Journal of Magnetics 13(1), 23-29 (2008)

Characteristics of $Mn_xSi_{1-x}Te$ Compound Studied by Electron Magnetic Resonance and Other Experiments

Sung-Ho Na*, Heung-Chul Kim, Jung-Woo Park, and Jang-Whan Kim

Department of Physics, Pusan National University, Pusan 609-735, Korea

(Received 15 February 2008)

The magnetic and other physical characteristics of $Mn_xSi_{1-x}Te$ have been investigated by electron magnetic resonance (EMR), X-ray diffraction (XRD) and other experiments. $Mn_xSi_{1-x}Te$ is found to have corundum structure for manganese contents up to 10% and also to be ferromagnetic for temperatures below 80 K. While ferromagnetic resonance signal coexists with the usual paramagnetic resonance signal, invariance of the g-factor inferred from the electron paramagnetic resonance signals throughout all temperature ranges clearly confirms that the manganese ions are in the electronic $3d^5$ state. The temperature dependence of EMR line-width is the same as other diluted magnetic semiconductors. From the EMR signals relaxation times T_2 and T_1 of $Mn_xSi_{1-x}Te$ compounds are estimated to be about 4.4×10^{-10}s and 9.3×10^{-8}s respectively and are found to vary slightly with temperature or composition change. Exchange narrowing of the EMR line-width becomes dominant for the sample in which the substitution ratio, x = 30%. For one sample, in which x = 0.5%, spin glass-like behavior is indicated by EMR signals for temperatures lower than 60 K. This behavior may authentic for samples within a certain range of x.

Keywords : electron magnetic resonance, ferromagnetism, EMR line-width, g-factor, diluted magnetic semiconductor, spin glass

1. Introduction

$Mn_xSi_{1-x}Te$ belongs to the diluted magnetic semiconductor (DMS) species [1] and contains manganese ions in Si_2Te_3 corundum structure. Ferromagnetic hysteresis is found for $Mn_xSi_{1-x}Te$ below 80 K. Above 80 K the compound is found to be paramagnetic. The g-factor inferred from EMR signal of $Mn_xSi_{1-x}Te$ is found constant under different temperature conditions as well as different manganese and silicon contents. The manganese ions in $Mn_xSi_{1-x}Te$ must therefore be free from spin orbit coupling and are believed to be in the $3d^5$ electronic state so as Mn^{2+} [2]. At 77 K, the ferromagnetic resonance signal is found together with the electron paramagnetic resonance signal. This coexistence suggests non-uniform distribution of the manganese ions within the crystal. As other diluted magnetic semiconductors [1, 3], the EMR signal line-width of the $Mn_xSi_{1-x}Te$ compound increases exponentially as the temperature decreases. Although there are other factors possibly influencing the line-width of the $Mn_xSi_{1-x}Te$ EMR signal, dipolar broadening and exchange narrowing [4] are believed to be the main mechanisms involved here. The EMR line-width of the samples gradually increases with x up to 10%, but is reduced significantly for the sample when x = 30%. This is the so-called exchange narrowing and is due to excessive manganese ion concentration. It is consistent with crystal structure instability as seen from XRD patterns. The EMR intensity is another measure of magnetic susceptibility. For one sample in which x = 0.5%, The EMR intensity was seen to gradually decreased with temperature for temperatures below 60 K. It then decreased almost linearly below 30 K. From this temperature dependence of EMR intensity, $Mn_xS_{i-x}Te$ is thought to be a spin glass-like material.

*Corresponding author: Tel: +82-51-510-3399
Fax: +82-51-513-7664, e-mail: sunghona@pusan.ac.kr

2. Characterizations

The Bridgman method, which is a conventional technique to grow bulk DMS crystals, was used to make $Mn_xSi_{1-x}Te$ samples for x = 0.5%, 3%, 5%, 10%, and 30%. Correct stoichiometric amounts of high purity manganese, silicon, and tellurium were mixed and heated above

ⓒ 2008 Journal of Magnetics

melting point in a Bridgman crucible. The crucible was moved downwards very slowly to the low temperature region at a rate of approximately 1 mm per hour. Samples of $Mn_xSi_{1-x}Te$ having a flake occurrence were acquired. XRD patterns confirmed the Si_2Te_3 corundum structure of these samples.

The selected conditions of the x-ray diffraction experiments are as follows:

- Cu target,
- λ = 1.5406 A,
- continuous scan with speed of 2.00 deg/min,
- 40 kV, 30 mA,
- divergence slit = 1.00 deg,
- scatter slit = 1.00 deg,
- receiving slit = 0.30 mm.

