One-dimensional magnetism and the phase transition in $VOMoO_4$

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Abstract. A crystal of VOMoO$_4$ was grown, which has a structure containing V–O–V–O linear chains along the c-axis. There a vanadium ion carries a spin of $\frac{1}{2}$ per ion. The magnetic susceptibility was measured in the region from 2 to 300 K up to 55 kG. The temperature dependence shows a broad maximum around 100 K. This is a characteristic of a 1D antiferromagnet. Fitting to the uniform 1D Heisenberg model is very good in the higher temperature region. This suggests the onset of antiferromagnetic order around 100 K. At 34 K, however, χ shows a kink followed by a ferromagnetic hump at lower temperature. This suggests some magnetic phase transition. At 2 K a slight hysteresis was observed in the magnetic field dependence. The above behaviour was interpreted as the process of transfer from 1D to weak 3D interaction, according to lowering temperature. Lattice parameters increased with decreasing temperature below 100 K, then showed a hump around 30 K. This anomalous behaviour corresponds to the above magnetic results. It has been concluded that VOMoO$_4$ is a one-dimensional antiferromagnet. We also suggest the existence of a weak ferromagnetic ordered state such as canted or ferri-magnetism by the V–O pairs in the lower temperature region.

1. Introduction

Molybdenum oxide has many kinds of crystal phase with different molybdenum to oxygen ratios. Most of the crystals constitute a slightly modified perovskite structure, that is mainly constructed by MoO$_6$ octahedra. They often crystallize with low-dimensional symmetry, and easily contain large cavities in ordered configurations [1–4]. For example, Mo$_4$O$_{11}$ possesses a quasi-two-dimensional crystal structure. It contains two-dimensional layers of cavities formed by a periodic lack of oxygen ions. The layers are situated with a periodic configuration in the crystal. In case of one-dimensional potassium molybdenum bronze, long crevices extend along the b-axis. Those contain the potassium ions in an ordered configuration [3].

   We are trying to substitute different kinds of impurity into molybdenum oxide [5, 6]. Our purpose is to control the dimensional configuration of impurity ions, and accordingly to control the direction and distance of inter-impurity interaction. In the present work, we have grown a crystal of a new one-dimensional ferromagnet by substitution of vanadium. The crystal does not necessarily contain big cavities, but the magnetic chain structure is the characteristic. The problem of the magnetic order in a low-dimensional spin system has been attracting many workers [7–16]. Most of the observed ordering has been explained by the Haldane gap or spin–Peierls transition, and sometimes by the Mott transition. In the present crystal the situation of phase transition in a lower temperature region is somewhat different [5, 6] from the previously reported mechanism.

2. Experiment

The crystal was prepared by chemical vapour transport of a mixture of MoO_3 and VO_2. More details were given earlier [5, 6]. The obtained fine crystals have the appearance of rectangular prisms, and their typical size is $50 \times 50 \times 80$ μm^3. Quantitative analysis was performed using an EDS type electron probe microanalyser (EPMA, JED-2001 from JEOL). From the results we found that Mo:V $\cong$ 1:1. The crystal structure was examined by the powder x-ray diffraction method, where monochromated Cu Kα, produced by 40 kV and 200 mA, was used (MAC, Japan). The diffraction pattern is very similar to that of $VOMoO_4$ suggested by Eick and Kihlborg [17]. Simulation by a Rietveld program was performed for two different chemical formulae, $VOMoO_4$ and $MoOVO_4$, where the program 'RIETAN'94' had been kindly supplied by F Izumi [18, 19]. The peak intensities of the former formula gave a quite good fit to the present measured ones, while the latter was ruled out. Thus the chemical formula and the crystal structure of the present compound were concluded to be those of $VOMoO_4$ given by [17]. The crystal structure determined by [17] is tetragonal ($P4/n$), where the parameters, a and c, of 6.6078 and 4.2646 Å, respectively at room temperature. Their suggested structure is shown in figure 1, and the details will be described in section 4. The temperature dependence of the spectrum in the present crystal was checked down to 10 K. The results were analysed by using the above 'RIETAN'94'.

