Essigsäurelösung bis zur Entfärbung titriert. Darauf gibt man 70 ml einer 0,5-*n*. methanolischen Jodlösung (Zusatz von 5 g KJ pro 100 ml) zu; man rührt weitere 10 Stdn. bei −40 °C und noch 2 Stdn. bei Zimmertemperatur. Das überschüssige Jod wird mit Natriumthiosulfat zurücktitriert. Die Lösung wird mit Natriumbicarbonat versetzt und dreimal mit Wasser gewaschen. Die ätherische Phase wird über Natriumsulfat getrocknet und eingedampft. Der Rückstand wird mit 200 ml Petroläther (Sdp. 50−70 °C) aufgekocht. Beim Abkühlen fallen 3 g 4-Benzoyl-triphenylcarbinol aus. Die Mutterlauge enthält im wesentlichen Benzophenon. Das 4-Benzoyl-triphenylcarbinol hat nach nochmaligem Umkristallisieren aus Petroläther einen Schmelzpunkt von 120−121 °C (Lit.: 125 °C [14], 116 °C [15]). Es gibt mit dem nach WITTIG und HOPF [14] dargestellten Präparat keine Schmelzpunktsdepression und wurde durch IR-, NMR- und Massenspektroskopie identifiziert.

2. *UV-Spektren von 4-Benzoyl-triphenylcarbinol und 1.1′-Diphenylglykol*

Das Spektrum von 4-Benzoyl-triphenylcarbinol verläuft ähnlich wie dasjenige von Benzophenon;

Maximum der Vorbande:	$\lambda = 329$ nm,	$\varepsilon = 267$,
Maximum der Hauptbande:	$\lambda = 260$ nm,	$\varepsilon = 26300$.

Das UV-Spektrum von 1.1′-Diphenylglykol gleicht dem des Benzpinakols, es ist etwas nach kürzeren Wellenlängen verschoben.

	[nm]	
Extinktionsmaxima:	$\lambda = 264$,	$\varepsilon = 320$
	$\lambda = 258$,	$\varepsilon = 420$
	$\lambda = 252$,	$\varepsilon = 375$
Schultern:	$\lambda = 280$,	$\varepsilon = 200$
	$\lambda = 247$,	$\varepsilon = 310$.

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[14] G. WITTIG u. W. HOPF, Chem. Ber. **65**, 766 [1932].
[15] M. DELACRE, Bull. Soc. chim. belges (4), **5**, 958 [1909].

Interpretation of the Ligand Field Spectra of Nickel (II) Octahedral complexes *

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Although the ligand field theory of cubic fields for all d^n, $n = 1$ to 9, electronic configurations is well-known [1], application of the theory to experimental situations does not seem to be completely clear. By considering the case of the d^8 electronic configuration encompassed by fields of octahedral symmetry as an example, we shall show here how the theory can be applied for the fitting of experimental data. Let us, for the present, confine our attention to the triplet states of the d^8 configuration, and thus consider only the spin-allowed transitions in the spectra of the corresponding octahedral systems. The theory needed for this purpose will be sketched briefly.

According to the principle of the hole formalism, both the d^8 and d^2 configurations give rise to the same RUSSELL-SAUNDERS terms of which ^3F and ^3P are of highest spin-multiplicity [2]. When perturbed

* Portions of this material were included in a paper presented by the author at the 50th Canadian Chemical Conference and Exhibition of The Chemical Institute of Canada, Royal York Hotel, Toronto, Canada, June 4–7, 1967.

[1] See for instance (a) C. J. BALLHAUSEN, "Introduction to Ligand Field Theory", McGraw-Hill Book Company, Inc., New York, N. Y., 1962. (b) J. S. GRIFFITH, "The Theory of Transition-Metal Ions", The University Press, Cambridge, England, 1961. (c) C. K. JØRGENSEN, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1962.

[2] E. U. CONDON and G. H. SHORTLEY, "The Theory of Atomic Spectra", Cambridge University Press, Cambridge, Cambridge and New York 1957.

by cubic ligand fields, V_C, these terms give rise to the states $^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}$, and $^3T_{1g}$, respectively, of which $^3A_{2g}$ is the ground state for the d^8 octahedral system. The energies of these states are given by:

$$\begin{aligned} {}^3A_{2g}({}^3F) &= -8B - 12Dq \\ {}^3T_{2g}({}^3F) &= -8B - 2Dq \\ {}^3T_{1g}({}^3F) &= -8B + 6Dq \\ {}^3T_{1g}({}^3P) &= +7B \\ \langle {}^3T_{1g}({}^3F) | V_C | {}^3T_{1g}({}^3P) \rangle &= 4Dq \end{aligned} \quad (1)$$

where Dq and B are the cubic ligand field and the Racah electron correlation parameters, respectively. If the off-diagonal element of equation (1) is neglected, the transition energies in the weak-field scheme are [3]:

$$\begin{aligned} {}^3A_{2g}({}^3F) &\rightarrow {}^3T_{2g}({}^3F) = 10Dq \\ {}^3A_{2g}({}^3F) &\rightarrow {}^3T_{1g}({}^3F) = 18Dq \\ {}^3A_{2g}({}^3F) &\rightarrow {}^3T_{1g}({}^3P) = 12Dq + 15B\,. \end{aligned} \quad (2)$$