A Superconducting Quantum Interference Device (SQUID) and Vibrating Sample Magnetometer (VSM) were used in this study to measure the induced magnetization of the samples. The SQUID magnetometer used for this study is MPMS-7 from the Quantum Design. The LakeShore model 7300 VSM in KBSI Busan Branch was also used for this study. Several M-H hysteresis loops and magnetic susceptibility temperature dependence curves were acquired by this VSM. The attainable temperature range was between 40 K and room temperature.

EMR experiments were carried for the samples with two commercial EMR units. An X-band EPR spectrometer Bruker 300 EMX was used with 9.74 GHz microwaves generated by the Klystron. The EMR experiment was normally performed between 140 K and room temperature, although samples were also immersed in liquid nitrogen for an EMR experiment at T = 77 K. For one sample, the EMR experiment was carried out at 5 K, using He flow. These two latter experiments were done with Jeol JEX-PX 2000.

3. Results and Discussion

X-Ray diffraction patterns (θ–2θ) are acquired as Fig. 1. The crystal structures of $Mn_xSi_{1-x}Te$ compounds generally coincide with corundum structure of Si_2Te_3 (hexagonal, $P\bar{3}1c$, a = 7.429 A, c = 13.471 A), which is an extended type of hexagonal close packed structure and which is also the only stable silicon tellurium compound [5]. It is found that the crystal structure of $Mn_xSi_{1-x}Te$ compound slightly deviates from Si_2Te_3 structure as x increases to 20% and almost loses that Si_2Te_3 structure for x = 30%. It should be noted that the tellurium deficiency in the samples of this study, though significant in amount, does not alter the whole crystal structure.

The magnetic susceptibilities of the samples acquired by VSM are in Fig. 2. Three samples of x = 0.5%, 5%, and 10% show a ferromagnetic character below the Curie temperature around 80 K and are paramagnetic for higher temperatures. But the other sample in which x = 3% exhibits only paramagnetic behavior and there is evidence, of its being contaminated, such as its reddish color. Hysteresis curves of $Mn_xSi_{1-x}Te$ samples in which x = 0.5% and 10% are given in Fig. 3.

A brief interpretation of the magnetic character of $Mn_xSi_{1-x}Te$ is the following. First the $Mn_xSi_{1-x}Te$ crystals, except one sample of x = 3%, showed ferrimagnetic or ferromagnetic property below 80 K. But their Curie temperatures are all the same, so that the magnetic moments in these samples are believed not to be uniformly distributed throughout the sample but rather concentrated in separate smaller regions, in which the magnetic moments exist with same density. By extrapolation from the inverse susceptibility curve, the Curie-Weiss temperature of the $Mn_xSi_{1-x}Te$ sample in which x = 0.5% is found to be approximately −25 K. This

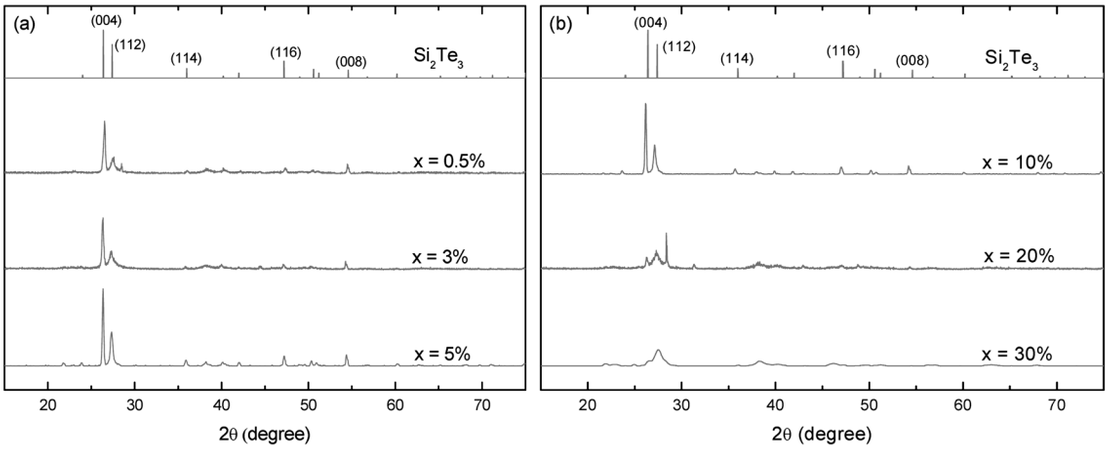

Fig. 1. X-Ray Diffraction Pattern of $Mn_xSi_{1-x}Te$: x = 0.5%, 3%, 5%, 10%, 20%, and 30%.