The static magnetic susceptibility was measured down to 10 G and to 2 K by a SQUID magnetometer from Quantum Design, USA. The sensitivity is 1×10^{-8} emu, which is equivalent to 10^{-5} emu mol^{-1} for the magnetization of the present sample. The absolute accuracy is limited by the contained magnetic impurities, but the relative accuracy, for example, the temperature dependence, is approximately 0.1% or better. Special care was required to determine the zero-point of the magnetic field, because a superconducting solenoid often keeps a resultant field with current of zero. The field values were corrected by a palladium sample as a standard. The absence of ferromagnetic impurity was also checked.

3. Results

3.1. Crystal structure

The x-ray spectrum at room temperature is shown in figure 2 together with the Miller indices. The analysed results are almost consistent with that of Eick and Kihlborg [17]. Though the orthorhombic symmetry is rather satisfactory in the present crystal, the difference between *a* and *b* is less than 0.3% at room temperature. The lattice parameters *a*, *b* and *c* are 6.6044, 6.5965 and 4.2710 Å, respectively with the error of ±0.0020 Å. No remarkable change of the line shape of the spectrum was observed when the temperature was reduced to 4 K. The lattice parameters, however, showed an anomalous behaviour. The temperature dependence of *a* and *c* is shown in figure 3. The decrease of *c* with decreasing temperature is nearly consistent, if we consider the usual thermal expansion coefficient. The temperature change of *a* is rather small. Below about 100 K both of them go up towards maxima around 30 K.

3.2. Magnetism

In a lower temperature region, the measured susceptibility, χ, shows a Curie-like upturn characteristic of extrinsic paramagnetic impurities. It mainly comes from the trace of MoO_3, one of the starting materials. Measured χ in 50 G was plotted as a function of $1/T$ as seen
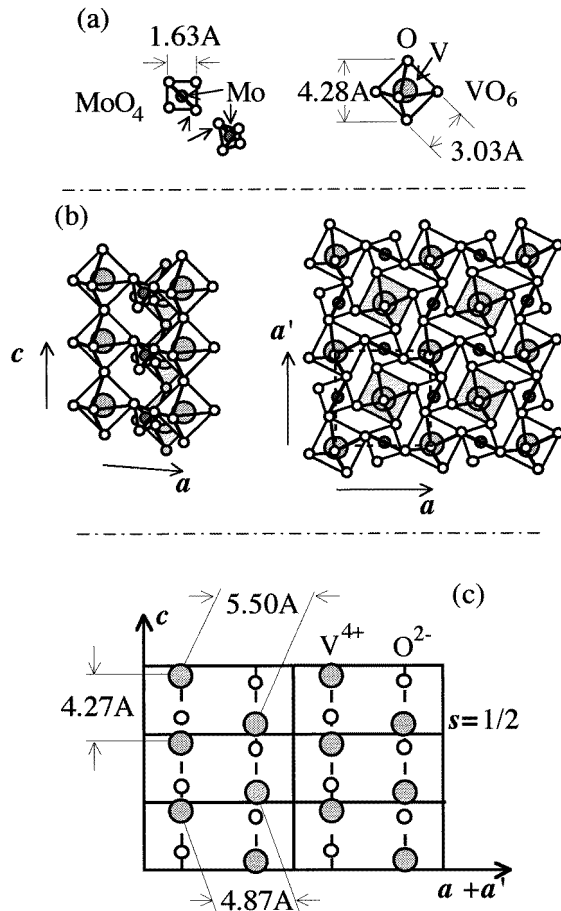
Figure 1. The crystal structure of VOMoO$_4$ suggested by Eick and Kihlborg [17]. (a) The crystal is constituted from MoO$_4$ tetrahedra and VO$_6$ octahedra. The numbers attached to the polyhedra are the respective inter-ion spacings, which were estimated according to the bond theory. (b) The white and shaded octahedra lie in front of and behind the page, respectively. The unit cell is shown by a dashed square. (c) The crystal is redrawn highlighting the V–O chain structure along the c-axis. Molybdenum should be non-magnetic, using all d electrons for the bond. Four more bonding electrons are supplied by V. The resultant one electron on V^{4+} forms a spin of $\frac{1}{2}$.

in figure 4(a), where the field value is low enough to satisfy the Curie law. The impurity part, χ_{imp}, was estimated as $1.2 \times 10^{-3}/T$ emu mol^{-1} from the gradient below 7 K, where the extrinsic Curie component is dominant. The measured results, calculated extrinsic part and the subtracted intrinsic susceptibility are plotted in figure 4(b). More details of the intrinsic susceptibility of VOMoO$_4$ are shown in figure 5. Two remarkable characteristics are seen there: one is a broad maximum around 100 K, and the other is the phase transition at 34 K.

