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Nuclear magnetic resonance in $BaCl_2 . 2H_2O$.[*]

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Silvidi & McGrath (1960) studied the orientations of the water molecules in $BaCl_2 . 2H_2O$ using the nuclear magnetic resonance (NMR) technique of Pake (1948). Their *p–p* (proton–proton) directions are represented by *A*, *B*, *C* and *D* in Fig. 1, and given in Table 1 in terms of $\pm\alpha_0$, β_0 and $\pm\gamma_0$, the angles that the directions make with the $\pm a$, b and $\pm c$ axes respectively. The *p–p* distances are given in Table 1 in terms of *r*. Recent neutron diffraction studies by Padmanabhan, Busing & Levy (1963) resulted in a structure which is in conflict with that proposed by Silvidi & McGrath. The hydrogen positions obtained by neutron diffraction were used to calculate the *p–p* vectors represented by I, I′, II and II′ in Fig. 1 and Table 1. The present work was undertaken to resolve this conflict.

The NMR spectra were obtained with a 'wide line' Varian spectrometer operating at 16 $mc.sec.^{-1}$. A calibrated drive was used to sweep the frequency through resonance. The first derivative spectra were recorded by standard lock-in detection techniques. Resonance diagrams obtained by rotating the crystal about two different axes of rotation, namely [101] and [$\bar{1}$01], were used to determine the *p–p* vectors. The planes of rotation are indicated by broken lines in Fig. 1. The observed *p–p* directions are shown in Fig. 1 and are to be compared with the directions obtained from the neutron diffraction structure. The comparison is shown in greater detail in Table 1 where the *p–p* separations are also given.

The observed *p–p* vectors were determined from resonance diagrams obtained by plotting the angular variation of the positions of maximum absorption. According to Pedersen & Holcomb (1963) the component lines are generally asymmetrical owing to the interaction between neighboring proton pairs, and precise results are obtained if the centres of gravity of the component lines are taken to represent positions of the component lines. The recorded resonance spectra for $BaCl_2 . 2H_2O$ were sufficiently complicated (8 lines for every spectrum) to prevent determination of the centres of gravity of the individual lines. In view of this and the experimental uncertainties involved because of the weak signals found for $BaCl_2 . 2H_2O$, the agreement between the observed *p–p* vectors and the neutron diffraction results is surprisingly good.

It is obvious from Fig. 1 that the present NMR results can be reconciled with the results obtained by Silvidi & McGrath provided that their *p–p* vectors are rotated about the *b* axis. The crystal edges parallel to [101] and [$\bar{1}$01] must have been mistakenly identified by Silvidi & McGrath as the *a* and *c* axes. If this view is accepted then a simple transformation produces the displacement of vectors pointed out in Fig. 1. Whether they considered [101] to be *a* or *c* is irrelevant since they obtained similar results from both rotations.

The structure proposed by Silvidi & McGrath is unacceptable on stereochemical grounds. Each of their arrangements *A*, *B*, *C* and *D* has one hydrogen atom in a position which is rather close to the two nearest Ba^{2+} neighbors; this position in the case of arrangement *A*, for instance, is at 2·5 Å from Cl^- and at 2·8 and 2·4 Å from the two Ba^{2+} ions. This is in contrast with the more reasonable neutron diffraction structure where the important factor which determines the hydrogen positions is reported to be the prox-

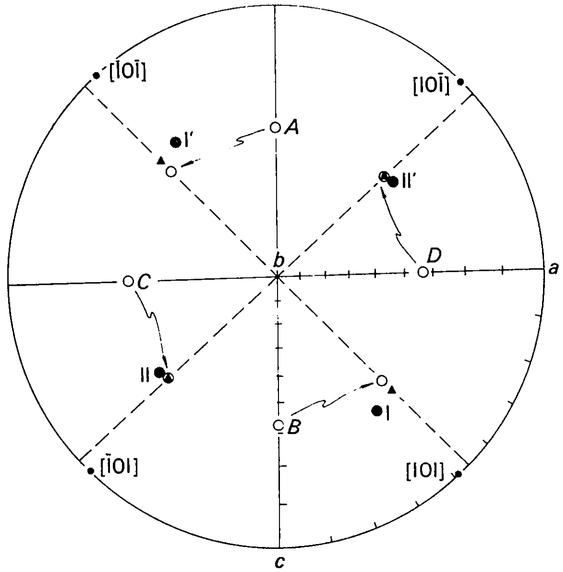

Fig. 1. A stereographic projection showing the *p–p* directions obtained from (*a*) the neutron diffraction structure represented by filled circles, (*b*) the present NMR investigation represented by filled triangles, (*c*) Silvidi & McGrath's NMR results represented by open circles (*A*, *B*, *C* and *D*) and (*d*) the transformation of these vectors on the assumption that the [101] and [$\bar{1}$01] directions are mistakenly identified as the *c* and *a* axes, respectively.

