

Mössbauer Studies of Ferrous Ions in Metal Dichlorides

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(Received, Sept. 5, 1977)

Abstract

Mössbauer spectra of Fe^{57} in MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 were investigated at several temperatures between 77K and 623K. The asymmetry of intensities of the quadrupole doublet was observed and it became more distinct with increasing temperature. The recoil-free fractions decreased with increasing temperature. The absolute value of the mean square displacement of lattice vibrations was estimated from the values of the ratio of intensities of two absorption peaks and of the recoil-free fractions. The isomer shift of Fe^{2+} increased with the ionic radius of the host metal.

Introduction

The ground and the first excited states of Fe^{57} have the nuclear spin of $I = \frac{1}{2}$ and of $I = \frac{3}{2}$, respectively. The excited state splits into two energy levels by a quadrupole interaction, although the ground state remains unsplit. For the $I = \frac{3}{2}$ to $I = \frac{1}{2}$ transition, a quadrupole doublet appears on a Mössbauer spectrum. If a recoil-free fraction is isotropic, angular dependences of the intensities of two absorption peaks are

<i>Transition</i>	<i>Angular Dependence</i>	
$\left(\frac{3}{2}, \pm\frac{3}{2}\right) \leftrightarrow \left(\frac{1}{2}, \pm\frac{1}{2}\right)$	$\frac{3}{2}(1 + \cos^2\theta)$	(1)
$\left(\frac{3}{2}, \pm\frac{1}{2}\right) \leftrightarrow \left(\frac{1}{2}, \pm\frac{1}{2}\right)$	$1 + \frac{3}{2} \sin^2\theta$	

where θ is an angle between the maximum principal axis of the EFG tensor and incident γ rays. In the case of powder samples, an intensity is averaged over all directions and both the absorption peaks have the same intensities. However, if a recoil-free fraction is anisotropic, the intensities of two absorption peaks are generally not equal even for powder samples. Because an angular dependence of the intensity is the product of the angular dependence described by the equation (1) and that of a recoilfree fraction which depends on an anisotropy of lattice vibrations. The effect has been found by Goldan-

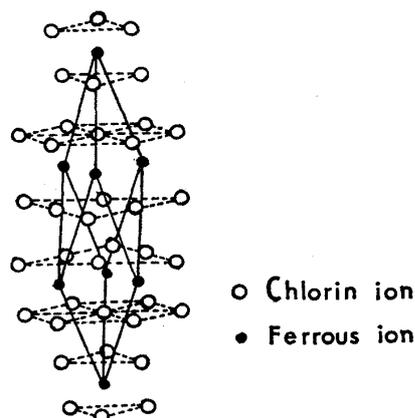


Fig. 1. Crystal structure of CdCl_2 type.

skaa and Karyagin, and the phenomenon observed for powder samples has been called as the Goldanskii-Karyagin effect.¹⁾

The crystal structure of the CdCl_2 type has a layer structure and is shown in Fig. 1. A metallic ion is surrounded by six chlorine ions octahedrally and is immersed in a trigonal field parallel to the c axis. The atomic layers normal to the c axis are Cl, Metal, Cl, Cl, Metal, Cl, ... as seen in the figure. The crystal is easily cloven because of the weak bonding between two Cl layers adjacent to each other. From the difference between the intra-plane and the inter-plane bonding strengths, an anisotropy of lattice vibrations is expected, and consequently an anisotropy of two absorption peaks is also expected. Therefore the observations of the Mössbauer spectrum were carried out using the compounds with the CdCl_2 structure, namely, FeCl_2 , and 2% Fe^{57} doped MgCl_2 , MnCl_2 , CoCl_2 , NiCl_2 and CdCl_2 at several temperatures between 77K and 623K.

Experimental

Anhydrous samples were prepared by dehydration of commercial reagents with crystalline water. The procedure we used was the following. In the case of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, powders put in a glass tube were completely dehydrated by pumping under slowly increasing temperature to about 120°C . Then, the temperature was raised to 350°C to sublime and exclude FeCl_3 . In other cases, separately prepared solutions of $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ (M: Mg, Mn, Co, Ni, Cd) and of $\text{Fe}^{57}\text{Cl}_2$ were mixed so that Fe^{57} at the rate of 2% of the metal ions might be distributed homogeneously in the sample. The water of the solutions was evaporated by pumping until the hydrous compounds were obtained. After that the similar procedures as the case of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were performed to get the anhydrous samples. In the case of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, an aqueous solution of NH_4Cl was added to the solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to produce $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in order to prevent the decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ during the process of dehydration.

Powder samples thus obtained were very deliquescent, so that a great precaution against rehydration was paid throughout the experiment. Before taking the sample out from the glass tube, a small amount of grease was as quickly as possible put on the inside wall of the glass tube near its mouth and adsorbed water and gases in grease were completely removed by pumping. Then the sample at the bottom of the tube was soaked with the melted grease. After filling dry N_2 gas into the tube, the sample was taken out for mounting on a holder which was made of a small size of an acrylic plastic plate. The plastic holder has a shallow hollow at the center with an area of 1 cm^2 and of 0.3 mm in depth. The greased powder was packed in it and tightly covered with a vinyl tape. This procedure prevented rehydration of the sample. The measurements were carried out up to room temperature using the samples prepared as mentioned above. But in the cases of the measurements at 473K and 623K , some improvements were required because an acrylic plastic holder and grease could not be used. A powder sample was sandwiched between two aluminum foils of $50\ \mu\text{m}$ in thickness. The sandwiched sample was put between two copper plates with a hole of 12 mm in diameter for γ ray transmission at each of their centers and was bolted at four corners. This process was carried out in a flow of dry N_2 gas. The sample thus prepared was mounted in a vacuum part of a metal dewar. The dewar was cooled down by mixture of dry ices and ethylalcohol so that water and other gases, which were emitted from a set of the heated sample holder and might give undesirable effects on the sample, could be trapped around it. A hot part and a cold finger were connected with a thin stainless steel plate which

