

Determination of the Exchange Integrals in β -MnO₂[†]

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Magnetic susceptibility and specific heat of the β -MnO₂ powder specimen have been measured in the range 20 to 300°K and 77 to 100°K respectively. The measurements have also been made for the paramagnetic inelastic neutron scattering at room temperature by using time-of-flight method. The values of the Weiss temperature, of the Néel temperature and of the average full width at half maximum of the neutron energy distribution (Gaussian) have been determined as 1050°K, 92°K and 13 meV respectively. The exchange integrals (J_n) are determined by combining these experimental data with the theoretical relations between exchange interactions and physical properties and by assuming $J_1/J_2=1.60$: $J_1=8.9$ (antiferromagnetic), $J_2=5.5$ and $J_3=-1.3^\circ\text{K}$, where J_1 is the exchange integral between nearest neighbours (in the $\langle 001 \rangle$ direction), J_2 acts between next nearest neighbours ($\langle 111 \rangle$ direction) and J_3 refers to third-neighbour coupling.

§ 1. Introduction

Beta manganese dioxide (β -MnO₂) is a tetragonal antiferromagnetic crystal ($T_N=92^\circ\text{K}$), which has the spin structure of the proper screw type proposed by Yoshimori¹⁾ on the basis of neutron diffraction data given by Erickson.²⁾ The spin structure is such that the spins, aligned parallel in the c plane, screw along the c axis with a pitch of $(7/2)c$. Therefore, along the c axis the magnetic unit cell is seven times as large as the chemical unit cell.

In the crystal there are three main exchange interactions with exchange integrals J_1 , J_2 and J_3 as shown in Fig. 1, where J_1 is the exchange integral between nearest neighbours (in the $\langle 001 \rangle$ direction), J_2 acts between next nearest neighbours ($\langle 111 \rangle$ direction) and J_3 refers to third-neighbour coupling ($\langle 100 \rangle$ or $\langle 010 \rangle$ direction). Yoshimori¹⁾ has shown, from the condition stabilizing the screw structure with a pitch of $(7/2)c$, that J_1/J_2 is 1.60, J_3/J_2 smaller than 0.31 and that a rough estimation of J_2 is 7.2°K (*i. e.* $16J_2 \approx 80 \text{ cm}^{-1}$), on the assumption that both J_1 and J_2 are positive (antiferromagnetic).*

The purpose of the present paper is to determine the exchange integrals in β -MnO₂ more definitely. Generally, in order to determine these

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* Here J_1 and J_2 represent J_2 and J_1 in Yoshimori's notation respectively.

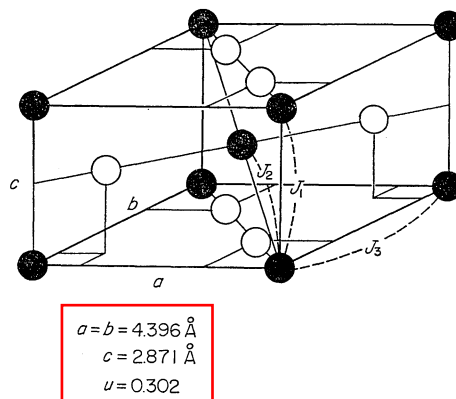


Fig. 1. The crystal structure of β -MnO₂ and the dominant exchange integrals therein. Solid circles represent Mn⁴⁺ ion, open circles O²⁻ ion.

values it is most effective to measure the spin wave dispersion relation by means of coherent inelastic neutron scattering. Since no single crystal of β -MnO₂ was available, measurements of paramagnetic scattering, *i. e.* incoherent inelastic scattering, were made; the method is suitable for determining the exchange integrals in a polycrystal.

This method was introduced by Van Vleck³⁾ and discussed more completely by de Gennes⁴⁾ and by Collins and Marshall.⁵⁾ According to their theories, neutron energy distribution is expected to be near Gaussian at large scattering angles, and the full width at half maximum (FWHM) of the Gaussian distribution is directly related to exchange integrals. This method is particularly powerful

for a simple cubic magnetic system which has a single exchange integral.

