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OF FERROUS IONS IN CUBIC ICE

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MÖSSBAUER EFFECT OF FERROUS IONS IN CUBIC ICE

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## ÖSSZEFOGLALÓ

A Mössbauer-abszorpció és a differenciális termoanalízis összekapcsolásával kimutatjuk, hogy a fagyasztott vas/II/-perklorát oldatban lévő  $\text{Fe}^{2+}$  ionokon a jég köbös fázisának hatását nem lehet észlelni.

## ABSTRACT

By combining Mössbauer absorption and differential thermal analysis it has been demonstrated that  $\text{Fe}^{2+}$  ions in frozen ferrous perchlorate solution are unaffected by the presence of the cubic phase of the ice.

## РЕЗЮМЕ

Путем сочетания абсорбции Мессбауера с дифференциальным термическим анализом было доказано, что наличие кубической фазы льда не воздействует на ионы  $\text{Fe}^{2+}$  в замороженном растворе перхлората железа (II).

In early investigations of frozen aqueous solutions using Mössbauer spectroscopy [1,2], the temporary disappearance of absorption near  $-90^{\circ}\text{C}$  was attributed to ionic motion during the transformation from cubic to hexagonal phase which occurs in pure Ice I at this temperature [3]. Since the absorbers were made under normal pressure and Ice  $I_c$  normally forms from high pressure phases of Ice III, V and in condensation from vapour, special mechanisms were invoked. Further studies [4,5], however, have suggested that the low-temperature phase of the frozen solution consists, at least in the region surrounding the impurity ions, of a glassy or amorphous variety of ice of approximately eutectic composition. Upon heating to about  $-110^{\circ}\text{C}$  the glass softens, causing the Mössbauer effect to vanish. At about  $-90^{\circ}\text{C}$ , the supercooled liquid recrystallizes. The Mössbauer effect returns, to remain until the eutectic melting point is reached at about  $-40^{\circ}\text{C}$ . Clarification of the situation has been helped by the use of differential thermal analysis /DTA/ [5,6].

We report here a study in which ice crystals were made from aqueous solutions of ferrous perchlorate under conditions of high pressure to assure the formation of the cubic phase. Evidence for the formation of Ice  $I_c$  was found in DTA measurements on the Mössbauer absorbers.

Samples of 1 ml ferrous perchlorate solution were placed in a sealed die and compressed at 5 kbar. In that condition, the die was cooled in liquid nitrogen over a period of 10 minutes. A few minutes after thermal equilibrium was reached, the frozen solution was forced from the die, being broken into small crystals in the process. Some of these were pressed into a brass cylinder 7 mm in diameter and 3 mm thick and held in place with thin aluminum caps. The cylinder contained a differential thermocouple whose junctions were at the centre of the sample and on the outer surface of the brass. The absorber was mounted on the cold finger of a liquid nitrogen cryostat surrounded by styrofoam insulation. The temperature was measured by a third thermocouple in contact with the absorber.

Two types of experiment were carried out. In the first series, the transmission of 14 keV gamma rays from an unsplit fixed source was measured with a multichannel scaler. Because the large isomer shift of ferrous ion brings one of the quadrupole split absorption peaks into resonance near zero velocity, the Mössbauer fraction can be measured rapidly. Alternate 20-second scaling periods were used to measure off-resonance background transmission, with the source oscillating. The absorber warmed over a period of 2 hours from  $-190^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ . The  $T$  and  $\Delta T$  measured by the single and double thermo-

couples were monitored using recorders synchronized with the multiscaler. Absorbers containing 3.5, 5.0 and 7.0 molar %  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in water were studied in this way.

In a further experiment, full Mössbauer spectra were made with an absorber containing 3.5 molar % solution at temperatures of  $-180^\circ\text{C}$ ,  $-130^\circ\text{C}$  and  $-115^\circ\text{C}$ . In each case the temperature was held constant within a few degrees for the measurement.

Figure 1 is a composite graph taken from the three multiscaling runs. The DTA curve for pure water is shown for comparison. In Figure 2 the absorption spectra are shown for the 3.5 molar % solution. The quadrupole splittings, line widths and isomer shifts are shown in Table I, where they are compared with similar data for an absorber of the same concentration made under atmospheric pressure.

. TABLE 1

T / $^\circ\text{C}$ /	"Pressurized Ice"			"Normal Ice"		
	$E_Q$	I.S. /mm/sec/	FWHM	$E_Q$	I.S. /mm/sec/	FWHM
-180	3.34 (2)	1.54 (2)	0.44 (3)	3.32 (1)	1.52 (1)	0.48 (1)
-125	3.27 (2)	1.52 (2)	0.42 (4)	3.25 (2)	1.50 (2)	0.50 (3)
-115	3.17 (3)	1.52 (3)	0.52 (4)	3.23 (1)	1.49 (1)	0.52 (1)

The thermal measurements clearly indicate the Ice III, V  $\rightarrow$  Ice I<sub>c</sub> transformation of at least some part of the absorber at  $-120^\circ\text{C}$ . This fraction decreases with increasing solute concentration, disappearing at the eutectic concentration of 7 %. At the same time, the dip at  $-100^\circ\text{C}$  and the subsequent peak at  $-80^\circ\text{C}$ , corresponding to the softening and recrystallization of amorphous ice, increase with concentration in exactly the manner observed with solutions frozen at normal pressure. Despite these quantitative changes in the DTA curves, no important variation in the Mössbauer data occurred from run to run. Most importantly, no change in intensity was found at  $-120^\circ\text{C}$ .

