Low Temperature Physics/Fizika Nizkikh Temperatur, 2021, vol. 47, No. 10, pp. 938–941

Effect of hydrostatic pressure on the magnetic susceptibility of MnF_2 single crystal

A. S. Panfilov and G. E. Grechnev

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine
Kharkiv 61103, Ukraine
E-mail: panfilov@ilt.kharkov.ua

Received June 2, 2021, published online August 26, 2021

For the classical antiferromagnet MnF_2 with $T_N \simeq 67$ K, the pressure dependence of static magnetic susceptibility χ at $T > T_N$ was studied for the first time. The measurements of $\chi(P)$ were carried out at fixed temperatures 78, 140, and 300 K using a pendulum-type magnetometer and helium gas pressure P up to 2 kbar. The experimental data on the pressure derivative of magnetic susceptibility, $d\ln\chi/dP$, were analyzed within the Curie–Weiss law for $\chi(T)$ behavior, yielding estimate of the pressure derivative of paramagnetic Curie temperature $d\Theta/dP = -(0.31 \pm 0.05)$ K/kbar and value $(1/\Theta)d\Theta/dP = (3.5 \pm 0.5)$ Mbar^{-1}. The obtained experimental result is explained by the volume dependence of superexchange interaction between the magnetic moments of Mn^{2+} ions.

Keywords: MnF_2, magnetic susceptibility, superexchange, pressure effect.

1. Introduction

The use of high-pressure techniques in the magnetism of solids makes it possible to study the dependence of magnetic interactions on the interatomic distance and obtain valuable information on the nature of these interactions. In the case of magnetic insulators, which include the classical antiferromagnet MnF_2 ($T_N \simeq 67$ K), the efficiency of applying pressures is determined by the high sensitivity of the dominant superexchange interaction to changes in the parameters of the crystal lattice.

For MnF_2, the available experimental data on the effect of pressure on magnetic characteristics refer to various research methods. From measurements of the nuclear magnetic resonance frequency of the F^{19} nucleus as a function of pressure at the different temperatures [1, 2] the pressure derivative of the Néel temperature was deduced to be $dT_N / dP = +(0.30 \pm 0.03)$ K/kbar. This result is consistent with the expected enhancement of the superexchange interactions with decreasing interatomic distances under pressure. The source of indirect information on the pressure dependence of magnetic susceptibility is the value of volume magnetostriction, which is proportional to the pressure derivative of susceptibility, $d\chi / dP$. The estimate of this derivative, using the experimental data on magnetostriction in MnF_2 [3, 4], turns out to be negative ($d\chi / dP < 0$).

The first and so far the only study of the pressure effect on static magnetic susceptibility was carried out by Astrov, *et al.* [5]. The temperature dependence $\chi(T)$ of the polycrystalline sample of MnF_2 was measured near the Néel temperature at $P = 0$ and $P \simeq 1.9$ kbar in order to determine the shift of T_N under pressure. As a result, the reported value $dT_N / dP = (0.8 \pm 0.1)$ K/kbar seems to be somewhat overestimated and the observed positive pressure effect on χ ($d\chi / dP > 0$) is puzzling.

In this work, in order to refine the pressure effect on magnetic properties of MnF_2 the measurements of its magnetic susceptibility in the paramagnetic state were carried out with the application of hydrostatic pressure, using a homemade precision magnetometer of pendulum type. The aim of the work was to explore volume dependencies of the paramagnetic Curie temperature Θ and the superexchange interaction in MnF_2. The obtained experimental data were analyzed within simple approach based on the Curie–Weiss law for description of the temperature dependence $\chi(T)$ of MnF_2 in paramagnetic state.

2. Experimental details and results

The single-crystalline sample of MnF_2 was cut from the same material that was previously used in optical research [6]. The sample was in the shape of a parallelepiped with dimensions of about $5 \times 2 \times 0.55$ mm and mass of 21.8 mg. According to the literature data, the crystal structure of MnF_2 is a tetragonal rutile type and the AFM direction lies along the c axis. Features of the temperature dependence of its magnetic susceptibility at ambient pressure [7] is shown in Fig. 1.