The behaviour in the higher temperature region is enlarged in figure 5(b). It is quite similar to the previous results in a one-dimensional Heisenberg-like antiferromagnet [7–16]. This is reasonable considering the crystal structure of the present compound. It was
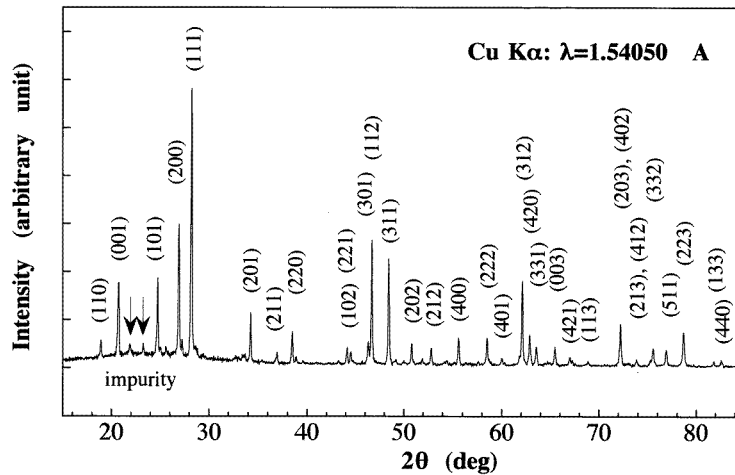
Figure 2. Powder x-ray diffraction spectrum at room temperature. A Cu Kα beam (40 kV, 200 mA) was used. Small peaks on the lower angle side must come from a resultant impurity of MoO_3.
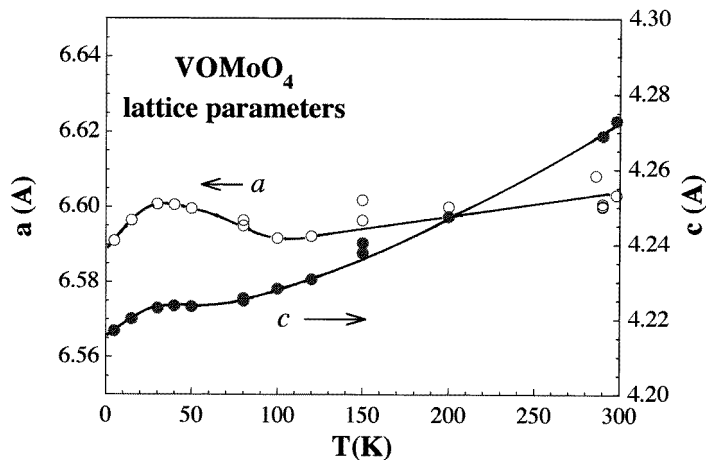

Figure 3. Temperature dependence of lattice parameters a and c. The decrease of c with decreasing temperature is nearly consistent, if we consider the usual thermal expansion coefficient. The small temperature change of a is rather strange. Below about 100 K both of them go up towards maxima around 30 K.

