.* B **55** R14 725
[6] Gao J, Xiong C S, Tang Y Q, Zhu H, Pi L, Zhu J S, Zhou G E and Zhang Y H 1997 *Chin. Sci. Bull.* **42** 1932

[7] Wohlfarth E P 1980 *Ferromagnetic Materials—a Handbook on the Properties of Magnetically Ordered Substances* vol 1 (Amsterdam: North-Holland)
Bancroft M H 1970 *Phys. Rev.* B **2** 2597
Anderson P W 1970 *Mater. Res. Bull.* **5** 549
[8] Goodenough J B 1970 *Landolt–Börnstein New Series* Group III, vol 4a (Berlin: Springer)
[9] Zener C 1951 *Phys. Rev.* **82** 403
[10] Wollan E O and Koehler W C 1955 *Phys. Rev.* **100** 545
[11] Mydosh J A 1993 *Spin Glasses: an Experimental Introduction* (London: Taylor and Francis)
Ito A, Aruga H, Kikuchi M, Syono Y and Takei H 1988 *Solid State Commun.* **66** 475
[12] Guo Yi-Cheng and Wang Zhen-Xi 1984 *Non-Crystalline Physics* (Beijing: Science) ch 3 (in Chinese)
Uhlmann D R 1978 *Metallic Glasses* (Metals Park, OH: American Society for Metals) ch 6
Mazurin O V 1977 *J. Non-Cryst. Solids* **25** 129
[13] Primak W 1953 *Phys. Rev.* **100** 1677
[14] Guy C N 1977 *Physica* B **86–8** 877