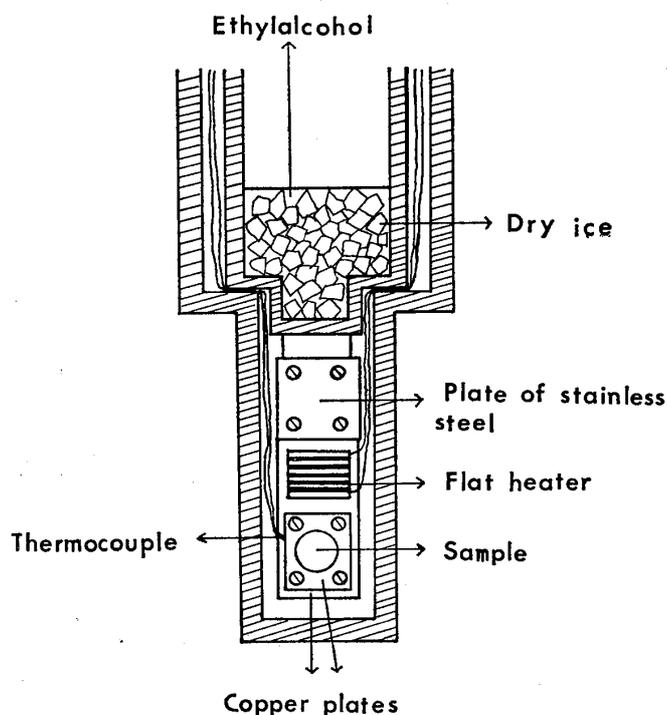


Fig. 2. The sample holder used for the measurements at 473K and 623K .

has low thermal conductivity, as shown in Fig. 2.

A constant acceleration spectrometer was used and calibrated with an Fe-metal absorber.

Experimental results and discussion

(A) Mean square displacement of lattice vibration

The Mössbauer spectra of Fe⁵⁷ in FeCl₂, CoCl₂ and NiCl₂ obtained at several temperatures between 77K and 623K are shown in Figs. 3, 4 and 5, respectively.* The spectra of MgCl₂, MnCl₂ and CdCl₂ at room temperature are shown in Fig. 6. At 77K the two absorption peaks had the same intensities within the experimental errors for all samples examined. This fact showed that there was no preferred orientation in the samples prepared as mentioned above. With increasing temperature the asymmetry of the quadrupole doublet increased as seen in the figures. The amount of absorption in CoCl₂ and NiCl₂ was found to be much decreased at 473K and 623K, that means a rapid decrement of a recoil-free fraction with increasing temperature for these compounds.

An asymmetry parameter A is defined as a ratio of intensities of two absorption peaks:

$$A = \frac{I \left(\begin{array}{c} \frac{3}{2} \rightarrow \frac{1}{2} \\ -\frac{3}{2} \rightarrow -\frac{1}{2} \end{array} \right)}{I \left(\begin{array}{c} \frac{1}{2} \rightarrow \pm \frac{1}{2} \\ -\frac{1}{2} \rightarrow \pm \frac{1}{2} \end{array} \right)}$$

$$= \frac{\int_0^\pi \exp \{ -(1/\lambda^2)(\langle u_{//}^2 \rangle - \langle u_{\perp}^2 \rangle) \cos^2 \theta \} \frac{3}{2} (1 + \cos^2 \theta) \sin \theta d\theta}{\int_0^\pi \exp \{ -(1/\lambda^2)(\langle u_{//}^2 \rangle - \langle u_{\perp}^2 \rangle) \cos^2 \theta \} (1 + \frac{3}{2} \sin^2 \theta) \sin \theta d\theta} \quad (2)^2$$

where I is the intensity of an absorption peak, λ is the wave length of the γ ray of 14.4 KeV divided by 2π and $\langle u_{//}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$ are the components of the mean square displacement of nuclear vibrations parallel and perpendicular to the z axis, respectively. The observed values of A for each sample are listed in Table 1, and their temperature dependences are shown in Fig. 7. The asymmetry is seen to increase with increasing temperature. The A values for FeCl₂, CoCl₂ and NiCl₂ at each temperature decreased in the order of FeCl₂, NiCl₂ and CoCl₂ except for the case of 201K. The reason for the exception observed at 201K is not certain now and a re-examination is necessary. The relationship between the asymmetry parameter A and $\langle u_{//}^2 \rangle - \langle u_{\perp}^2 \rangle$

* The two outermost small absorption lines came from hydrous compounds which were partially formed in the sample during being set into the dewar.