estimated that the maximum value, χ_{max}, is 9.2×10^{-4} emu mol^{-1}, at T_{max} of 100 K. These were compared with the calculation by Bonner and Fisher [7] according to the uniform Heisenberg model. They gave the relation of dimensionless numbers, $\chi J/g^2\mu_B^2$ and $k_B T/J$. Also given was the maximum value of the dependent variable as 7.346 at the independent one of 1.282. Here the J value is estimated as 78 K with 100 K for T_{max}, when we assume that vanadium is tetravalent. Moreover, the g factor is calculated as 1.614, making use of the above estimated J and the measured χ_{max}. With these parameters the measured points in the figure are scaled according to [7]. The thick solid curve was
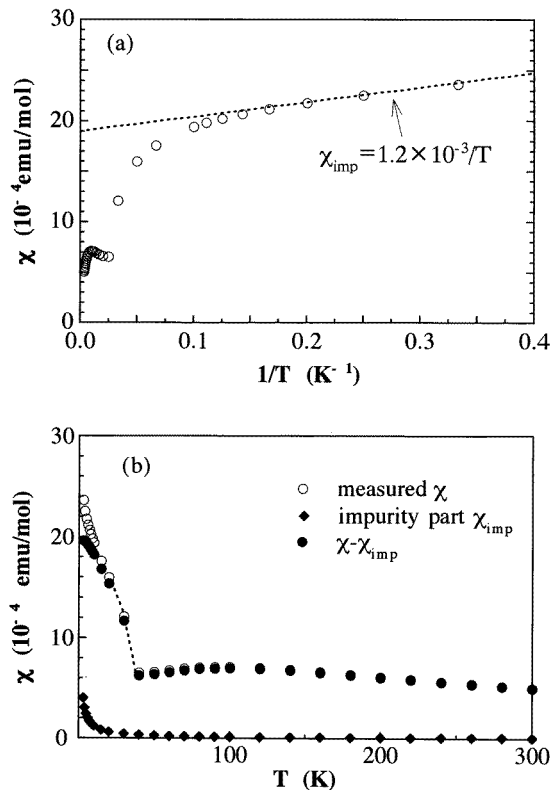
Figure 4. (a) Measured χ in 50 G was plotted as a function of $1/T$, where the field value is low enough to satisfy the Curie law. The extrinsic Curie component is dominant below 7 K. From the gradient there the impurity part, χ_{imp}, was estimated as $1.2 \times 10^{-3}T$ emu mol^{-1}. (b) The measured results, calculated impurity component and the subtracted intrinsic susceptibility are plotted as functions of temperature.

drawn following their calculated results. Their calculated results, however, are limited in the region of $k_B T/J < 2.5$ ($T < 200$ K in the present case). We need an approximate function to extrapolate to the higher temperature. The behaviour above 100 K shows the process of paramagnetic decay of the intrachain magnetic interaction. We assume that the spin system is almost perfectly paramagnetic around 200 K. In that case the dimensionality of system does not necessarily make sense. There spins should show the usual Curie-like temperature dependent behaviour. So we empirically gave a supplementary equation as

$$\chi = \left(0.0445 + \frac{6.57}{T}\right) \times 10^{-2} \ (\text{emu mol}^{-1}) \tag{1}$$

for temperatures above 200 K. The thick solid curve above 200 K was thus drawn, and is continuous to the one calculated by [7].

Both the measured points and calculated line are shown in figure 5(b), and show that the agreement is excellent. If we assume that the numerator in equation (1) gives the Curie constant, the effective number of Bohr magneton is estimated as 0.725 per formula unit. The value is almost consistent with the first prediction that vanadium is tetravalent. This number is reasonable considering the process of crystal growth, namely the shortage of moment per ion comes from defects of vanadium. It is also possible, that the too small
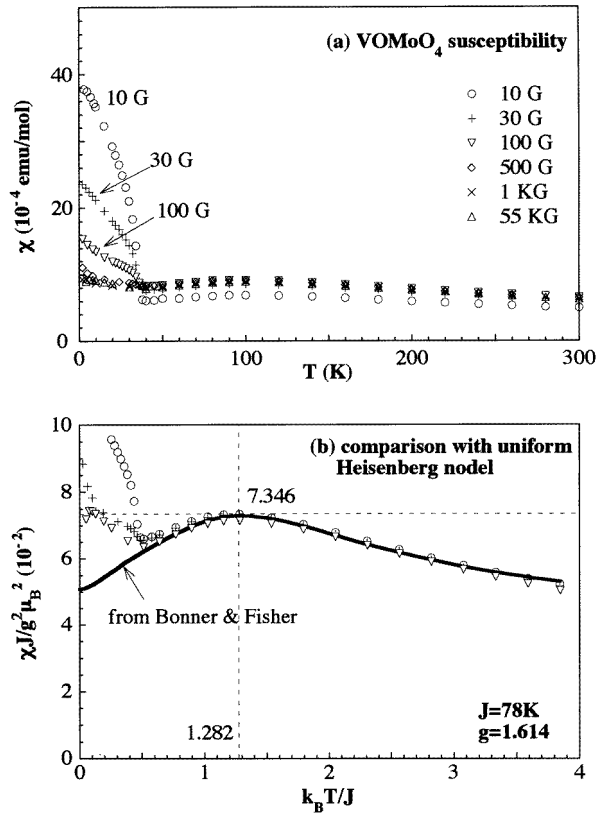
Figure 5. Temperature dependence of magnetic susceptibility of $VOMoO_4$ in different fields as a parameter. Here the Curie-like contribution of the impurity has already been subtracted. (a) Below T_c (= 34 K) χ increases and saturates toward 0 K. The magnitude of χ decreases with increasing field. This behaviour suggests a ferromagnetic transition. (b) Comparison with the susceptibility calculated by the uniform Heisenberg model.