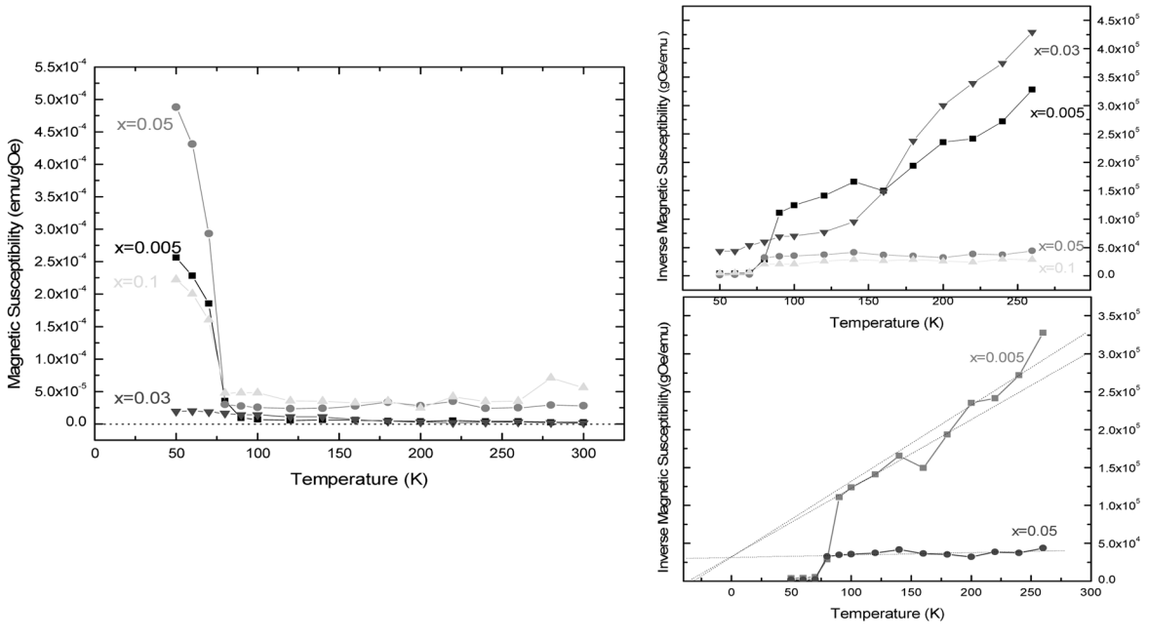

Fig. 2. Magnetic Susceptibility Curves of $Mn_xSi_{1-x}Te$ for x = 0.5%, 3%, 5%, and 10% and Inverse Magnetic Susceptibility Curves.