The earliest experimental study made by Brockhouse⁶⁾ in this direction is that on paramagnetic Mn_2O_3 . Several investigations have since been carried out on MnF_2 ,⁷⁾ MnO ,⁸⁾ a series of perovskite salts,^{9,10)} rare earth metals¹¹⁾ and chromium and ferrous halides.¹²⁾

In the case of $\beta\text{-MnO}_2$ there are three exchange integrals to be determined. Therefore determination of these integrals can be done by using the Yoshimori's theory¹⁾ with the data of the paramagnetic scattering, the Néel temperature and the Weiss temperature.

The magnetic susceptibility and the specific heat for powder $\beta\text{-MnO}_2$ have been measured in the range 20 to 300°K and 77 to 100°K respectively. Measurements of the paramagnetic scattering of neutrons at room temperature have been carried out by using time-of-flight method.

In § 2 the sample preparation, the experimental results on the magnetic susceptibility, on the specific heat and on the paramagnetic scattering of neutrons are described. The analysis of the exchange integral (J_n) is also presented. In § 3 the results of the analysis are discussed.

§ 2. Experiments and Analysis

2.1. Samples

Powder samples of $\beta\text{-MnO}_2$ were prepared from pure electrolytic manganese* and reagent quality nitric acid by the following procedure given by Kelley and Moore¹³⁾ and by Itoh and Takahashi.¹⁴⁾ The manganese nitrate ($\text{Mn}(\text{NO}_3)_2$) obtained by dissolving manganese into concentrated nitric acid was kept at 250°C in ambient atmosphere for two days. The product (MnO_2) was then heated up to 400°C in ambient atmosphere for a week. The most stable phase in the manganese dioxide in ambient atmosphere is $\beta\text{-MnO}_2$; all the manganese dioxides go to $\beta\text{-MnO}_2$ at about 400°C in ambient atmosphere.¹⁵⁾

Chemical analysis was made only for manganese by using the acetylacetone method;** the manganese to oxygen ratio thus determined was 1:2.02, which is satisfactory.

X-ray powder photographs taken at room temperature and at the lower temperatures (*i.e.* 40, 53, 60 and 70°K) showed neither lines other than those of $\beta\text{-MnO}_2$ nor changes in the symmetry of the

crystal structure below the Néel temperature.

Neutron diffraction pattern obtained at 4.2°K using the powder specimen was consistent with the Yoshimori's theory.*

2.2. Magnetic susceptibility

The powder magnetic susceptibility (χ_p) of $\beta\text{-MnO}_2$ was measured using a recording magnetometer¹⁷⁾ in the temperature range 20 to 300°K. The results are shown in Fig. 2 together with the

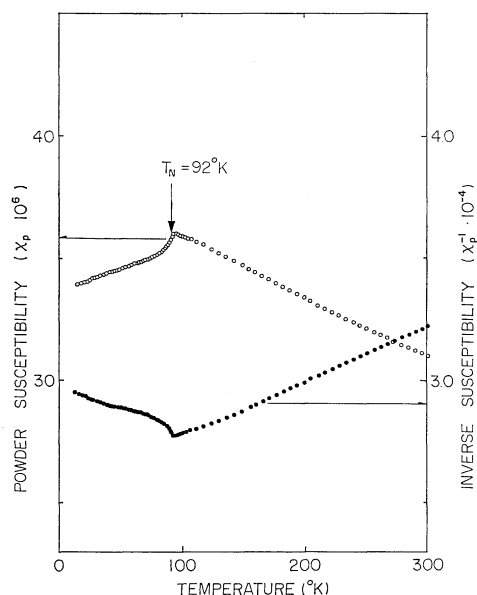


Fig. 2. The powder magnetic susceptibilities and the inverse magnetic susceptibilities vs. temperature.

inverse magnetic susceptibility.** The value of the Néel temperature (T_N) was determined from the figure as 92°K. In the temperature range higher than 150°K the Curie-Weiss law is satisfied; the Weiss temperature (θ_p), the molar Curie constant (C_M) and the paramagnetic effective Bohr magneton number (μ_{eff}) are 1050°K, 3.78 and 5.52

* This magnetic structure of $\beta\text{-MnO}_2$ has also been confirmed by Gonzalo and Cox.¹⁶⁾

** Magnetic susceptibility was first measured on the natural $\beta\text{-MnO}_2$ sample (by courtesy of Prof. G. Gattow). However the results showed that the sample is not good enough for the experiment determining the exchange integrals. Next measurements were carried out on the above-mentioned synthesized sample and on the Takahashi's sample (by courtesy of Prof. T. Takahashi). The results of magnetic susceptibilities were in good agreement with each other; magnetic susceptibilities of both samples have maxima at 92°K (T_N). Therefore the authors' synthesized sample was used in the following experiments.

