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MAGNETIC PROPERTIES OF MOLTEN CHLORIDE SYSTEMS
$MnCl_2$ - KCl, $CoCl_2$ - KCl AND $NiCl_2$ - KCl

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Magnetic susceptibilities of chloride systems containing paramagnetic ions $Mn^{2+}(3d^5)$, $Co^{2+}(3d^7)$ and $Ni^{2+}(3d^8)$ were measured with increasing temperatures from their solid states to molten states. The susceptibility of each system obeyed the Curie-Weiss law in the both states and jumped at the melting temperature. The magnetic moments increased on melting in the systems of Co^{2+} and $Ni^{2+}(L\neq0)$.

The molten salts have been usually studied by means of the high temperature X-ray diffraction, the electron and Raman spectroscopies, volume change, viscosity, enthalpy of mixing, electrical conductivity and diffusion coefficient. Recently the ESR1),2) and NMR3),4) methods have been applied to study the magnetic properties of molten chlorides. The magnetic susceptibilities of molten salts have been scarecely reported.5) In this work we measured the susceptibilities of the systems MCl_2 - KCl (M=Mn, Co, Ni) with increasing temperatures from their solid states to molten states. The results were discussed in connection with the structural change on melting.

The mixtures of MCl_2 and KCl of six different compositions were put into a quartz tube of 6 mmϕ. The tube was sealed off after being evacuated and heated at about 200°C for a few hours. The susceptibility was measured by a Faraday-type magnetic balance from room temperature to 900°C. Paramagnetic molar susceptibility χ_M was calculated by the formula $F = (m/M)\chi_M H(dH/dx)$. The standard substance was $CuSO_4\cdot5H_2O$ ($\chi_M = 1.41 \times 10^{-3}$ emu/mole at 21°C). The diamagnetism was corrected according to Selwood.6)

Fig.1 shows typical results of χ_M^{-1} vs. T for the system $MnCl_2$ - KCl. The relationship is linear, so this system obeys the Curie-Weiss law $\chi_M = N\mu_{eff}^2/3k(T+\theta)$. At the melting temperature a marked jump in susceptibility $\Delta\chi_M$ is seen except for a composition with the mole fraction of $MnCl_2$ $x(MnCl_2)=0.65$. The ratio of $\Delta\chi_M$ to χ_M is less than 0.1. Fig.2(a) and Fig.2(b) show the relationships of μ_{eff} and $\Delta\chi_M$ to $x(MnCl_2)$, respectively. The value of μ_{eff} is in good agreement with the spin only value of Mn^{2+} ion 5.92 B.M. in both solid state and molten state at any composition. Therefore, the energy level of Mn^{2+} ion is ground state, $^6A_{1g}$ (L = 0, S = 5/2). As shown in Fig.2(b), $\Delta\chi_M$ is negative for the region of $x(MnCl_2)>0.65$ and positive for the region of $x(MnCl_2)<0.65$. This behavior seems to be caused by the structural difference between the solid state and the molten state of each composition.