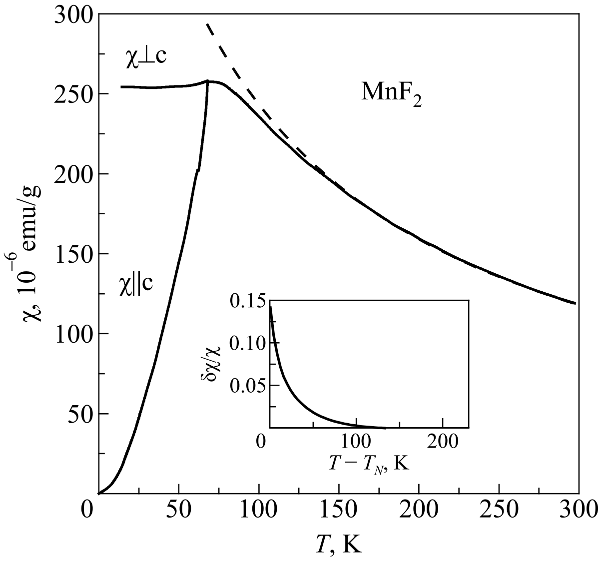

Fig. 1. Temperature dependence of magnetic susceptibility $\chi(T)$ for single crystal of $\mathrm{MnF_2}$ from Ref. 7 (solid lines). Dashed line is the Curie–Weiss model description, $\chi^{CW}(T) = C/(T-\Theta)$. The inset shows the deviation of $\chi(T)$ dependence from the Curie–Weiss behavior, $\delta\chi(T) = \chi^{CW}(T) - \chi(T)$, normalized to $\chi(T)$.

The measurements of the pressure effect on magnetic susceptibility of $\mathrm{MnF_2}$ were carried out under helium gas pressure P up to 2 kbar, using a pendulum type magnetometer [8]. In this device the sample was placed inside a small compensating coil located at the lower end of the pendulum rod. Under switching on magnetic field, the measure of the sample magnetic moment is the value of current through the coil, at which the sample moment is fully compensated by the magnetic moment of coil and magnetometer comes back to its initial position. To measure the pressure effects, the mechanical part of pendulum was inserted into a cylindrical non-magnetic pressure cell, which was placed inside a cryostat. In order to eliminate the effect on susceptibility of the temperature changes during applying or removing pressure, the measurements were performed at fixed thermostat temperatures. The relative errors of measurements of χ under pressure did not exceed 0.05 % for employed magnetic field $H = 1.7$ T (detailed analysis of the origin of errors and their magnitude is given in Ref. 8).

The experimental pressure dependencies of χ at fixed temperatures 78, 140, and 300 K are shown in Fig. 2. As seen, they are linear within experimental errors and the used range of pressures. The corresponding values of the normalized pressure derivative of χ, $(1/\chi)d\chi/dP \equiv d\ln\chi/dP$, are listed in Table 1 together with the values of χ at $P = 0$. Reasonable agreement of the values of χ at zero pressure with the literature data in Fig. 1 indicates a sufficiently high quality of our sample.

Note that since the magnetic susceptibility of $\mathrm{MnF_2}$ in the paramagnetic phase is isotropic, the data obtained correspond to an arbitrary choice of the sample orientation relative to the magnetic field direction.