* Johnson, Matthey and Co., Ltd., 99.99% pure.

** The authors are indebted to Dr. T. Ando for the chemical analysis.

respectively. A correction of the contribution of the Van Vleck paramagnetism to the Weiss temperature has been made.

The values of the Néel temperature and the Weiss temperature are not in agreement with those obtained by Bizette and Tsai¹⁸⁾ and by Bizette,¹⁹⁾ who gave the values of 84°K and 316°K* respectively. In § 3 a discussion on the discrepancy of the values of θ_p is given.

2.3. Specific heat

The specific heat measurements were made with powder sample of 53.8 g using an adiabatic type calorimeter in the temperature range 77 to 100°K; the results are plotted in Fig. 3. A sharp anomaly

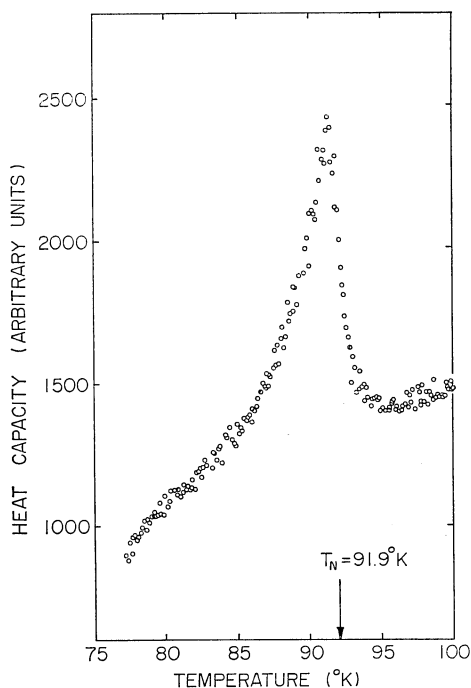


Fig. 3. The specific heat of β - MnO_2 .

ly in the specific heat appears at $91.9 \pm 0.2^\circ\text{K}$ corresponding to the second order phase transition between paramagnetic and antiferromagnetic phases. This value of the transition temperature is in good agreement with the above-mentioned value of the Néel temperature obtained from the magnetic susceptibility data and also with that of $92.12 \pm 0.05^\circ\text{K}$ determined by Kelley and Moore¹³⁾ from specific heat measurements.

* This value of 316°K is that of the powder sample; that of the single crystal is about 1300°K which is obtained from the Bizette's magnetic susceptibility data by the present authors. Only the value of 316°K has been cited so far.

2.4. Paramagnetic scattering

The paramagnetic scattering experiments were performed on a pulse type neutron spectrometer (PTNS-1) at JRR-2 reactor at Japan Atomic Energy Research Institute (JAERI), Tokai-mura. The wavelength of the incident neutrons was selected as 3.01Å. The measurements of the energy of the scattered neutrons were made by using the time-of-flight (TOF) technique. The sample used in this experiment was packed in an aluminium can ($30 \times 30 \times 5 \text{ mm}^3$).

The TOF spectra of the scattered neutrons were taken, at room temperature, at the scattering angles 20, 35, 45 and 65° . The spectra observed at 20 and 45° are shown in Fig. 4. The ordinate is in proportion to the differential scattering cross section per unit solid angle Ω per unit TOF t , $d^2\sigma/d\Omega dt$, and the abscissa is TOF. Also shown in the abscissa are the energy transfer to lattice $\hbar\omega$ ($\hbar\omega = E_0 - E_1$) and the momentum transfer $\kappa = k_0 - k_1$ ($\kappa = (k_0^2 + k_1^2 - 2k_0k_1 \cos \phi)^{1/2}$), where E_0 and E_1 are the incident and the scattered neutron energy respectively, k_0 and k_1 the incident and the scattered neutron wave vector respectively and ϕ the scattering angle.