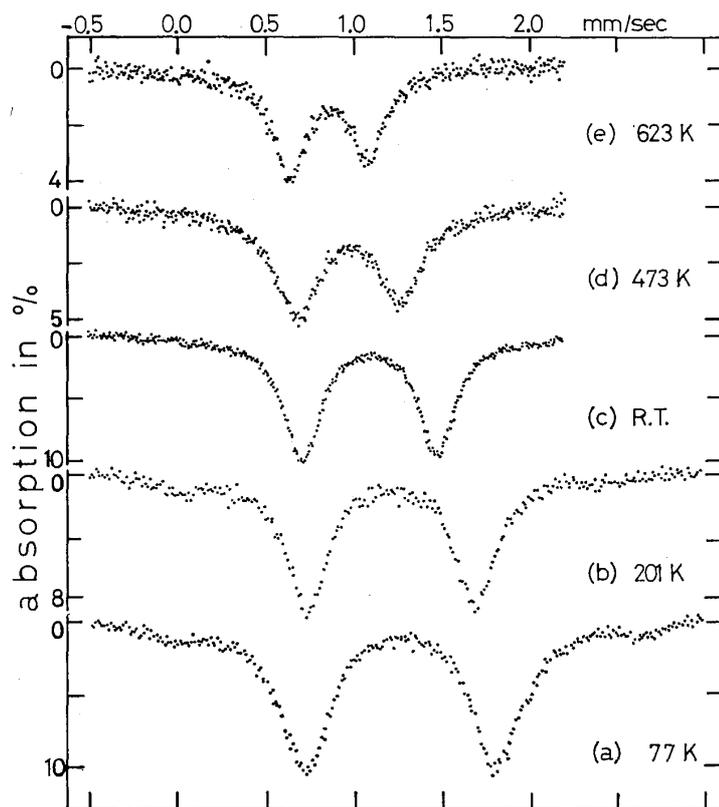


Fig. 3. Mössbauer spectra of Fe⁵⁷ in FeCl₂ at (a) 77K, (b) 201K, (c) room temperature, (d) 473K and (e) 623K.

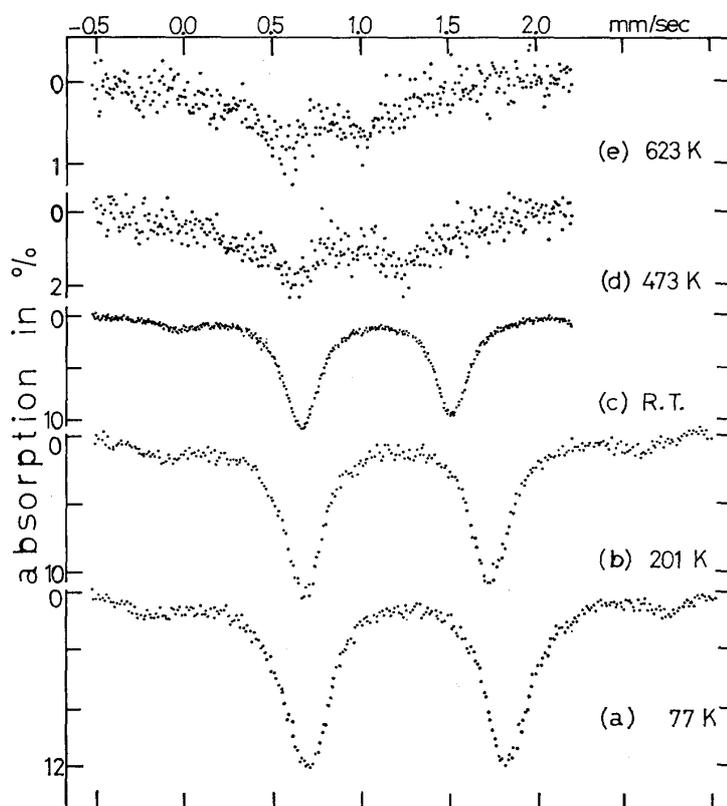


Fig. 4. Mössbauer spectra of Fe⁵⁷ in CoCl₂ at (a) 77K, (b) 201K, (c) room temperature, (d) 473K and (e) 623K.

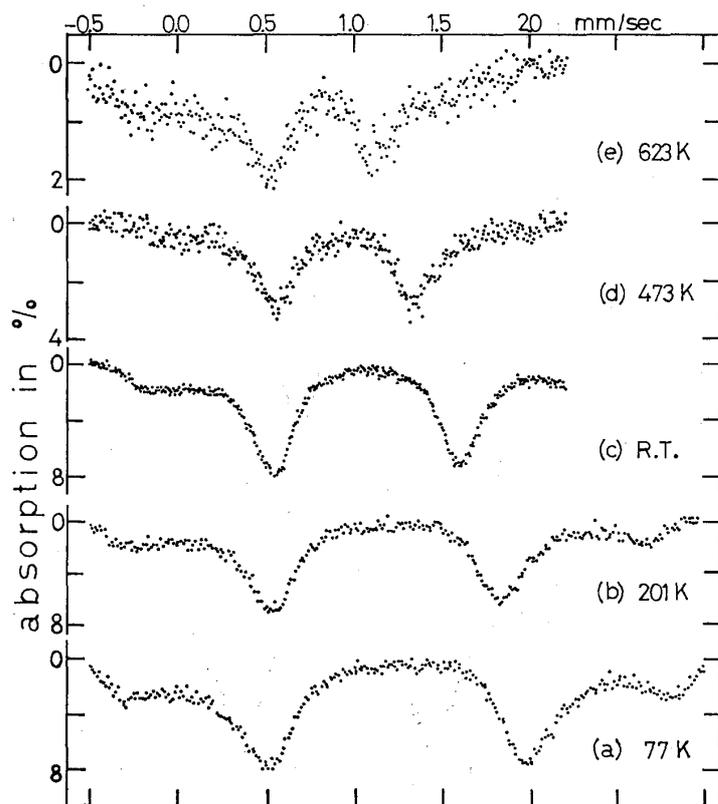


Fig. 5. Mössbauer spectra of Fe^{57} in $NiCl_2$ at (a) 77K, (b) 201K, (c) room temperature, (d) 473K and (e) 623K.