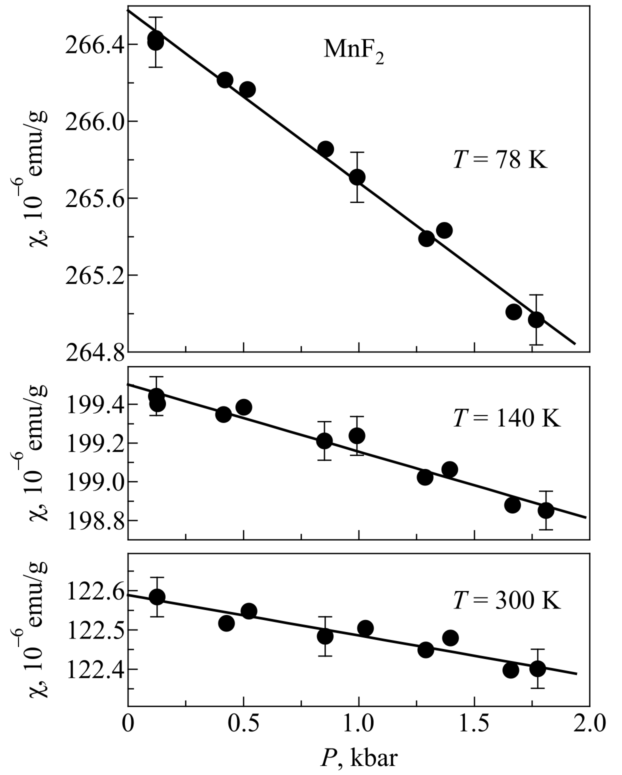

Fig. 2. Pressure dependence of magnetic susceptibility of $\mathrm{MnF_2}$ at different temperatures.

Table 1. Magnetic susceptibility χ at $P = 0$ and its pressure derivative $d\ln\chi/dP$ for $\mathrm{MnF_2}$ at different temperatures

T, K	$\chi, 10^{-6}$ emu/g	$d\ln\chi/dP$, Mbar^{-1}
78	266.6	-3.3 ± 0.4
140	199.5	-1.7 ± 0.3
300	122.6	-0.8 ± 0.2

3. Discussion

Analysis of the temperature dependence $\chi(T)$ for $\mathrm{MnF_2}$ (Fig. 1) shows that at T above of about 150 K it obeys Curie–Weiss (CW) law:

$$\chi(T) \simeq \chi^{CW}(T) = \frac{C}{T-\Theta} \tag{1}$$

with the Curie constant C corresponding to the effective magnetic moment of $\mathrm{Mn^{2+}}$ ion $\mu_{\mathrm{eff}} \simeq 5.9\,\mu_B$ and paramagnetic Curie temperature $\Theta \simeq -89$ K. Values of $\mu_{\mathrm{eff}} \simeq 5.9\,\mu_B$ and saturated magnetic moment $\mu_{\mathrm{sat}} \simeq 5.0\,\mu_B$ [9] coincide with the spin moment expected for the free $\mathrm{Mn^{2+}}$ ion with spin number $S = 5/2$. Therefore, it is quite reasonable to assume that the dependence of this moment [and Curie constant C in Eq. (1)] on pressure is weak. Then the effect of pressure on χ is determined only by the pressure dependence of Θ, as it follows from Eq. (1):

$$\frac{d\ln\chi(T)}{dP} \simeq \frac{d\ln\chi^{CW}(T)}{dP} \simeq \frac{1}{T-\Theta}\frac{d\Theta}{dP}. \tag{2}$$

Experimental values of $d\ln\chi / dP$ as a function of $1/(T-\Theta)$ are shown in Fig. 3. As can be seen, at high temperatures, where the Curie–Weiss law is fulfilled and Eq. (2) is valid, this dependence is close to linear. Its slope, indicated in Fig. 3 by the dashed line, determines the value of the derivative

$$d\Theta / dP = -(0.31 \pm 0.05)\ \mathrm{K/kbar}. \qquad (3)$$

As seen in Fig. 3, at temperatures below about 150 K, the magnitude of the pressure effect, $d\ln\chi / dP$, begins to gradually deviate from the values predicted by Eq. (2) and grows rapidly when approaching the Néel point. For MnF_2, a similar peculiarity near T_N was observed earlier in temperature dependence of magnetostriction [3], which is directly related to the pressure derivative of susceptibility. Taking into account a rapid increase in the deviation of $\chi(T)$ behavior from the CW law as the temperature approaches T_N (see Fig. 1) and the shift of T_N itself under pressure, an additional contribution to the magnitude of the pressure effect on $\chi(T)$, given by Eq. (2), can be represented as

$$\frac{d\ln\chi(T)^*}{dP} \simeq -\frac{1}{\chi(T)} \frac{\partial[\delta\chi(T)]}{\partial t} \frac{dt}{dP}, \qquad (4)$$

where the designations $\delta\chi(T) = \chi^{CW}(T) - \chi(T)$ and $t = T - T_N$ are adopted. When temperature approaches T_N the magnitude of this contribution grows rapidly and becomes comparable with the CW value determined by Eq. (2). So at $T = 78$ K, its estimation by Eq. (4) gives