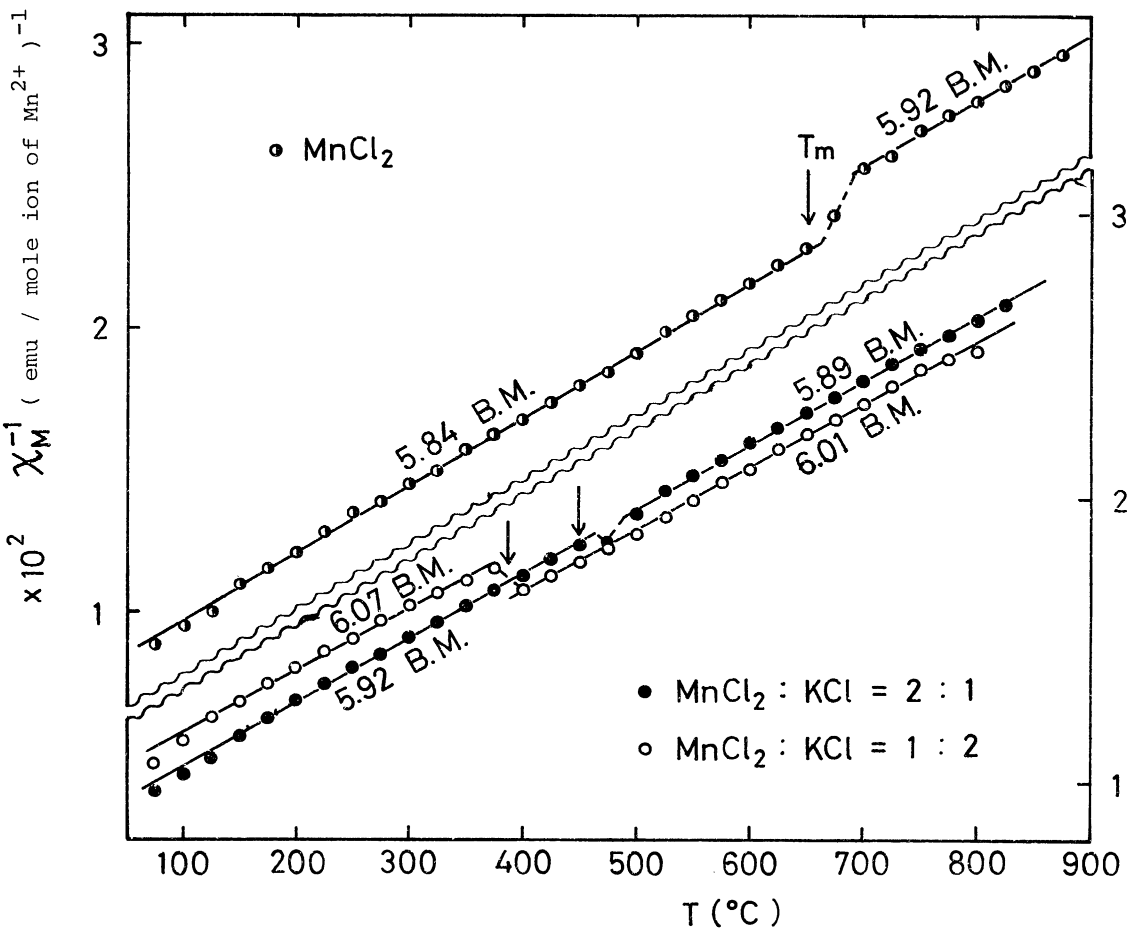

Fig.1 Temperature dependence of reciprocal susceptibility of the system $MnCl_2$ - KCl. (Attention to the χ_M^{-1} - scale.)

$MnCl_2$ has a layer structure of $CdCl_2$-type and an antiferromagnetic ordering below the Néel point of 1.9K$^{7)}$ as shown in Fig.3. The antiferromagnetic ordering between Mn^{2+}-layers across two Cl^--layers disappears above 1.9K. However, an exchange interaction that makes spins of Mn^{2+} ions parallel each other within a Mn^{2+}-layer will remain up to higher temperatures. At the melting point this parallel interaction will disappear owing to the collapse of the layer structure. Therefore, the susceptibility decreases on melting. In the molten state the octahedral $MnCl_6^{4-}$ ions seem to be dominant from the results of the Raman spectroscopies of $CdCl_2^{8)}$ and $MgCl_2^{9)}$ which have the $CdCl_2$-type structure.

Three compounds$^{10)}$ $KMnCl_3$, $K_3Mn_2Cl_7$ and K_4MnCl_6 are known in the region of $x(MnCl_2)<0.65$. Mn^{2+} ion has the octahedral coordination of six Cl^- ions in these compounds.$^{10)}$ There is a superexchange interaction, which makes spins of Mn^{2+} ions antiparallel each other, between Mn^{2+} ions through a neighboring Cl^- ion. At the melting temperature such an antiparallel interaction will disappear owing to the collapse of the solid structure. Therefore, the susceptibility increases on melting for KCl-rich compositions. Data of the Raman spectroscopies$^{8),9)}$ indicate that the tetrahedral $MnCl_4^{2-}$ ions and K^+ ions are dominant in their melts.