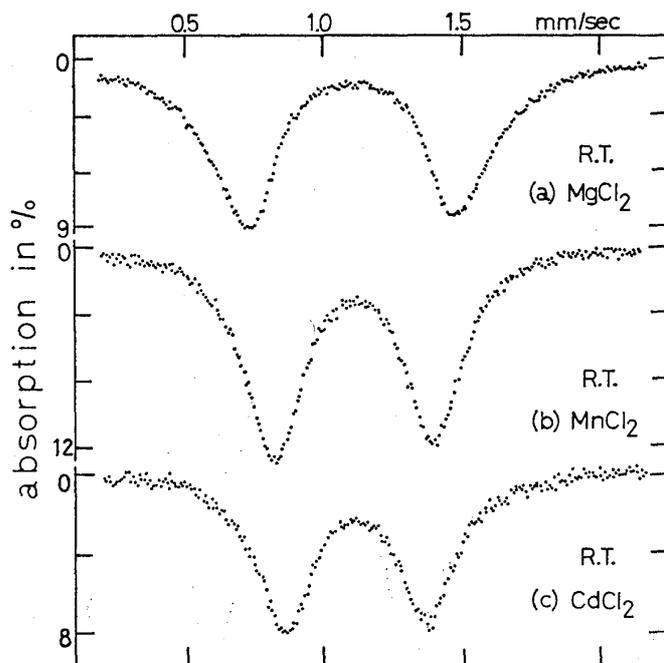
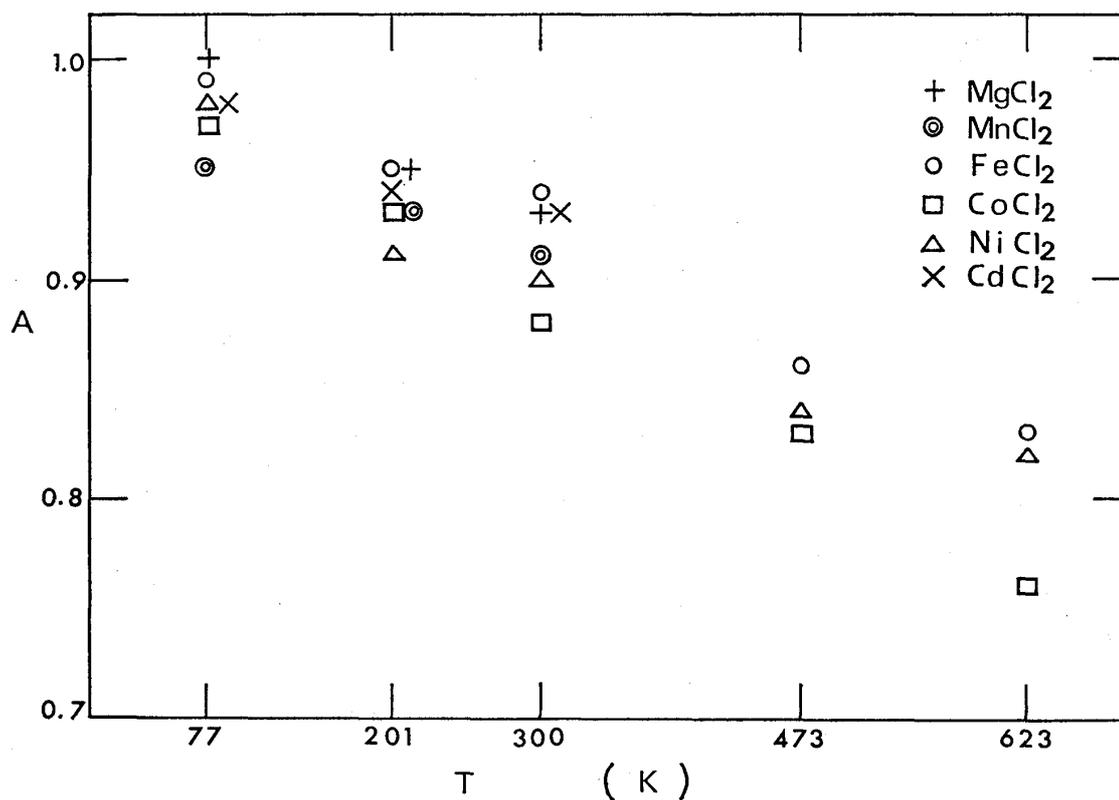


Fig. 6. Mössbauer spectra of Fe^{57} at room temperature in (a) $MgCl_2$, (b) $MnCl_2$ and (c) $CdCl_2$.

Table 1. The values of asymmetry parameter A for MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 at several temperatures.

Temp. (K)	77	201	R. T.	473	623
Sample					
MgCl_2 (2% Fe^{57})	1.00 ± 0.01	0.95 ± 0.02	0.93 ± 0.01		
MnCl_2 (2% Fe^{57})	0.95 ± 0.01	0.93 ± 0.02	0.91 ± 0.01		
FeCl_2	0.99 ± 0.02	0.95 ± 0.02	0.94 ± 0.02	0.86 ± 0.05	0.83 ± 0.04
CoCl_2 (2% Fe^{57})	0.97 ± 0.01	0.93 ± 0.01	0.88 ± 0.01	0.83 ± 0.12	0.76 ± 0.15
NiCl_2 (2% Fe^{57})	0.98 ± 0.02	0.91 ± 0.02	0.90 ± 0.01	0.84 ± 0.07	0.82 ± 0.10
CdCl_2 (2% Fe^{57})	0.98 ± 0.02	0.94 ± 0.05	0.93 ± 0.01		

Fig. 7. Temperature dependences of the asymmetry parameter A for MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 .

given by the equation (2) was used to obtain the values of $\langle u_{//}^2 \rangle - \langle u_{\perp}^2 \rangle$ from the observed values of A . The results are listed in Table 2. In all cases $\langle u_{//}^2 \rangle$ was larger than $\langle u_{\perp}^2 \rangle$. This fact means that the inter-plane bonding is weaker than the intra-plane bonding as expected from the crystal structure.

Table 2. The $\langle u_{\parallel}^2 \rangle - \langle u_{\perp}^2 \rangle$ values in MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 at several temperatures.