Table 1. *The directions and magnitudes of the p–p vectors obtained from the neutron diffraction structure, the NMR results of Silvidi & McGrath and the present NMR investigation*

	Neutron diffraction structure		NMR results of Silvidi & McGrath		Present NMR results	
	I, I′	II, II′	*A*, *B*	*C*, *D*	I, I′	II, II′
α_0	±58·7°	±47·2°	±90°	±32°	±53°	∓50°
β_0	63·3°	58·8°	50°	58°	63°	58°
γ_0	±44·1°	±58·0°	±32°	±90°	±49°	±56°
r	1·496 Å	1·548 Å	1·58 Å	1·58 Å	1·58 Å	1·57 Å

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imity of two Ba^{2+} ions to each water. The two Ba^{2+} ions and two H atoms are arranged approximately tetrahedrally about oxygen.

It must be understood that in investigating complicated hydrates, the NMR method is rather crude and inhibited with inaccuracies arising from (*a*) the difficulty encountered in determining the exact orientation of the axis of rotation of the crystal in the magnetic field, (*b*) the low signal-to-noise ratio observed in most diamagnetic substances which are the ones generally investigated, and (*c*) overlap of the resonance lines that makes it difficult to determine the positions of maximum absorption of these lines. The experimental uncertainties involved make it pointless to try and apply corrections for the effect of thermal vibrations on the resonance spectra (Pedersen, 1964), or worry about whether the centres of gravity of the lines or the positions of maximum absorption are used to plot the resonance diagram. However, for a quick determination of the approximate positions of hydrogen atoms in many and often complicated hydrates, the NMR method remains of great value (*cf.* Murty & El Saffar, 1962).

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Ein doppelt gekrümmter Neutronenleiter zur Unterdrückung der höheren Ordnung bei Neutronenbeugungsexperimenten.

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Ein Aufbau von Neutronendiffraktrometern am Ende von langen Neutronenleitern würde verschiedene Vorteile mit sich bringen (Maier-Leibnitz, 1966). Der Untergrund am Ausgang eines gekrümmten Neutronenleiters (Maier-Leibnitz & Springer, 1963) ist sehr viel kleiner als für Instrumente in unmittelbarer Reaktornähe. Es entfällt die schwere Abschirmung. Die Instrumente werden flexibler, die Platzverhältnisse günstiger und der Streuwinkelbereich kann bis zu 180° ausgedehnt werden. Wie hier gezeigt wird, lässt sich durch eine geeignete Ausführung des Neutronenleiters zudem noch erreichen, dass die zweite Ordnung vollständig unterdrückt wird.

Bei einem geraden Neutronenleiter (mit z als Achse) gilt für den Oeffnungswinkel α des austretenden Neutronenstrahls $\alpha = 2\Delta k/k_z$, wobei $k_z = 2\pi/\lambda$ und $\Delta k = 1{,}07 \times 10^{-2}$ Å^{-1}, wenn man Nickel als totalreflektierndes Wandmaterial verwendet. Abgesehen von Reflexionsverlusten und anderen Baufehlern des Neutronenleiters ist die Durchlässigkeit D unabhängig von der Wellenlänge konstant gleich eins. Ein einfach gekrümmter Neutronenleiter mit rechteckigem Querschnitt hat die Eigenschaft nach kleineren Wellenlängen hin immer weniger durchlässig zu werden (Maier-Leibnitz & Springer, 1963). In Fig. 1 ist die über den Querschnitt gemittelte Durchlässigkeit D als Funktion der Wellenzahl k_z aufgetragen. Die charakteristische Wellenzahl $k_{z,m}$ ist nach Maier-Leibnitz (1965) durch den Krümmungsradius ϱ und die Breite a des Neutronenleiters gegeben gemäss der Beziehung:

$$k_{z,m} = \Delta k \sqrt{\varrho/2a}$$

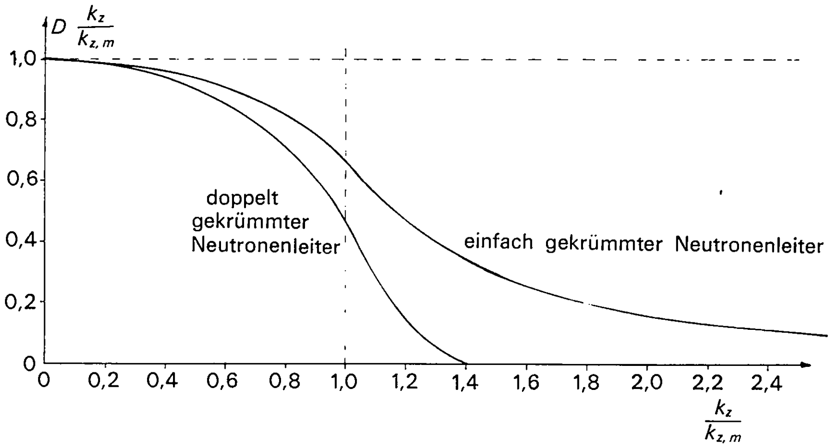

Fig. 1.