$$\frac{d\ln\chi(78\,\mathrm{K})^*}{dP} \simeq -1.35\ \mathrm{Mbar}^{-1} \qquad (5)$$

using the values $(1/\chi(T))\partial[\delta\chi(T)]/\partial t \simeq -0.0045\ \mathrm{K}^{-1}$ (see inset in Fig. 1) and $dt/dP = -dT_N/dP \simeq -0.30$ K/kbar [2]. For the same temperature, the CW contribution to the pressure effect on χ is determined by Eq. (2) to be

$$\frac{d\ln\chi^{CW}(78\,\mathrm{K})}{dP} \simeq -1.85\ \mathrm{Mbar}^{-1} \qquad (6)$$

As can be seen, the sum of both contributions at 78 K is in good agreement with the corresponding experimental value, $d\ln\chi / dP \simeq -3.3\ \mathrm{Mbar}^{-1}$, and this confirms the validity of the approach used.

The experimental data on the pressure dependence of Θ in MnF_2 can be expressed in the form of a "magnetic Grüneisen constant"

$$\gamma_m = -\frac{V}{\Theta}\frac{d\Theta}{dV} = \frac{B}{\Theta}\frac{d\Theta}{dP}. \qquad (7)$$

Here B is the bulk modulus. Using in Eq. (7) the room temperature value $B = 0.93$ Mbar, obtained by averaging the available literature data [10–12], we determine the γ_m value to be equal to

$$\gamma_m = 0.33 \pm 0.06. \qquad (8)$$

Since the value of Θ is proportional to the value of the superexchange interaction J, the volume dependence of J is related to the same value of γ_m, namely

$$\gamma_m = -\frac{d\ln J}{d\ln V}. \qquad (9)$$

The estimate for γ_m obtained in MnF_2 is reasonably consistent with the trend towards the value $\gamma_m = 10/3$ for a wide range of magnetic insulators, which was first pointed out by Bloch on the basis of analysis of the available experimental data [13]. The origin and validuty of the "10/3" rule for the volume dependence of superexchange interactions was discussed, for example, in Refs. 14, 15. It was noted that this rule is not universal and requires some adjustments taking into account the individual characteristics of materials, such as features of structural properties, type of crystal bonds, etc. In addition, when evaluating value of γ_m, along with the dominant superexchange, it is necessary to consider other contributions to the magnetic interactions [16, 17].

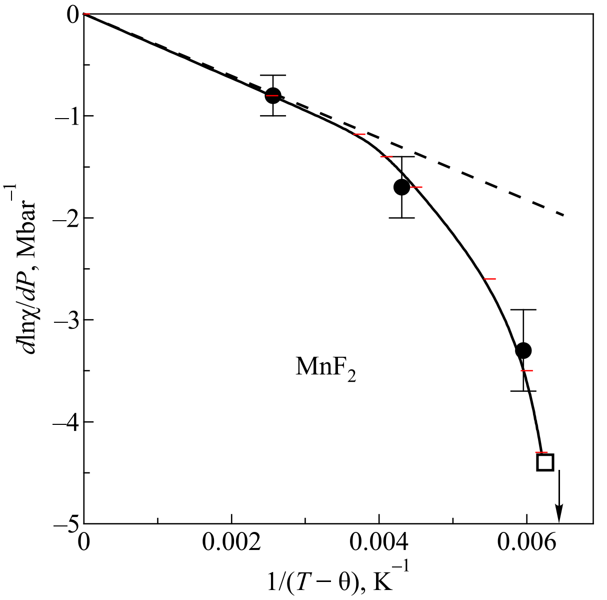

Fig. 3. Pressure derivative of magnetic susceptibility $d\ln\chi / dP$ in MnF_2 as a function of $1/(T-\Theta)$; (●) – our data, (☐) – estimate from the magnetostriction data of Ref. 4 at $T = 70$ K. Solid line is a polynomial fit of the experimental data; dashed straight line corresponds to a model description by Eq. (2). The arrow marks $T = T_N$.