Temp. (K)	77	201	R. T.	473	623
Sample					
MgCl_2 (2% Fe^{57})	$\times 10^{-18} \text{ cm}^2$ 0.00 ± 0.001	$\times 10^{-18} \text{ cm}^2$ 0.76 ± 0.15	$\times 10^{-18} \text{ cm}^2$ 1.14 ± 0.11	$\times 10^{-18} \text{ cm}^2$	$\times 10^{-18} \text{ cm}^2$
MnCl_2 (2% Fe^{57})	0.76 ± 0.08	1.14 ± 0.23	1.44 ± 0.14		
FeCl_2	0.15 ± 0.03	0.76 ± 0.15	0.95 ± 0.19	2.4 ± 0.7	3.2 ± 1.1
CoCl_2 (2% Fe^{57})	0.46 ± 0.05	1.14 ± 0.11	1.75 ± 0.18	3.2 ± 1.6	6.2 ± 3.7
NiCl_2 (2% Fe^{57})	0.30 ± 0.06	1.44 ± 0.29	1.56 ± 0.16	2.9 ± 1.0	3.4 ± 1.7
CdCl_2 (2% Fe^{57})	0.30 ± 0.06	0.95 ± 0.29	1.14 ± 0.11		

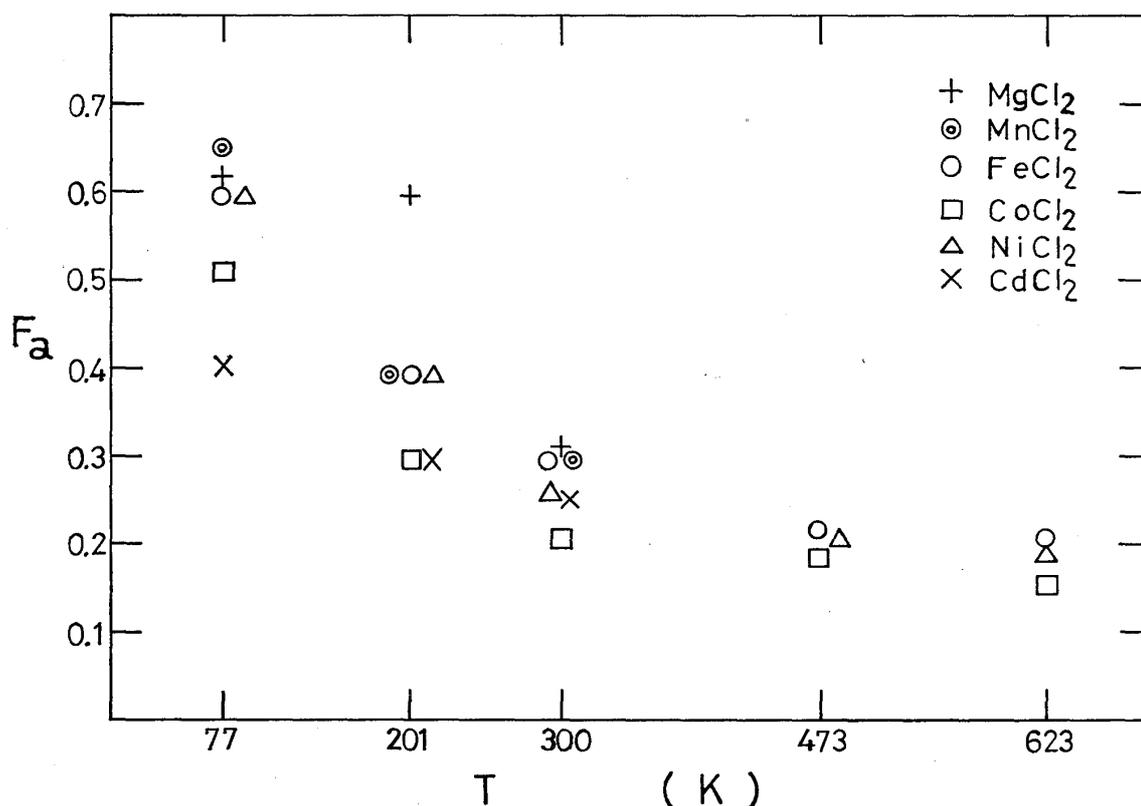
In order to get the absolute values of $\langle u_{\parallel}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$, another information is needed. The recoil-free fraction F_a is denoted as:

$$F_a = \exp \{ -(1/3\lambda^2)(\langle u_{\parallel}^2 \rangle + 2\langle u_{\perp}^2 \rangle) \} \quad (3)$$

Therefore, $\langle u_{\parallel}^2 \rangle + 2\langle u_{\perp}^2 \rangle$ can be calculated from the value of F_a . The F_a value is obtained as follows. The relationship between F_a and an effective thickness T_a of the sample is expressed as $T_a = n_a \sigma_0 F_a$, where suffix "a" for T , n and F denotes the absorber, n_a means the number of Mössbauer nuclei on a unit area, whose value was chosen as $(5.3 \pm 0.2) \times 10^{18} / \text{cm}^2$ throughout the experiment. The σ_0 is a cross section of absorption, which has been known to be $2.56 \times 10^{-18} \text{ cm}^2$,³⁾ for the relevant transition of Fe^{57} . The T_a was estimated using a relationship between T_a and $\Gamma_{\text{exp}} / \Gamma'$.⁴⁾ The Γ' means a natural width of an excited state of a nucleus. In the case of Fe^{57} , Γ' has the value of 0.097 mm/sec. The Γ_{exp} is a full width at a half maximum of the observed absorption peak. The numerical value indexed to W , which is used as a parameter in the Fig. 2 in the reference 4), indicates a shape of an absorption line. As the value increases from zero, a shape of an absorption line approaches from Lorentzian to Gaussian. As the shape of the absorption line in our case was approximately Lorentzian, we used the line for $W_{1/2}$ in the analysis. There were two absorption peaks in our spectrum, and, accordingly, the F_a value was obtained by summing up the f_a values of the left and right absorption peaks. The F_a values thus obtained are listed in Table 3 and their temperature dependences are shown in Fig. 8. The recoil-free fraction decreased with increasing temperature as expected. The F_a values of FeCl_2 , CoCl_2 and NiCl_2 at each temperature decreased in the order of FeCl_2 , NiCl_2 and CoCl_2 in the same manner as the A value did. This fact indicates that CoCl_2 has the weakest lattice bonding in average among these three salts.