Corrections for the neutron counts were made on the background, absorption by the sample, air scattering in flight path and counter efficiency by using IBM 7044 computer at JAERI.²⁰⁾

The corrected differential cross section ($d^2\sigma/d\Omega dt$)_{corr} was converted to the differential cross section per unit solid angle Ω per unit energy transfer $\hbar\omega$, $d^2\sigma/d\Omega d\omega$, by the expression

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \frac{1}{k_1^3} \left(\frac{d^2\sigma}{d\Omega dt} \right)_{\text{corr}}. \quad (1)$$

On the other hand, the magnetic cross section for the scattering of neutrons in a polycrystalline system of paramagnetic N spins is

$$\frac{d^2\sigma}{d\Omega d\omega} = N \left(\frac{\gamma e^2}{m_n c^2} \right)^2 \frac{k_1}{k_0} |F(\kappa)|^2 P(\kappa, \omega), \quad (2)$$

where $F(\kappa)$ is the usual magnetic form factor. According to Collins and Marshall⁵⁾, $P(\kappa, \omega)$ is given as

$$P(\kappa, \omega) \propto \exp \left\{ -\frac{(\hbar\omega)^2}{2\langle(\hbar\omega)^2\rangle} \right\}^*, \quad (3)$$

where $\langle(\hbar\omega)^2\rangle$ is the second moment of $P(\kappa, \omega)$; it is related with the exchange integral by the following formula.

* Since the data were not good enough for discussion of the shape of $P(\kappa, \omega)$, analysis of $P(\kappa, \omega)$ was made on the approximation that $P(\kappa, \omega)$ is a Gaussian.

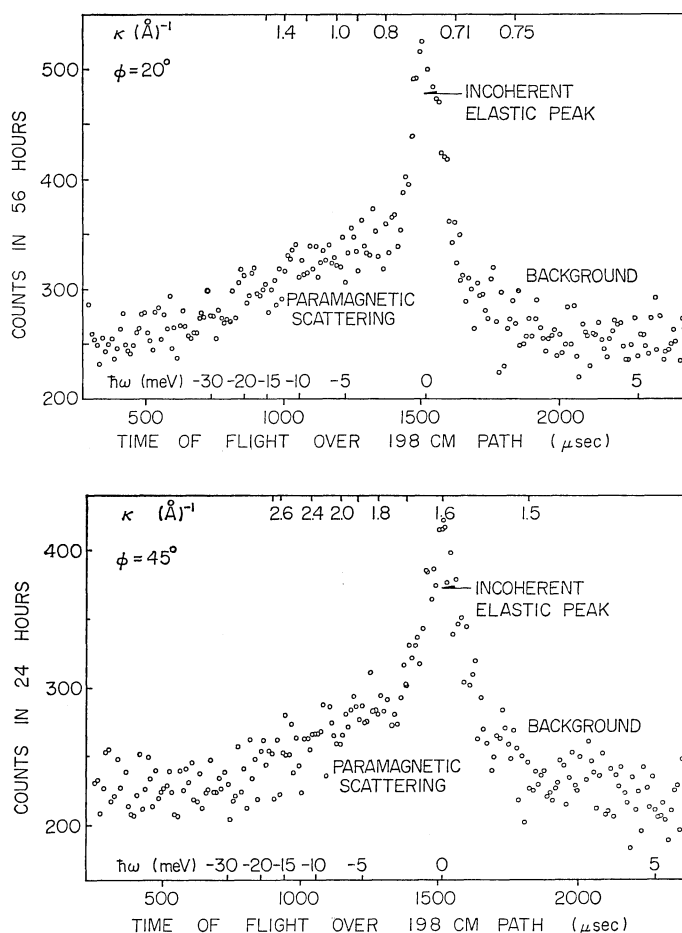


Fig. 4. The time-of-flight spectra scattered through the angles of 20 and 45° from powder β -MnO₂ at room temperature. The scales on the upper and the lower part of the figure show the momentum and energy transfer respectively.

$$\langle (\hbar\omega)^2 \rangle = \frac{8}{3} S(S+1) \sum_n z_n J_n^2 \left\{ 1 - \frac{\sin(\kappa R_n)}{\kappa R_n} \right\}, \quad (4)$$

where J_n , z_n and R_n are the exchange integral, co-ordination number and distance of the n th co-ordination shell from any given atom.

Therefore at large scattering angles (*i.e.* $\kappa R_n > \pi$) $P(\kappa, \omega)$ is a Gaussian.