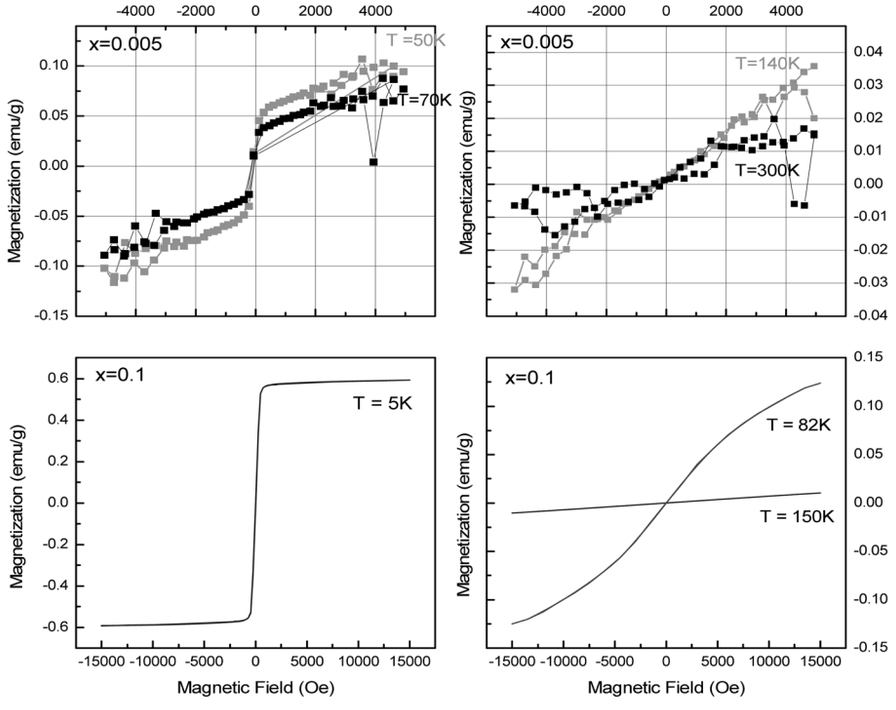

Fig. 3. Magnetization Loop of $Mn_xSi_{1-x}Te$ for x = 0.5% and 10%.

sample can also be regarded as ferrimagnetic from its inverse magnetic susceptibility [6].

Two other samples of $Mn_xSi_{1-x}Te$ with x = 5% and 10%, which both exhibit ferromagnetic behavior in magnetic susceptibility, do not show any noticeable change in susceptibility for T > 80 K. It is not clear why these two samples show constant magnetic susceptibility for T > 80 K. Van Vleck or Pauli paramagnetism can not be the cause [7, 8]. The fact that the Curie temperatures of three samples, x = 0.5%, 5%, and 10%, are almost the same and not altered by manganese content differences, needs explanation. If the manganese ions were randomly distri-

buted in the samples as ideal diluted magnetic semiconductor, the Curie temperature should depend on manganese content. Since this is not the case here, it is believed that the manganese ions in these samples are not distributed randomly in the crystal structure but quite possibly are gathered into “islands” of uniform manganese density. Tellurium deficiency in the samples, as discussed earlier, could be the main cause of this. The $Mn_xSi_{1-x}Te$ sample with x = 3% exhibits paramagnetism but its paramagnetic behavior is not genuine and can be divided into two different temperature ranges, T < 140 K and T > 140 K. This kind of magnetic character can not be simply categorized. It is possible that this sample is a mixture of two different magnetic structures, each having their own respective Curie-Weiss temperatures of −30 K and 110 K.

Typical EMR signals are shown in Fig. 4. At selected temperatures EMR absorption signals are acquired for $Mn_xSi_{1-x}Te$ samples in which x = 0.5%, 3%, 5%, 10%, and 30%. EMR signals measured at room temperature and at 77 K are drawn together in Fig. 5.

The EMR signal acquired for $Mn_xSi_{1-x}Te$ samples are Lorentzian in shape. The intensity of the signals is seen to increase as temperature decreases. The temperature dependence of the EMR signal intensity down to 140 K of $Mn_xSi_{1-x}Te$ samples with x = 0.5%, 3%, 5%, 10%, and 30% is shown in Fig. 6. Though not precise, an exponential decrease in EMR intensity with respect to temperature increase can be easily seen in this figure. The same data plotted on a logarithmic scale in the adjacent figure confirm the exponential dependence of the Boltzmann factor.