Table 3. The values of recoil-free fractions F_a in MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 at several temperatures.

Temp. (K)	77	201	R. T.	473	623
Sample					
MgCl_2 (2% Fe^{57})	0.63 ± 0.05	0.59 ± 0.05	0.30 ± 0.03		
MnCl_2 (2% Fe^{57})	0.65 ± 0.05	0.38 ± 0.04	0.29 ± 0.03		
FeCl_2	0.59 ± 0.05	0.38 ± 0.04	0.29 ± 0.03	0.21 ± 0.04	0.20 ± 0.04
CoCl_2 (2% Fe^{57})	0.52 ± 0.05	0.29 ± 0.04	0.21 ± 0.03	0.19 ± 0.06	0.16 ± 0.06
NiCl_2 (2% Fe^{57})	0.59 ± 0.06	0.38 ± 0.05	0.26 ± 0.03	0.21 ± 0.04	0.19 ± 0.05
CdCl_2 (2% Fe^{57})	0.40 ± 0.04	0.29 ± 0.04	0.25 ± 0.03		

Fig. 8. Temperature dependences of the recoil-free fraction F_a in MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 .

The absolute values of $\langle u_{\parallel}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$ can be obtained from the observed values of $\langle u_{\parallel}^2 \rangle - \langle u_{\perp}^2 \rangle$ and $\langle u_{\parallel}^2 \rangle + 2\langle u_{\perp}^2 \rangle$. The values of $\langle u_{\parallel}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$ are tabulated in Table 4 and those for FeCl_2 , CoCl_2 and NiCl_2 are shown in Fig. 9.

Table 4. The values of the components of the mean square displacement of lattice vibrations parallel and perpendicular to the z axis, i. e. $\langle u_{//}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$, in MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 at several temperatures.

Temp. (K)	77	201	R. T.	473	623
Sample					
MgCl_2 $\langle u_{//}^2 \rangle$	$\times 10^{-18} \text{ cm}^2$ 0.88 ± 0.22	$\times 10^{-18} \text{ cm}^2$ 1.51 ± 0.30	$\times 10^{-18} \text{ cm}^2$ 3.05 ± 0.30	$\times 18^{-18} \text{ cm}^2$	$\times 10^{-18} \text{ cm}^2$
(2% Fe^{57}) $\langle u_{\perp}^2 \rangle$	0.88 ± 0.22	0.75 ± 0.15	1.91 ± 0.19		
MnCl_2 $\langle u_{//}^2 \rangle$	1.33 ± 0.25	2.60 ± 0.52	3.31 ± 0.33		
(2% Fe^{57}) $\langle u_{\perp}^2 \rangle$	0.57 ± 0.11	1.46 ± 0.29	1.87 ± 0.19		
FeCl_2 $\langle u_{//}^2 \rangle$	1.10 ± 0.22	2.35 ± 0.47	2.99 ± 0.45	4.57 ± 1.37	5.20 ± 1.82
$\langle u_{\perp}^2 \rangle$	0.95 ± 0.19	1.61 ± 0.32	2.04 ± 0.31	2.16 ± 0.65	1.99 ± 0.70
CoCl_2 $\langle u_{//}^2 \rangle$	1.55 ± 0.23	3.11 ± 0.50	4.13 ± 0.41	5.30 ± 2.65	7.62 ± 4.57
(2% Fe^{57}) $\langle u_{\perp}^2 \rangle$	1.09 ± 0.16	1.97 ± 0.31	2.38 ± 0.24	2.09 ± 1.04	1.41 ± 0.85
NiCl_2 $\langle u_{//}^2 \rangle$	1.20 ± 0.24	2.80 ± 0.56	3.60 ± 0.36	4.90 ± 1.72	5.41 ± 2.71
(2% Fe^{57}) $\langle u_{\perp}^2 \rangle$	0.90 ± 0.18	1.36 ± 0.27	2.04 ± 0.20	2.00 ± 0.70	2.03 ± 1.02
CdCl_2 $\langle u_{//}^2 \rangle$	1.94 ± 0.39	2.99 ± 0.75	3.39 ± 0.34		
(2% Fe^{57}) $\langle u_{\perp}^2 \rangle$	1.64 ± 0.33	2.04 ± 0.51	2.25 ± 0.22		