The function $P(\kappa, \omega)$ is now obtained from the experimental cross section by the expression

$$\left(\frac{d^2\sigma}{d\Omega dt} \right)_{\text{corr}} \propto \frac{k_1^4}{k_0} \exp(-\alpha\kappa^2) \times \frac{\hbar\omega\beta}{1 - \exp(-\hbar\omega\beta)} P(\kappa, \omega). \quad (5)$$

The second factor is an approximate analytic expression for the Mn²⁺ magnetic form factor instead of that for the Mn⁴⁺ one, which have not been measured. The constant $\alpha = 0.17 \text{ \AA}^2$ is found to

give reasonable agreement with the Mn²⁺ experimental form factor.¹⁰⁾ The third is the detailed balance correction depending on the temperature, *i.e.* $\beta = 1/k_B T$, where k_B is the Boltzmann constant. The calculation of $P(\kappa, \omega)$ was performed on the above-mentioned computer.

Figure 5 shows $P(\kappa, \omega)$ plotted against energy transfer $\hbar\omega$ at the scattering angles 20 and 45°. The solid lines in Fig. 5 are the Gaussian best fitted to the experimental values by using the least mean square method. In Fig. 6 the full width at half maximum (FWHM) of the Gaussian, Γ , is plotted against scattering angle. The FWHM is determined from the following expression corrected for the width of the incident neutron spectrum:

$$\Gamma^2 = \Gamma_{\text{exp}}^2 - \Gamma_i^2, \quad (6)$$

where Γ_{exp} and Γ_i are the FWHM's of the experimental and the incident spectra respectively. As

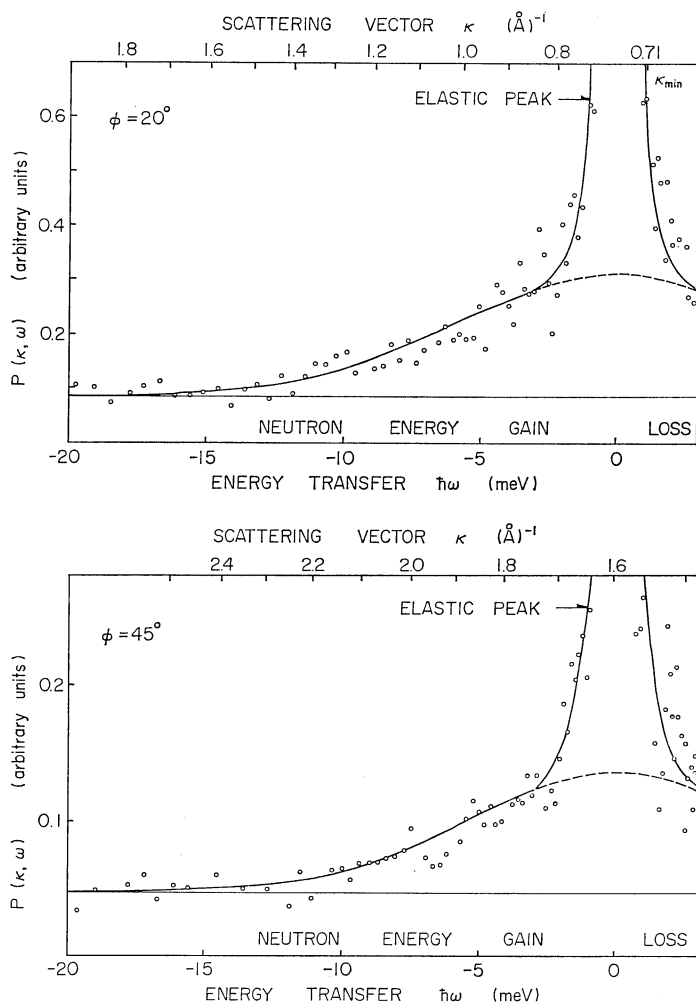


Fig. 5. $P(\kappa, \omega)$ plotted against energy transfer at the scattering angles of 20 and 45°. The solid lines show the Gaussian best fitted to experimental values.