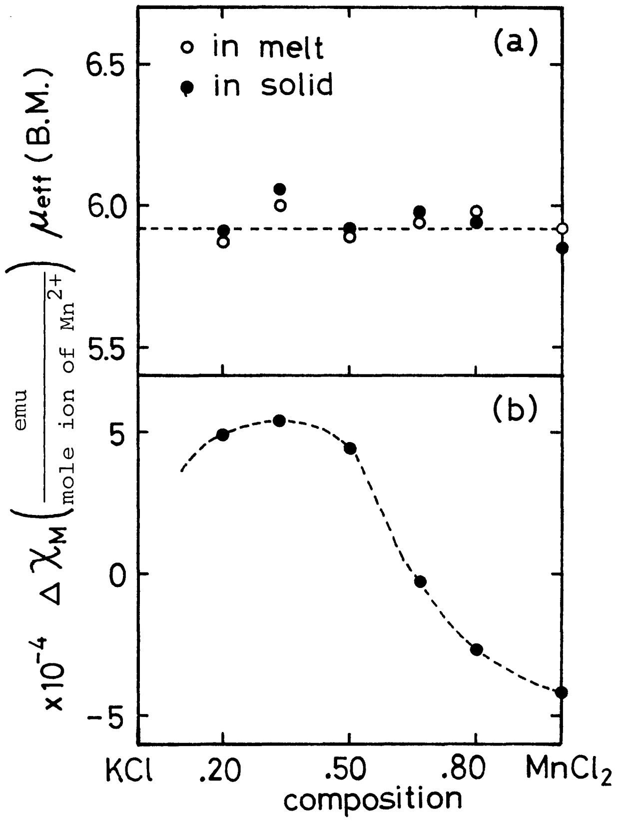

Fig.2 (a) Effective magnetic moments and (b) jump in the susceptibility of the system $MnCl_2$ - KCl.

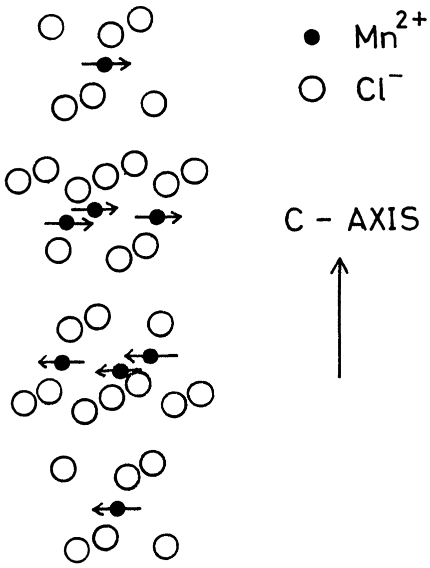

Fig.3 $MnCl_2$ - structure and antiferromagnetic ordering below 1.9K

Fig.4(a) shows μ_{eff} vs. x($CoCl_2$) in the system $CoCl_2$ - KCl. The value of μ_{eff} increases from 4.95 ∿ 5.18 B.M. to the higher value through the melting at any composition. These increments of μ_{eff} are attributable to the fact that the Co^{2+} ions in the melts are close to the free Co^{2+} ions. That is, the anisotropy of 3d-electron orbitals caused by long-range ordering of ions in the solid state collapses on melting, then a random distribution of farther neighbors outside the nearest Cl^- ions of Co^{2+}ions occurs in the molten state. Particularly the value 6.15 B.M. of μ_{eff} of a Co^{2+} ion for the specimen $CoCl_2$: KCl = 4:1 is close to 6.63 B.M. of μ_{eff} of a free Co^{2+} ion. In the system $NiCl_2$ - KCl (Fig.5(a)), the value of μ_{eff} of Ni^{2+} ion also increases through the melting at any composition. The data for a pure $NiCl_2$ could not be obtained because of its higher melting point (≃1000°C). As shown in Figs.4(b) and 5(b), the behavior of $\Delta\chi_M$ in the system $CoCl_2$-KCl and $NiCl_2$ - KCl are similar to that of the system $MnCl_2$ - KCl (Fig.2(b)). $\Delta\chi_M$ is positive for the smaller x($CoCl_2$) and x($NiCl_2$) compositions, and negative and almost zero for the larger x($CoCl_2$) and x($NiCl_2$) compositions, respectively.