The overall g-factors inferred are 1.993±0.002 and are

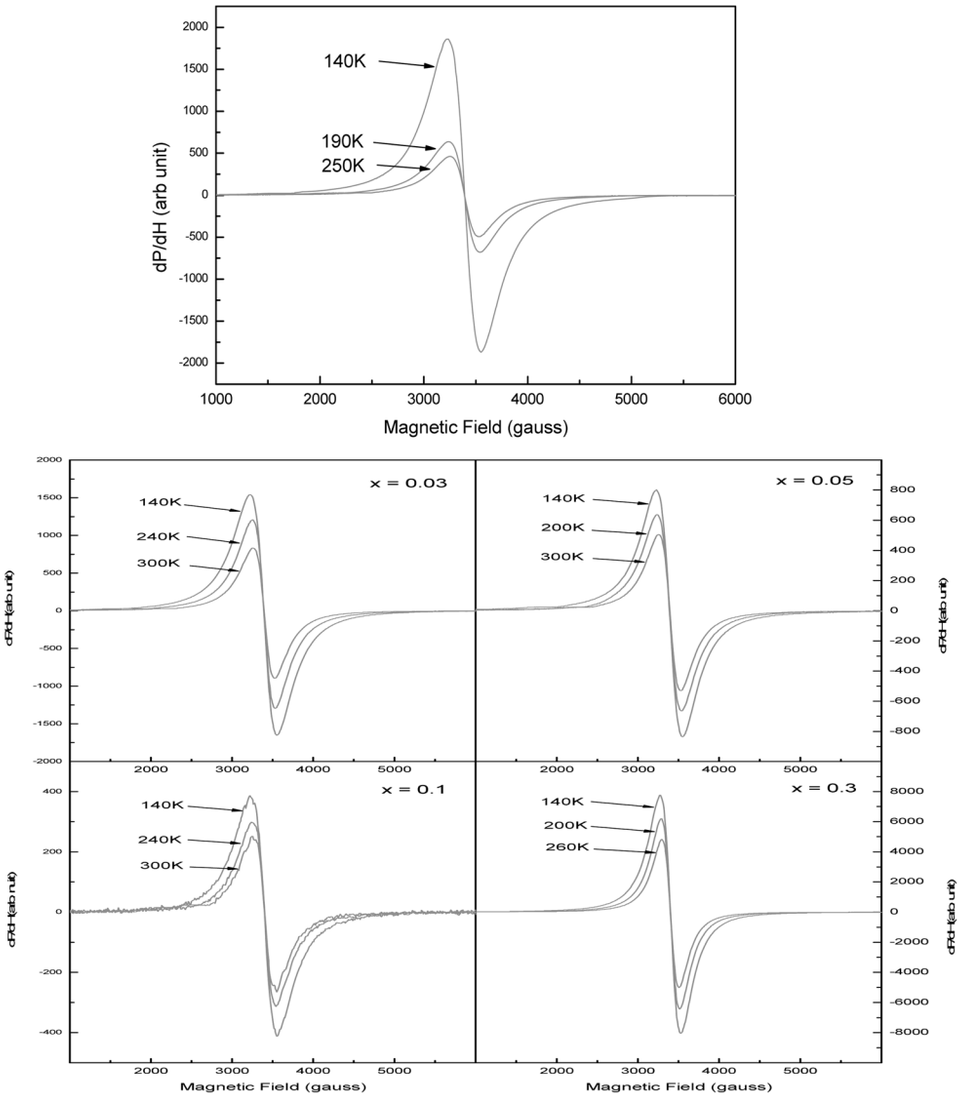

Fig. 4. Typical EMR signals of the samples of $Mn_xSi_{1-x}Te$.

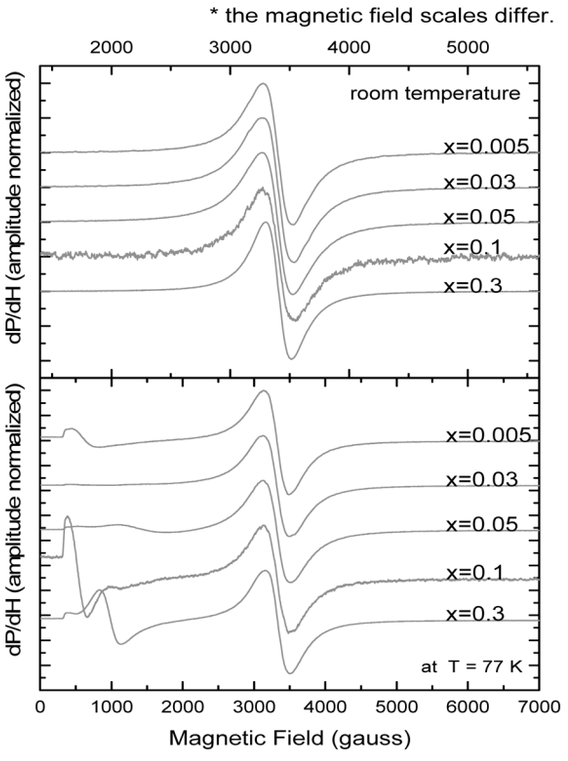

Fig. 5. EMR signals of the samples of $Mn_xSi_{1-x}Te$ (at room temperature and at 77 K).