The Mössbauer spectra give further evidence that most, if not all, of the iron ions are associated with the glassy fraction of the absorber and that they are unaffected by the appearance of the cubic phase of ice, which must be occurring elsewhere in the material.

These experiments seem to provide strong evidence for the segregation of the solution upon freezing into two components, one containing  $\text{Fe}(\text{ClO}_4)_2$  solution of approximately eutectic composition, the other pure ice.

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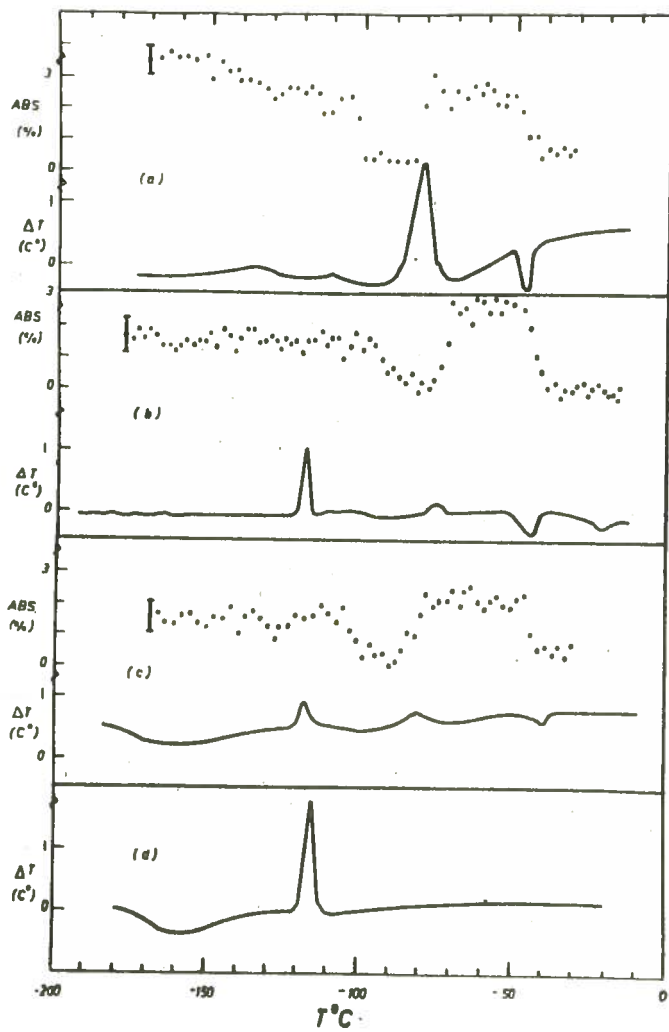


Fig. 1

DTA and zero velocity Mössbauer absorption as functions of temperature and solute concentration: /a/ 7.0 molar %; /b/ 3.5 molar %; /c/ 5.0 molar % ferrous perchlorate in water; /d/ DTA of pure ice.