value of g comes from the same origin. The ordinate of figure 5(c) may give either g or the number of Bohr magnetons, when the other is fixed in value. If we fix g to 2, alternatively we obtain $0.807\mu_B$ per formula unit. This is consistent with the above estimated number from equation (1), and is more reasonable than the too small g value.

Another characteristic behaviour is the sharp rise of χ below a critical temperature, T_c. From the derivative of $\chi(T)$, T_c was determined as 34 K. With decreasing temperature χ increases and saturates toward 0 K. Here the magnitude of χ is larger in lower fields, and saturates above about 1 kG. This behaviour looks like a ferromagnetic transition. Molar magnetization at 2 K in 50 G is 4.2×10^{-2} emu mol^{-1}, which is quite small for an ordinary ferromagnet. Though the numerical value is small for an ordinary ferromagnet, a slight hysteresis around zero field is also observed at 2 K at least (figure 6). Figures 7(a) and (b) show the field dependence of magnetization, M. Below T_c a tendency of saturation of M toward higher field is observed, while M is linear with field above T_c. In detail the function $M(B)$ is given as $M(B) = \chi_1 B + \delta M(B)$. Here χ_1 changes from 9.65×10^{-4} at 2 K to 8.33×10^{-4} at 40 K with the unit of emu mol^{-1}. Deviation, $\delta M(B)$, from the linear term

is plotted in figure 7(b) with a parameter, T. The behaviour suggests that the mechanism of magnetism is not simple below T_c. It looks that two types of temperature dependence, at least, compete there.
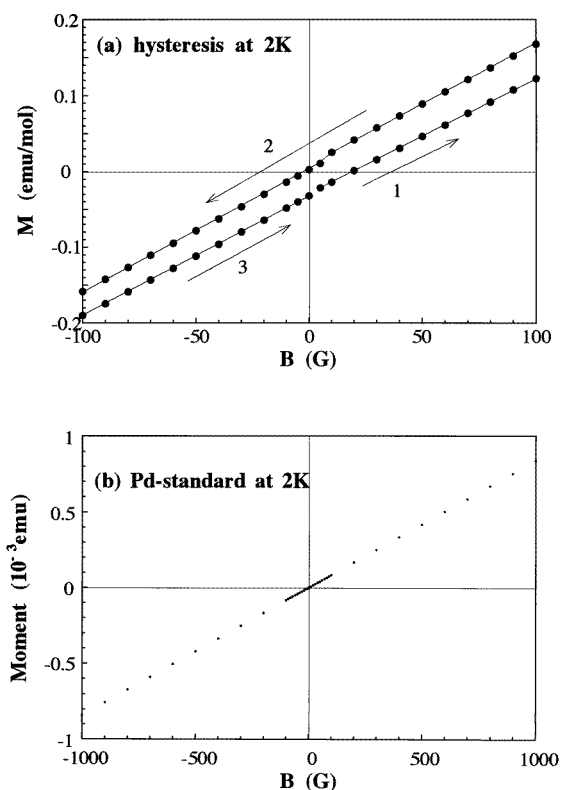

Figure 6. (a) Hysteresis around zero field measured at 2 K. (b) Measured result for palladium as a standard sample is shown for comparison.