4. Concluding remarks

As far as we know, the dependence of magnetic susceptibility of the antiferromagnet MnF_2 on hydrostatic pressure at temperatures above T_N has been properly measured for the first time. From the analysis of the obtained experimental data, it was determined that the paramagnetic Curie temperature Θ and the effective exchange interaction J increase in magnitude with increasing pressure. The corresponding estimate of the magnetic Grüneisen parameter turns out to be close to the value $\gamma_m \simeq 10/3$ inherent in the superexchange interaction.

Acknowledgments

We express our deep gratitude to N. F. Kharchenko for providing a single-crystal sample of MnF_2 and some comments on the text.

---

1. G. B. Benedek and T. Kushida, *Phys. Rev.* **118**, 46 (1960).
2. P. Heller and G. B. Benedek, *Phys. Rev. Lett.* **8**, 428 (1982).
3. Y. Shapira, R. D. Yacovich, C. C. Becerra, S. Foner, and E. J. McNiff Jr, *Phys. Lett. A* **55**, 363 (1976).
4. V. I. Nizhankovskii, *Eur. Phys. J. B* **78**, 449 (2010).
5. D. N. Astrov, S. I. Novikova, and M. P. Orlova, *Sov. Phys. JETP* **37**, 851 (1960).
6. N. F. Kharchenko, O. V. Miloslavskaya, and A. A. Milner, *Fiz. Nizk. Temp.* **31**, 1081 (2005) [*Low Temp. Phys.* **31**, 825 (2005)].
7. C. Kittel, *Introduction to Solid State Physics*, John Wiley Sons Inc., Hoboken, New Jersey (2004), pp. 321–360.
8. A. S. Panfilov, *Fiz. Nizk. Temp.* **41**, 1318 (2015) [*Low Temp. Phys.* **41**, 1029 (2015)].
9. J. Strempfer, U. Rutt, S. P. Bayrakci, Th. Bruckel, and W. Jauch, *Phys. Rev. B* **69**, 014417 (2004).
10. D. Gerlich, S. Hart, and D. Whittal, *Phys. Rev. B* **29**, 2142 (1984).
11. R. M. Hazen and L. W. Finger, *J. Phys. Chem. Solids* **42**, 143 (1981).
12. E. Stavrou, Y. Yao, A. F. Goncharov, Z. Konôpková, and C. Raptis, *Phys. Rev. B* **93**, 054101 (2016).
13. D. Bloch, *J. Phys. Chem. Solids* **27**, 881 (1966).
14. K. C. Johnson and A. J. Sievers, *Phys. Rev. B* **10**, 1027 (1974).
15. G. A. Garcia and R. Ingalls, *J. Phys. Chem. Solids* **37**, 211 (1976).
16. R. Ritter, L. Jansen, and E. Lombardi, *Phys. Rev. B* **8**, 2139 (1073).
17. L. J. De Jongh and R. Block, *Physica B* **79** 568 (1975).

Вплив гідростатичного тиску на магнітну сприйнятливість монокристала MnF_2

A. S. Panfilov, G. E. Grechnev

Для класичного антиферомагнетика MnF_2 з $T_N \simeq 67$ К вперше досліджено залежність від тиску статичної магнітної сприйнятливості χ при $T > T_N$. Вимірювання $\chi(P)$ проведено при фіксованих температурах 78, 140 та 300 К за допомогою маятникового магнітометра під тиском газу гелію P до 2 кбар. Експериментальні дані про похідну магнітної сприйнятливості по тиску, $d\ln\chi / dP$, проаналізовано за законом Кюрі–Вейсса для опису поведінки $\chi(T)$. Оцінено похідну по тиску для парамагнітної температури Кюрі, $d\Theta/dP = -(0{,}31 \pm \pm 0{,}05)$ К/кбар та величини $(1/\Theta)d\Theta/dP = (3{,}5 \pm 0{,}5)$ Мбар$^{-1}$. Отриманий експериментальний результат пояснюється об’ємною залежністю суперобмінної взаємодії між магнітними моментами іонів Mn^{2+}.

Ключові слова: MnF_2, магнітна сприйнятливість, суперобмін, вплив тиску.