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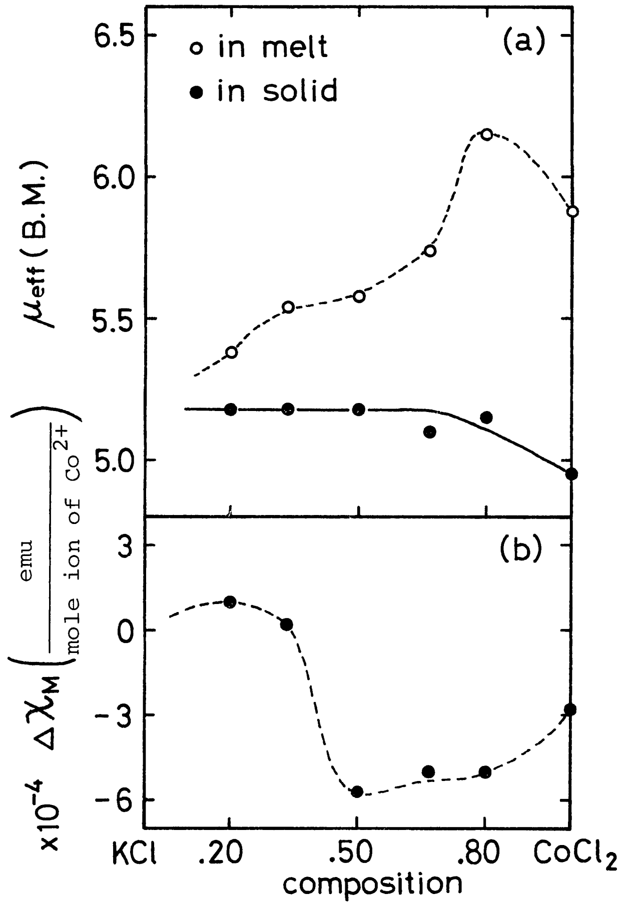

Fig.4 (a) Effective magnetic moments and (b) jump in the susceptibility of the system $CoCl_2$ - KCl.

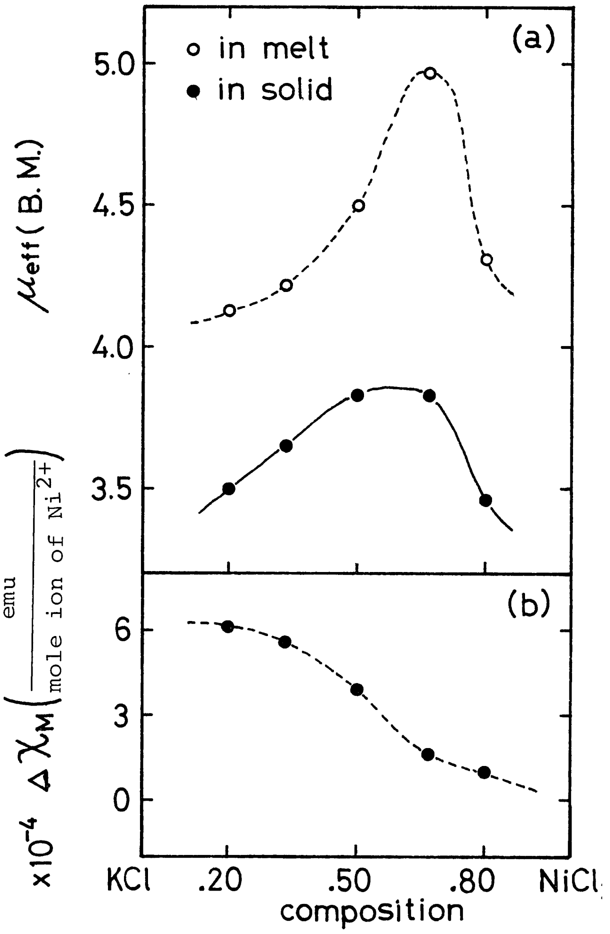

Fig.5 (a) Effective magnetic moments and (b) jump in the susceptibility of the system $NiCl_2$ - KCl.

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