4. Discussion

The suggested structure by Eick and Kihlborg [17] of VOMoO$_4$ is sketched in figures 1(a), (b) and (c). The crystal is constructed of infinite linear arrays of apex-sharing VO$_6$ octahedra, running parallel to the c-axis. The arrays are bundled through MoO$_4$ tetrahedra. Every octahedron shares oxygen ions in the aa'-plane with four surrounding tetrahedra. The white and shaded octahedra lie in front of and behind the page, respectively. The unit cell is shown by a dashed square in figure 1(b). Molybdenum should be non-magnetic, using all d electrons for bonding. Four more bonding electrons are supplied by V, and the resultant one electron on V^{4+} carries a spin of $\frac{1}{2}$. That is expected to construct a V–O spin chain structure along the c-axis. The numerical values attached to the figures are the respective inter-ion spacings, which were estimated on the basis of bond theory [20]. The length of the c-axis is almost consistent in comparison to the calculated bond length of O^{2-}–V^{4+}–O^{2-}, when the coordination number is 6. Parameter a (a') is rather small compared to the values expected by bond theory, and MoO$_4$ tetrahedra are predicted to be much compressed. We
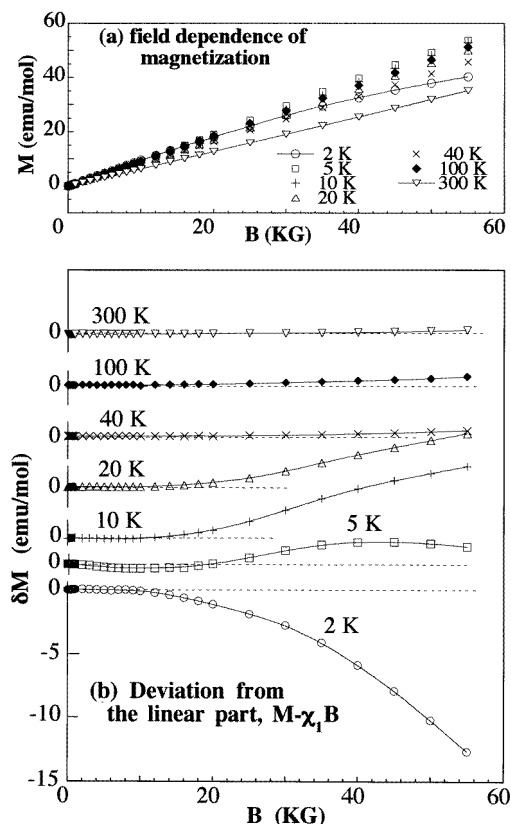
Figure 7. (a) Field dependence of magnetization. The function $M(B)$ is given as $M(B) = \chi_1 B + \delta M(B)$. Here χ_1 changes from 9.65×10^{-4} to 8.33×10^{-4} (emu mol^{-1}), while temperature changes from 2 K to 40 K. (b) Deviation, $\delta M(B)$, from the respective linear part of the field is plotted with T as a parameter.

expect that an inter-chain interaction cannot be negligible in the lower temperature region. More details of the structure are also described in [17]. This says that the metal–oxygen bonding along the c-axis is parallel to it, but those in the aa'-plane are a little tilted from a- or a'-axes. The distance between V and O ions is not homogeneous inside a single chain. It changes alternatively with the ratio of about 6 to 4. As shown in figure 1(c), the V–V distances between the nearest neighbouring chains are approximate to the separation in a single chain. It is, however, clear from figure 1(b) that the overlap of d wave functions on V is not direct between the different chains. That means the exchange interaction should be weak. This is the reason why we assume the present crystal is a one-dimensional magnet.

The behaviour of χ above T_c reproduces well the T dependence of a 1D antiferromagnet. We saw the reasonable decrease of lattice parameter along the c-axis with decreasing temperature. The T dependence in the range from $T_{\max}$ to T_c shows the intrachain magnetic ordering process. Shiozaki [6] measured χ in fields parallel and perpendicular to the c-axis. This suggested that spins on V^{4+} tend to align along the c-axis below $T_{\max}$. The obtained g is 1.614, which is too small, and is not reasonable. If we fix g at 2, the same calculation alternatively gives the effective moment as $\langle \mu \rangle = 0.807 \mu_B$. We attribute the small number to defects in the vanadium site. That is consistent with the value obtained from equation (1).