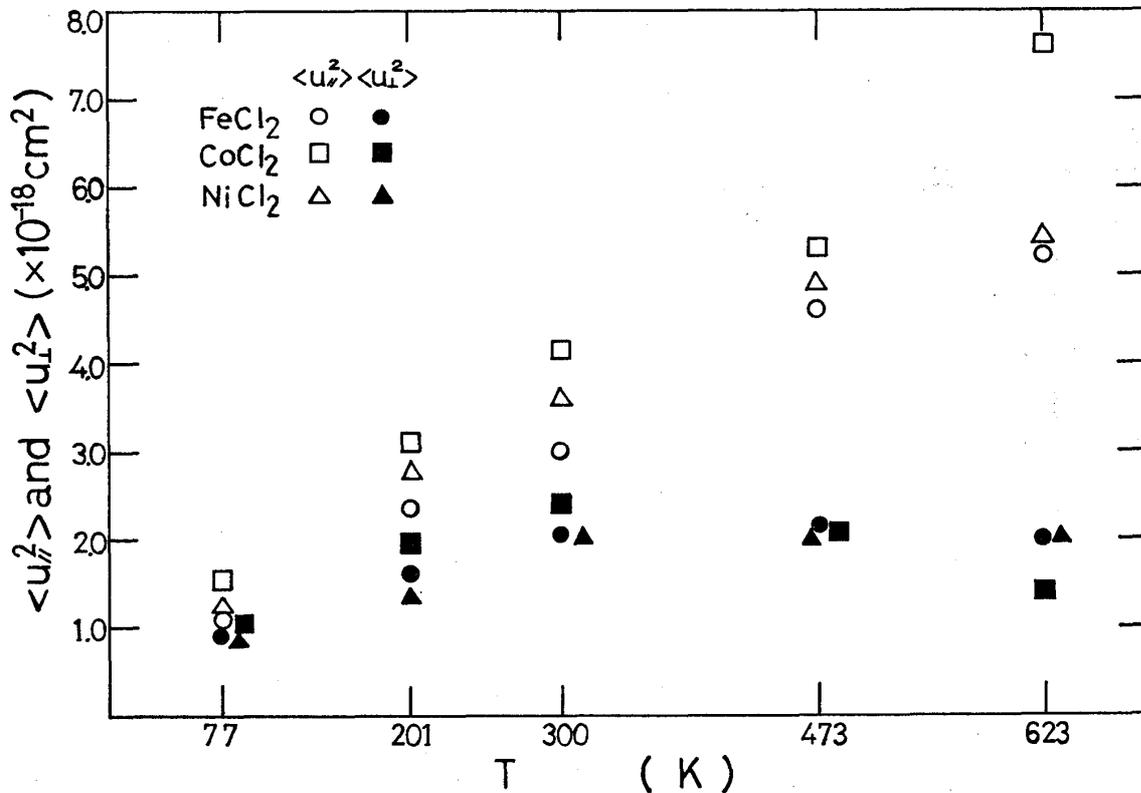


Fig. 9. Temperature dependences of the components of the mean square displacement of lattice vibrations, $\langle u_{//}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$, in FeCl_2 , CoCl_2 and NiCl_2 .

The values of $\langle u_{ij}^2 \rangle$ increased remarkably with increasing temperature, especially in the case of CoCl_2 at 623K, but those of $\langle u_{\perp}^2 \rangle$ showed rather small increment. The fact indicates that the increase of the anisotropy of lattice vibrations at high temperature results from the increase in $\langle u_{ij}^2 \rangle$. The remar-

Table 5. The values of center shifts δ in MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 at several temperatures.

Temp. (K)	77	201	R. T.	473	623
Sample					
MgCl_2 (2% Fe^{57})	mm/sec 1.29 ± 0.01	mm/sec 1.22 ± 0.01	mm/sec 1.09 ± 0.007	mm/sec	mm/sec
MnCl_2 (2% Fe^{57})	1.30 ± 0.01	1.22 ± 0.01	1.10 ± 0.007		
FeCl_2	1.27 ± 0.01	1.20 ± 0.01	1.08 ± 0.007	0.96 ± 0.011	0.85 ± 0.011
CoCl_2 (2% Fe^{57})	1.26 ± 0.01	1.19 ± 0.01	1.07 ± 0.007	0.91 ± 0.018	0.84 ± 0.021
NiCl_2 (2% Fe^{57})	1.24 ± 0.01	1.17 ± 0.01	1.06 ± 0.007	0.93 ± 0.014	0.81 ± 0.018
CdCl_2 (2% Fe^{57})	1.23 ± 0.007	1.17 ± 0.007	1.11 ± 0.007		