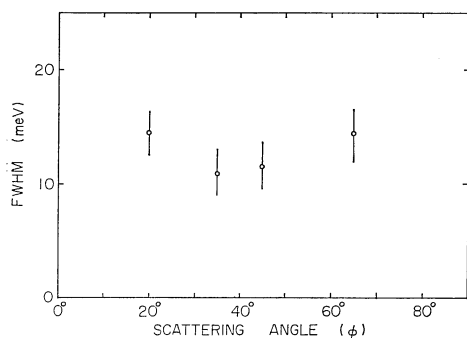


Fig. 6. The full width at half maximum (FWHM) of the Gaussian plotted against scattering angle.

shown in Fig. 6 the observed values of Γ are nearly constant with respect to the scattering angle within the experimental errors. The average of FWHM (denoted by Γ_a) is 13 meV.

2.5. Determination of the exchange integrals

The second moment of $P(\kappa, \omega)$ is related with Γ_a by the following relation

$$\Gamma_a^2 = 8 \ln 2 \cdot \langle (\hbar\omega)^2 \rangle. \quad (7)$$

From eqs. (4) and (7) an equation for the exchange integrals is given by

$$\Gamma_a^2 / (8 \ln 2) = \{2S(S+1)/3\} (8J_1^2 + 32J_2^2 + 16J_3^2), \quad (8)$$

where $S=3/2$ for Mn^{4+} ion.

On the other hand, Yoshimori has shown that the Néel temperature and the Weiss temperature in this screw type structure are given in the molecular field approximation¹⁾ as follows:

$$k_B T_N = \{S(S+1)/3\} (4J_1 + 8J_2/J_1 - 8J_3), \quad (9)$$

and

$$k_B \theta_p = \{S(S+1)/3\} (4J_1 + 16J_2 + 8J_3). \quad (10)$$

These three equations (*i. e.* eqs. (8), (9) and (10)) are the basic ones for the exchange integrals in β -MnO₂. It was expected, at the beginning of the present work, that these simultaneous equations for J_n can be solved by substituting the experimental data of Γ_a , T_N and θ_p . It was revealed however, that there were no solutions between eqs. (8) and (10), because the value of θ_p was very much larger than that expected from the molecular field approximation. Under these circumstances, in order to determine the individual values of the three J_n , the relation $J_1/J_2=1.60$ was used instead of eq. (10); the relation was given by Yoshimori¹¹ as the condition stabilizing the screw structure with a pitch of $(7/2)c$. The values of the three J_n can be determined as the solution of eqs. (8) and (9) and the above-mentioned relation. The exchange integrals thus obtained are: $J_1=8.9$, $J_2=5.5$ and $J_3=-1.3^\circ\text{K}$. The experimental error on J_n is estimated to be 15%.

§ 3. Discussion

It was the purpose of this investigation to determine the three main exchange integrals in β -MnO₂

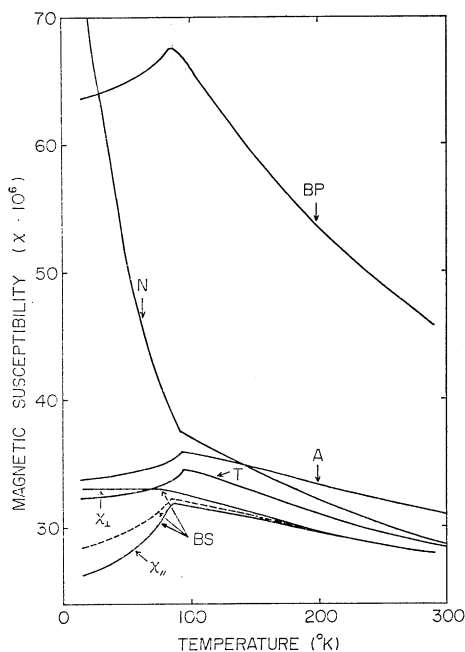


Fig. 7. The observed magnetic susceptibilities vs. temperature; A, BP, BS, N and T curves are that on the authors' synthesized sample, the Bizette's powder sample, the Bizette's single crystal, the natural sample and the Takahashi's synthesized sample respectively. The broken curve is the powder magnetic susceptibility χ_p expected from χ_\perp and χ_\parallel .

from the simultaneous equations concerned with J_n given in § 2.5 without introducing any other assumption. This purpose is, however, not fully successful, because there is no solution between eqs. (8) and (10). One of the reason of this is that the value of the Weiss temperature θ_p is very large as 1050°K .