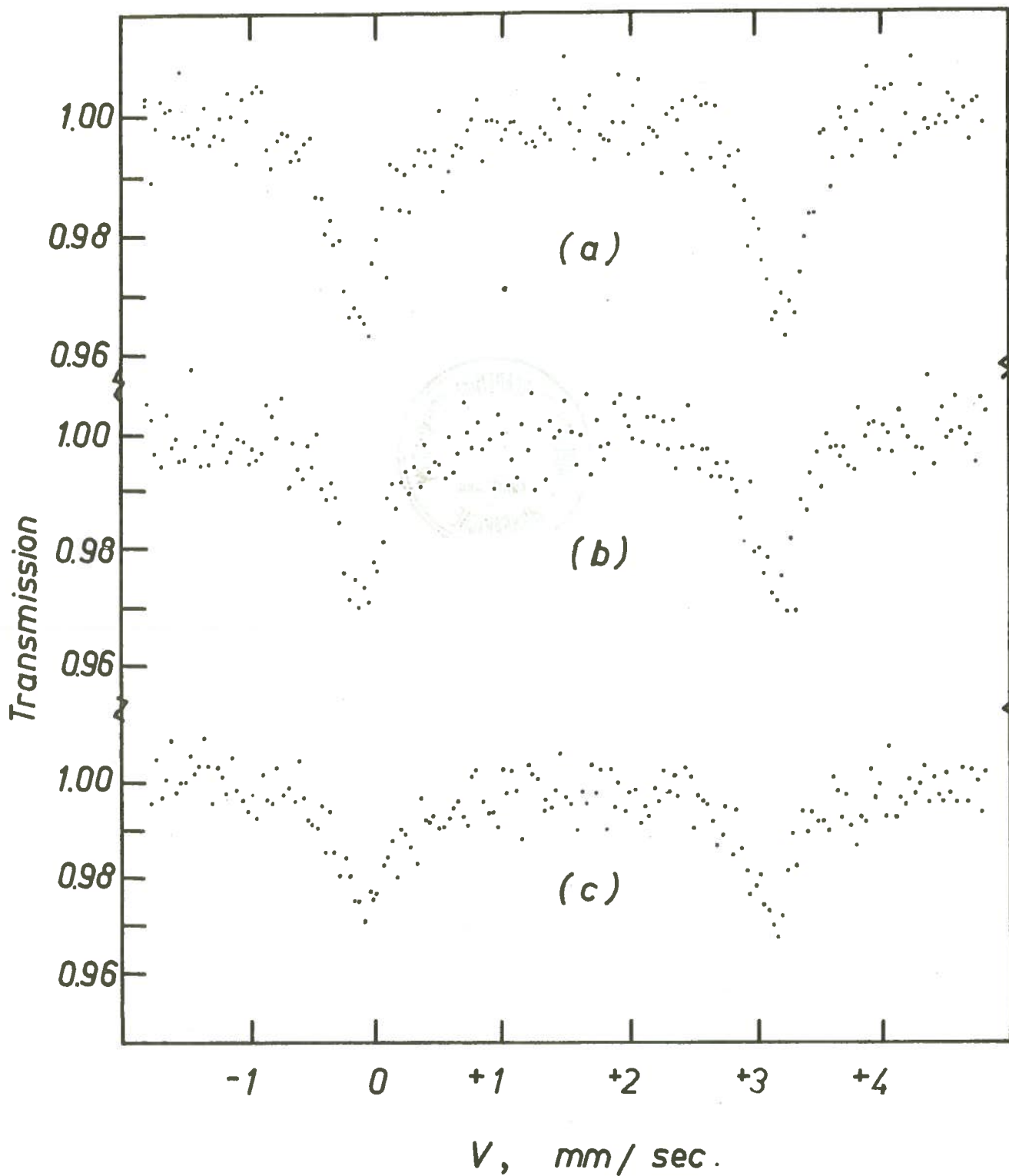
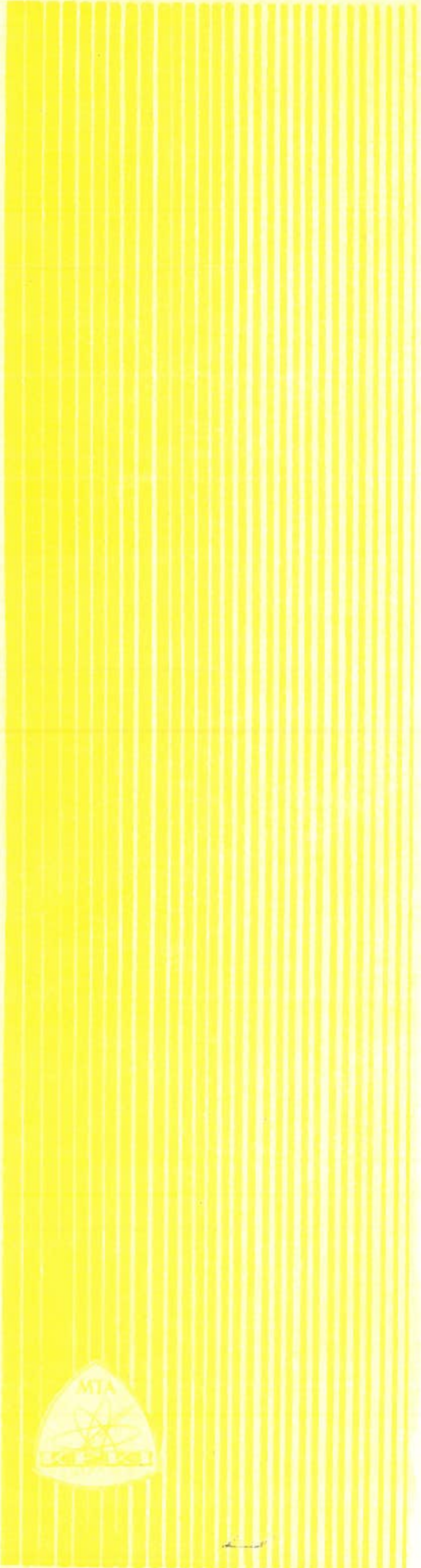


Fig. 2

Mössbauer spectra of 3.5 molar % ferrous perchlorate solution  
at /a/  $-180^{\circ}\text{C}$ ; /b/  $-140^{\circ}\text{C}$ ; /c/  $-110^{\circ}\text{C}$ .







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