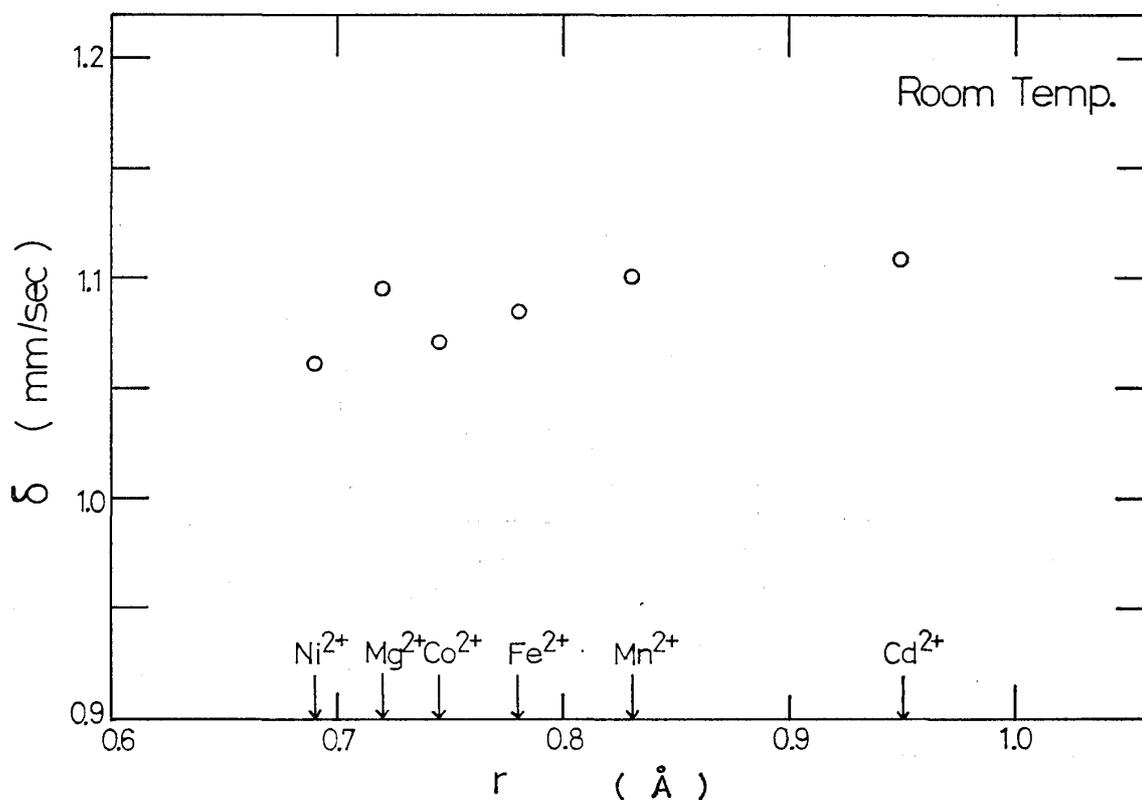


Fig. 10. Dependence of the center shift δ on the ionic radius of host metals at room temperature.

kable feature observed for CoCl_2 at 623K may be related to the fact that the sublimation temperature of CoCl_2 is the lowest among the samples used here. Further experiments will be needed for the detailed discussion.

(B) Center shift

The observed center shifts are listed in Table 5. A relation between the center shift and the ion radius of the host metal at room temperature is shown in Fig. 10. The center shifts increased as the radii of the host metallic ions became large. This observation can be interpreted as the result of the difference of isomer shifts of Fe^{2+} ions in each compounds. When Fe^{2+} ions are introduced into a host lattice with larger metallic ions, the covalency between Fe^{2+} ions and the ligands is expected to decrease, and consequently isomer shifts of Fe^{2+} ions are increased.

The temperature dependences of the center shifts are shown in Fig. 11. The observed change with temperatures can be interpreted as the second order Doppler shift.

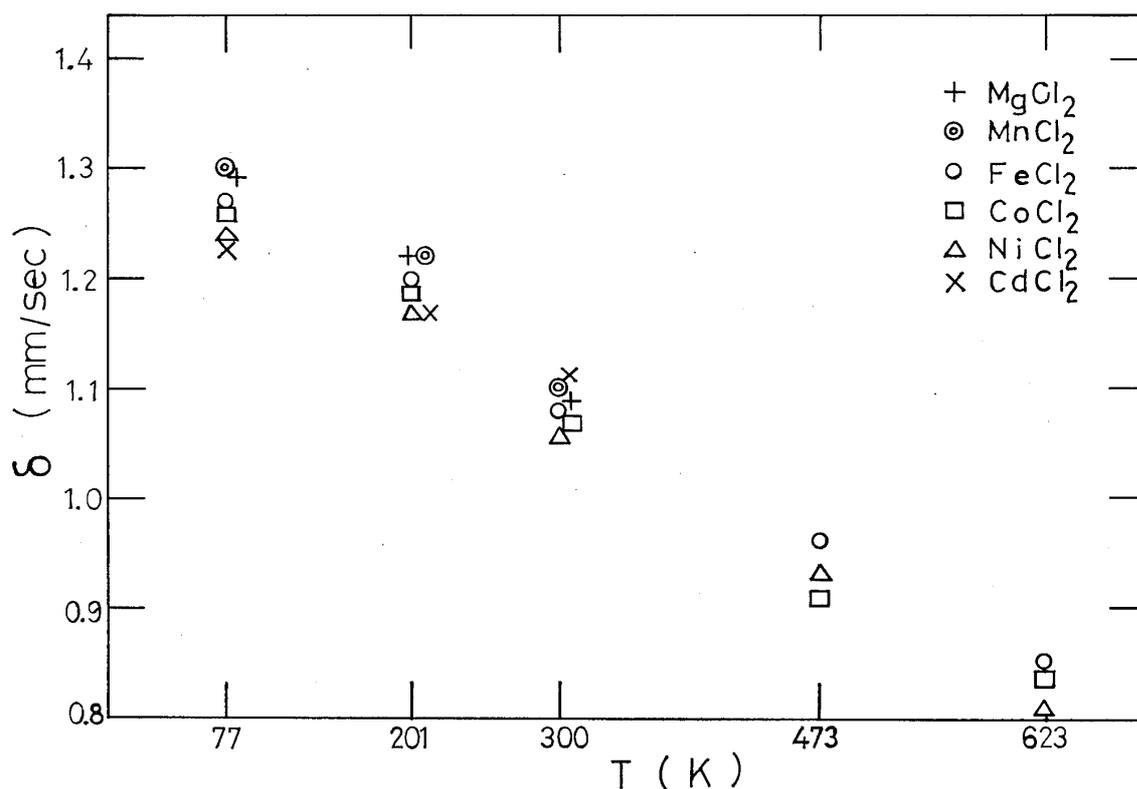


Fig. 11. Temperature dependences of the center shifts δ for MgCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 and CdCl_2 .

Acknowledgments

One of the authors, T. Tamaki, would express her sincere thanks to Professor Sadato Yabuki for his encouragement during completing the manuscript.

References

- 1) V. I. Goldanskii, E. F. Makarov and V. V. Khrapov: *Phys. Letters*, **3** (1963), 344; V. I. Goldanskii, E. F. Makarov, I. P. Suzdalev and I. A. Vinogradov: *Phys. Rev. Letters*, **20** (1968), 137.
- 2) V. I. Goldanskii and R. H. Herber (Ed.): *Chemical Applications of Mössbauer Spectroscopy*, p. 104, Academic Press, (1968).
- 3) J. G. Stevens and V. E. Stevens (Ed.) *Mössbauer Data Index*, Plenum, (1974).
- 4) G. Lang: *Nuclear Instruments and Methods*, **24** (1963), 425.