As described in § 2.2, the magnetic susceptibilities were measured on the natural β -MnO₂ sample (denoted by N), the Takahashi's synthesized sample (T) and the above-mentioned authors' synthesized sample (A). These results are shown in Fig. 7 together with that of the Bizette's single crystal (BS) and powder sample (BP).^{18,19} The magnetic susceptibility vs. temperature curves of the three samples A, T and BS show rather similar behaviour; the values of the magnetic susceptibility in the measured temperature range are quite consistent with each other. The values of the sample N increase abruptly with decreasing temperature below about 92°K ; this abnormal behaviour might be attributed to a contribution from the impurity in the sample N to the paramagnetic part. The sample N was therefore omitted from the subject of the discussion on θ_p .

On the other hand, the temperature dependence of the magnetic susceptibility of the sample BP is quite different from those of the other samples; the value of the magnetic susceptibility is about two times larger than that of the others.

The samples A, T and BP were all prepared by the thermal decomposition of manganese nitrate $\text{Mn}(\text{NO}_3)_2$;^{14,18,19} in particular the sample A was treated by heating at 400°C in ambient atmosphere for a week in order to get a purer β -MnO₂. The sample BS was made by the calcination of the natural manganite $\text{Mn}(\text{OH})\text{O}$ single crystal.^{18,19}

The experimental values of θ_p for these samples obtained by using Curie-Weiss law were as follows. The value of the sample BP has been reported as 316°K and that of the other three samples T, A and BS are 850, 1050 and 1300°K respectively; the latter values are about three to four times larger than the former one. There will be no solution between eqs. (8) and (10), if $\theta_p \gtrsim 190^\circ\text{K}$. These values, except for that of the Bizette's samples (BP and BS), were corrected for a contribution due to the Van Vleck paramagnetic term (about $1 \times 10^{-6} \text{ emu/g}$); the magnitude of the correction to θ_p is about 50°K for the sample A. The reason why these values of θ_p are very larger than that expected from the molecular field approximation, is not clear. However, if there is a small

amount of impurity in the sample, the magnetic susceptibility should be affected by the impurity and the sample would have a larger value of θ_p . In the β -MnO₂, it is very difficult to synthesize a perfectly stoichiometric sample. The impurity might be the other phase of the manganese dioxide and/or the different valent manganese (Mn²⁺ and Mn³⁺).

In the present situation, it is impossible to use the values of θ_p of the samples BS, T and A, while there is no reason for using the value of θ_p of the sample BP. Moreover the value of T_N of that sample is different from that of the sample A. It can thus not be helped to give up to determine J_n from the experimental value of θ_p by using eq. (10).

On the other hand, the value of T_N and of Γ_a will be much less affected by such impurities. The values of the T_N obtained from the measurements of the magnetic susceptibility and of the specific heat are in very good agreement with each other; the values are also in agreement with that obtained by Bizette and Tsai¹⁸⁾ and by Bizette¹⁹⁾ within a 10% relative error.

At large scattering angles $P(\kappa, \omega)$ is almost a Gaussian, but in small scattering angles ($\kappa R_n \approx \pi$), it also has a little part of Lorentzian,⁵⁾ which contributes to the FWHM (Γ). However, analysis of $P(\kappa, \omega)$ was done on the assumption that $P(\kappa, \omega)$ is a Gaussian, because the data good enough for the discussion of the shape of $P(\kappa, \omega)$ was not obtained.

The scattering cross section and the intensity of the scattered neutrons decrease with increasing scattering angle. Therefore the experimental error on Γ increases with increasing scattering angle. The experimental errors on the exchange integrals (J_n) are directly connected with that on Γ through eq. (8) in § 2.5; they are about 15%.

In general there is the phonon scattering superposed on the paramagnetic scattering. A rough estimation shows that in the case of the β -MnO₂ the phonon scattering intensity is about 12% of the paramagnetic scattering one. The contribution of the phonon scattering to the FWHM (Γ) is therefore quite small and can be neglected. This phonon part can perfectly be excluded if the neutron spin spectroscopy technique²¹⁾ is used.

In order to determine the exchange integrals in β -MnO₂ more precisely, it is necessary to synthesize a single crystal and to measure the spin wave dispersion relation using the coherent inelastic neutron scattering techniques.

The above-mentioned discussion is developed

inconnection with that the molecular field theory can be applied to the β -MnO₂. However, the experimental results of the magnetic susceptibility of the β -MnO₂ may suggest that it is not adequate to discuss this material only with that theory.

Acknowledgements

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