The behaviour below T_c is more complicated. We can see from figure 7(b) the increase of moment with increasing field near T_c. Such a behaviour is somewhat antiferromagnetic, if the spin system is ordered. With descending temperature and with rising field the system changes to a ferromagnetic tendency, though the magnetization is quite small for an ordinary ferromagnet. For example, it is 4.2×10^{-2} emu mol^{-1} at 2 K in 50 G. We suggest the existence of a weak ferromagnetic ordered state such as canted or ferri-magnetism by the V–O pair. Comparison with the temperature dependence of lattice parameters suggests that the magnetic transition is accompanied by some kind of crystal strain. The behaviour of c is almost understood, but that of a is strange. Change of a is small through the present temperature region, but is remarkable between T_c and 0 K. Once a increases below T_c, and then decreases towards 0 K. Any strong interaction, however, is not to be expected between V^{4+} ions in the aa'-plane, because they are separated by MoO$_4$ tetrahedra. The magnetic transition must be limited mainly to the inside of the chains. First spins tend to align in an anti-parallel manner just below T_c and in lower fields. At lower temperature and in higher fields the parallel configuration is induced. The mechanism of the modulation of a accompanied by the above situation is not clear. The present crystal has a rotational freedom around the c-axis, but attempting to modulate the in-plane symmetry around magnetic V^{4+} ions is not successful, so far without change of c.

A neutron diffraction experiment was tried to understand the magnetic structure, but the intensity of scattering from vanadium is not strong enough yet. The simultaneous configuration of moments in the crystal needs more research.

5. Conclusions

A crystal of VOMoO$_4$ has been grown by the chemical vapour transport method. The crystal has a one-dimensional magnetic chain structure. The magnetic property in the higher temperature region exactly reflects this structure. The temperature dependence of susceptibility is accompanied by a broad maximum around 100 K. It has been explained by the model of a one-dimensional uniform Heisenberg antiferromagnet. The intrachain exchange coefficient has been estimated as 78 K. At 34 K the system goes through a magnetic phase transition to a lower temperature phase. In the new phase ferro- and antiferro-magnetic field dependence appears to compete at different temperatures. Contribution of intra- and, probably, inter-chain interaction increases at lower temperature. It has been suggested that the result brings in an ordered state carrying a weak moment such as canted or ferri-magnetic phases. Research on the detail of the magnetic structure is in progress in the whole temperature range.

Acknowledgments

References

[1] Magneli A 1948 *Acta Chem. Scand.* **2** 861–71
[2] Kihlborg L 1959 *Acta Chem. Scand.* **13** 954–62

[3] Graham J and Wadsley A D 1966 *Acta Crystallogr.* **20** 93–100
[4] Parmentier M, Gleitzer C and Tilley R J D 1980 *J. Solid State Chem.* **31** 305–11
[5] Narushima K and Shiozaki I 1997 *Solid State Commun.* **101** 99–102
[6] Shiozaki I 1998 *J. Magn. Magn. Mater.* **177–181** 261–2
[7] Bonner J C and Fisher M E 1964 *Phys. Rev.* **135** A640–58
[8] Hatfield W E 1981 *J. Appl. Phys.* **52** 1985–90
[9] Haldane F D M 1983 *Phys. Lett.* **93A** 464–8
[10] Haldane F D M 1983 *Phys. Rev. Lett.* **50** 1153–6
[11] Torrance J B 1987 *Low-Dimensional Conductors and Superconductors (NATO ASI Series B Physics 155)* ed
        D Jerome and L G Caron (New York: Plenum) pp 113–33
[12] Renard J P, Verdaguer M, Regnault L P, Erkelens W A C, Rossat-Mignod J and Stirling W G 1987 *Europhys.
        Lett.* **3** 945–52
[13] Renard J P, Verdaguer M, Regnault L P, Erkelens W A C, Rossat-Mignod J, Stirling W G and Vettier C
        1988 *J. Appl. Phys.* **63** 3538–42
[14] Hase M, Terasaki I and Uchinokura K 1993 *Phys. Rev. Lett.* **70** 3651–4
[15] Nishi M, Fujita O and Akimitsu J 1994 *Phys. Rev.* B **50** 6508–10
[16] Isobe M and Ueda Y 1996 *J. Phys. Soc. Japan* **65** 1178–81
[17] Eick H A and Kihlborg L 1966 *Acta Chem. Scand.* **20** 722–9
[18] Izumi F 1993 *The Rietveld Method* ed R A Young (Oxford: Oxford University Press) ch 13
[19] Kim Y-I and Izumi F 1994 *J. Ceram. Soc. Japan* **102** 401
[20] For example, Smith F G 1963 *Physical Geochemistry* (Reading, MA: Addison-Wesley)