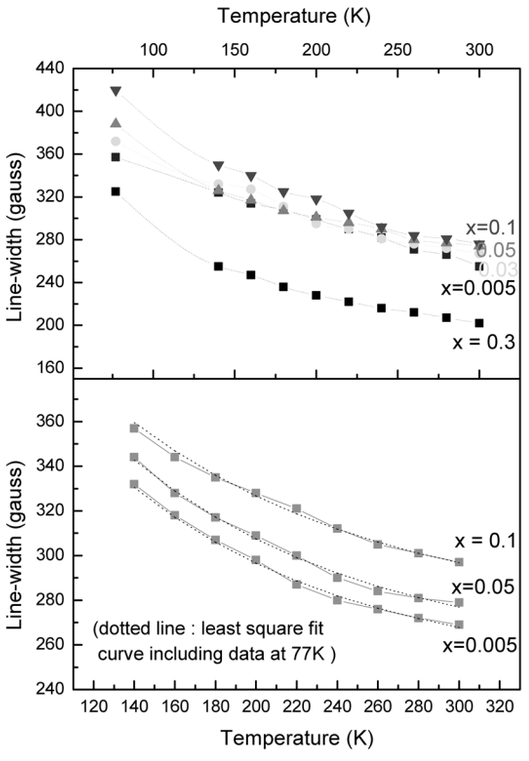

Fig. 7. EMR line-widths and their least square fit of the samples of $Mn_xSi_{1-x}Te$.

not changing with respect to the manganese content or temperature. The g-factor of the contaminated sample records 1.991 in all temperature ranges, and is the largest deviation. If the manganese ions in these samples had orbital angular momentum, there should be g-factor variations for differing temperatures due to spin-orbit coupling. It is therefore believed that the electronic state of the manganese ions in these sample is $Mn^{2+}(3d^5)$, which has zero angular momentum. EMR amplitudes of all samples decrease exponentially with increasing temperature. The deviation of the $Mn_xSi_{1-x}Te$ compound g-factor from 2.0023 – the free electron g-factor, to 1.993 is believed to be mainly associated with the sp-d bonding of manganese ions (d orbital) with tellurium and silicon ions [1]. At T = 77 K two separated absorption signals are recorded together. One is recorded at 600 to 1000 gauss and this corresponds to an effective g-factor of about 7-10. The other signals are the usual paramagnetic EMR absorption signals. The low field absorption signals are believed to be caused by neighboring manganese ions in the crystal

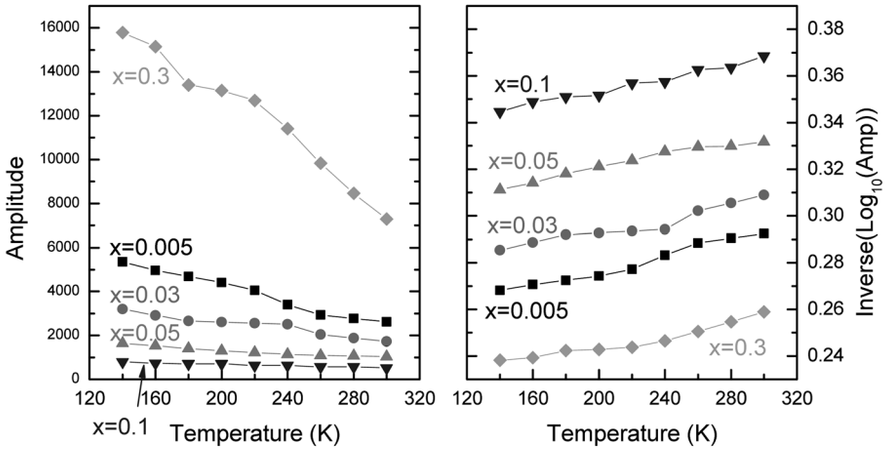

Fig. 6. EMR signal intensity and Inverse of its logarithm for $Mn_xSi_{1-x}Te$ with x = 0.5%, 3%, 5%, 10%, and 30%.

simultaneously absorbing microwave radiation while they undergo transitions from alpha states to beta states under the imposed magnetic fields. This phenomenon has been called as ferromagnetic resonance - i.e. FMR. So the Curie temperature must be higher than 77 K and in fact is assumed to be about 80 K by consideration of this FMR signal taken together with the magnetic susceptibility measurements.

The line-widths (peak to peak magnetic field) of the EMR signals for $Mn_xSi_{1-x}Te$ compounds are varied by differing composition as well as temperature. All samples of $Mn_xSi_{1-x}Te$ show larger line-widths for lower temperatures. In fact, this is a general EMR characteristic of DMS [3, 9]. The line-width variations of the EMR sample signals as function of temperature are drawn in Fig. 7. As the manganese content increases from 0.5% to 3%, 5%, and 10%, the line-width increases. This tendency is believed to be due to dipolar broadening. But for a sample with a Mn content of 30%, the EMR line-width is smaller than all of the other samples. There is no plausible explanation for this observation except for the possibility that exchange narrowing dominates over dipolar broadening in that particular sample, where the manganese ion content increases up to 30% and exceeds the limit concerned. The exponential dependence of the EMR line-width has been suggested by Sayad and Bagat [9].

A least squares fit of the exponential temperature dependence of the EMR line-width are first acquired for x = 0.5%, 5%, and 10% and plotted in Fig. 7. The relation is then expressed as the following.

$$\Gamma=\Gamma_0+\Gamma_1 \exp(-T/T_0) \tag{1}$$

Γ_0 and Γ_1 are estimated to be about 250 gauss each and the corresponding value of T_0 is about 120 K.

Using Bloch's formalism for describing the magnetic resonance [10], the relaxation times can be inferred from the line shape of EMR absorption signal:

$$\nu=\frac{\gamma h_1 T_2}{1+(T_2\Delta\omega)^2+\gamma^2 h_1 T_1 T_2} M_0 \tag{2}$$

where γ is magnetogyric ratio and h_1 is amplitude of oscillating magnetic field.

Since EMR absorption is proportional to ν and since the first two terms in the denominator usually dominate,

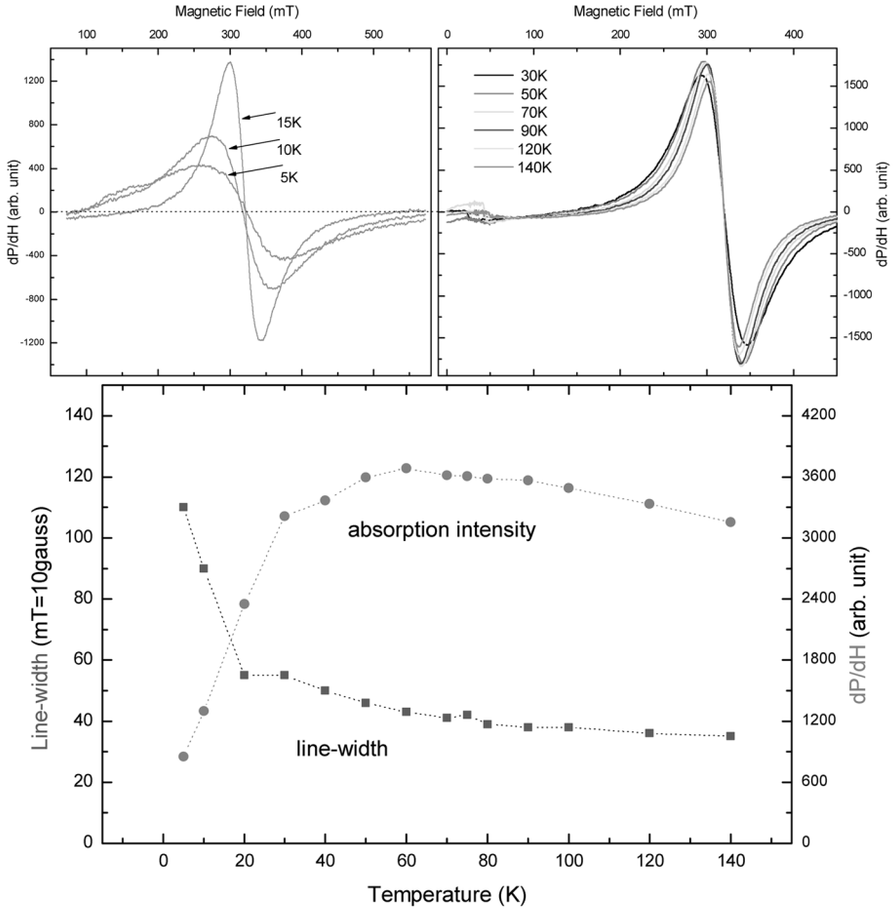

Fig. 8. Low temperature EMR signal (above) and temperature dependence of the signal intensity and line-width.

the spin-spin relaxation time T_2 can be estimated with the peak to peak line-width as the following.

$$T_2 = \frac{1}{(\omega_{1/2} - \omega_0)} = \frac{1}{\gamma(H_{1/2} - H_0)} = \frac{2}{\sqrt{3}\gamma\Delta H_{p-p}} \quad (3)$$

where p-p stands for peak to peak.

And near resonance center, the last term becomes much larger and so from the half absorption point yields spin-lattice relaxation time T_1 as the following.

$$T_1 = \frac{1}{\gamma^2 h_1^2 T_2} \quad (4)$$

The relaxation times, T_2 and T_1, for $Mn_xSi_{1-x}Te$ compounds at 200 K are estimated to be about 4.4×10^{-10}s and 9.3×10^{-8}s respectively and vary slightly with temperature or compositional change. For all samples, T_2 decreases about 15 percent and 30 percent as temperature changes from room temperature to 140 K and 77 K, respectively. And T_1 increases about 20 percent and 40 percent over the same respective temperature decrease. Estimates of T_2 and T_1 also slightly vary with manganese content variations. T_2 is smaller for higher manganese content except in the case of the $Mn_xSi_{1-x}Te$ sample in which x = 30%.

Low temperature EMR data from the $Mn_xSi_{1-x}Te$ sample in which x = 0.5%, are analyzed as the following. The EMR absorption signal records a maximum intensity at 60 K. Below 60 K, the absorption intensity decreases with decreasing temperature, while the line-width shows steady exponential increase, as seen in Fig. 8. From this EMR signal temperature dependence, the sample is believed to have spin-glass-like behavior below 60 K [11, 12]. The inferred g-factor remains at 1.993 except for temperatures below 10 K, where the EMR signal becomes unstable. The constant g-factor over all temperature ranges again confirms that the manganese ion must be in the $3d^5$ electronic state.

4. Conclusion

$Mn_xSi_{1-x}Te$ crystals of x = 0.5%, 3%, 5%, 10%, and 30% have been investigated by their EMR signal, XRD pattern, and magnetic susceptibility. The crystal structures of these compounds are found to be Si_2Te_3 corundum structure, but deviate from it as the manganese content increases to more than 10 percent. The $Mn_xSi_{1-x}Te$ crystals, except the sample of x = 3%, showed ferromagnetic or ferrimagnetic property below 80 K. The magnetic moments are not uniformly distributed in each sample but are possibly concentrated into separate confined regions, which may be called as island or cluster. The magnetic moment concentration in those island regions are believed to be slightly less than the concentration of $Mn_xSi_{1-x}Te$ crystals of x = 30%, where exchange narrowing effect become dominant in EMR. Other major features of electron magnetic resonance and analyzed results are followings. The g-factors of all $Mn_xSi_{1-x}Te$ samples as inferred from their EMR signals remain constant as 1.993 regardless of variations in composition and temperature. From the constant g-factor, the state of manganese ions in these samples is clearly known to be $Mn^{2+}(3d^5)$. Ferromagnetic resonance signals with g-factor about 10 exist for temperatures below 80 K. The temperature dependence of the EMR line-width of these samples is the same as those for other DMS. From the EMR signal shape the relaxation times T_2 and T_1 of $Mn_xSi_{1-x}Te$ compounds at 200 K are estimated to be about 4.4×10^{-10}s and 9.3×10^{-8}s respectively and are found to slightly change with temperature or composition change. It is also revealed that a $Mn_xSi_{1-x}Te$ sample with x = 0.5% behaves as a spin glass at temperatures below 60 K.

Acknowledgement

We thank Dr. Eatons at the University of Denver, Department of Chemistry and Biochemistry for useful discussions concerning this study. We thank Dr. Choi, S. N., Dr. Won, M. S. and Dr. Kim, Y. C also for useful discussions and other help concerning this study. The first author would like to express his thanks to God, the Eternal Father and the Lord Jesus Christ.

References

[1] J. Furdyna, J. Appl. Phys. **64**, R29 (1988).
[2] W. Gordy, Theory and Applications of Electron Spin Resonance, Wiley (1980).
[3] R. Kremer and J. Furdyna, Phys. Rev. B **31**(1), 1 (1985).
[4] C. Poole and H. Farach, Relaxation in Magnetic Resonance, Academic Press (1971).
[5] A. Hanaveld, W. Van Der Veer, and F. Jellinek, Rec. Tray. Chim., Pay-Bas **87**(3), 255 (1968).
[6] D. Craik, Magnetism: Principles and Applications, Wiley (1995).
[7] C. Kittel, Introduction to Solid State Physics, 7th ed. (1996).
[8] N. Ashcroft and N. Mermin, Solid State Physics, Harcourt College Publisher (1976).
[9] H. Sayad and S. Bhagat, Phys. Rev. B **31**(1), 591 (1985).
[10] F. Bloch, Phys. Rev. **70**, 460 (1946).
[11] S. McAlister, J. Furdyna, and W. Giriat, Phys. Rev. B **29**(3), 1310 (1984).
[12] M. Mezard, Spin Glass Theory and Beyond, World Scientific (1987).