The exact energy equations including configuration interaction between the two $^3T_{1g}$ states are as follows:

$$\begin{aligned} {}^3A_{2g}({}^3F) &\rightarrow {}^3T_{2g}({}^3F) = 10Dq \\ {}^3A_{2g}({}^3F) &\rightarrow {}^3T_{1g} = 1/2\,\{(15B + 30Dq) \\ &\quad - [(15B - 10Dq)^2 \\ &\quad + 12B(10Dq)]^{1/2}\} \\ {}^3A_{2g}({}^3F) &\rightarrow {}^3T_{1g} = 1/2\,\{(15B + 30Dq) \\ &\quad + [(15B - 10Dq)^2 \\ &\quad + 12B(10Dq)]^{1/2}\} \end{aligned} \quad (3\,a)$$

When full configuration interaction is included, the $^3T_{1g}$ eigenfunctions will be mixtures of both $^3T_{1g}(^3F)$ and $^3T_{1g}(^3P)$ eigenvectors and, hence, the RUSSELL-SAUNDERS labels are not further specified for the $^3T_{1g}$ excited states in equation (3 a).

The exact transition energies of equation (3 a) can also be derived starting from the strong-field coupling scheme, thus demonstrating the confluence of the two descriptive processes. In the strong-field scheme, the ground configuration $(t_{2g}^6 e_g^2)$ gives rise to the ground state $^3A_{2g}$ and the excited configurations $(t_{2g}^5 e_g^3)$ and $(t_{2g}^4 e_g^4)$ to the excited states $^3T_{2g}$, $^3T_{1g}$, and $^3T_{1g}$, respectively. The energies of these states are [4]:

$$\begin{aligned} {}^3A_{2g}(t_{2g}^6 e_g^2) &= -12Dq - 8B \\ {}^3T_{2g}(t_{2g}^5 e_g^3) &= -2Dq - 8B \\ {}^3T_{1g}(t_{2g}^5 e_g^3) &= -2Dq + 4B \\ {}^3T_{1g}(t_{2g}^4 e_g^4) &= +8Dq - 5B \\ \langle {}^3T_{1g}(t_{2g}^5 e_g^3) | \Sigma e^2/r_{ij} | {}^3T_{1g}(t_{2g}^4 e_g^4) \rangle &= 6B \end{aligned} \quad (4)$$

where $\Sigma e^2/r_{ij}$ is the electron correlative perturbation. As before, if configuration interaction between the two $^3T_{1g}$ states is neglected, the energies of the spin-allowed transitions will be given by:

$$\begin{aligned} {}^3A_{2g}(t_{2g}^6 e_g^2) &\rightarrow {}^3T_{2g}(t_{2g}^5 e_g^3) = 10Dq \\ {}^3A_{2g}(t_{2g}^6 e_g^2) &\rightarrow {}^3T_{1g}(t_{2g}^5 e_g^3) = 10Dq + 12B \\ {}^3A_{2g}(t_{2g}^6 e_g^2) &\rightarrow {}^3T_{1g}(t_{2g}^4 e_g^4) = 20Dq + 3B\,. \end{aligned} \quad (5)$$

When configuration interaction is taken into account, the above equations will be modified as follows:

$$\begin{aligned} {}^3A_{2g}(t_{2g}^6 e_g^2) &\rightarrow {}^3T_{2g}(t_{2g}^5 e_g^3) = 10Dq \\ {}^3A_{2g}(t_{2g}^6 e_g^2) &\rightarrow {}^3T_{1g} = 1/2\,\{(15B + 30Dq) \\ &\quad - [(15B - 10Dq)^2 \\ &\quad + 12B(10Dq)]^{1/2}\} \\ {}^3A_{2g}(t_{2g}^6 e_g^2) &\rightarrow {}^3T_{1g} = 1/2\,\{(15B + 30Dq) \\ &\quad + [(15B - 10Dq)^2 \\ &\quad + 12B(10Dq)]^{1/2}\}. \end{aligned} \quad (3\,b)$$

The configurations of the two excited states, $^3T_{1g}$, are not included in equation (3 b), as these eigenfunctions are now admixtures of both the $^3T_{1g}(t_{2g}^5 e_g^3)$ and $^3T_{1g}(t_{2g}^4 e_g^4)$ eigenvectors. Since the weak-field and strong-field sets of basis functions are connected by unitary transformations, calculations carried to completion must yield identical results in both the schemes. Therefore, the energy values given in equations (3 a) and (3 b) turn out to be the same. The appropriate transformation matrices which can be derived are as follows [5]:

	$^3A_{2g}(t_{2g}^6 e_g^2)$	$^3T_{2g}(t_{2g}^5 e_g^3)$	$^3T_{1g}(t_{2g}^5 e_g^3)$	$^3T_{1g}(t_{2g}^4 e_g^4)$
$^3A_{2g}(^3F)$	$+i$			
$^3T_{2g}(^3F)$		$+i$		
$^3T_{1g}(^3F)$			$+i\sqrt{1/5}$	$+i\sqrt{4/5}$
$^3T_{1g}(^3P)$			$+i\sqrt{4/5}$	$-i\sqrt{1/5}$

[3] (a) C. J. BALLHAUSEN, Kgl. Danske Videnskab-Selskab, Mat.-fys. Medd. **29**, nr 8 [1955], (b) L. E. ORGEL, J. chem. Physics **23**, 1004 [1955].

[4] (a) Y. TANABE and S. SUGANO, J. physic. Soc. Japan **9**, 753 [1954]; (b) **9**, 766 [1954].

[5] The derivation and significance of such unitary transformation matrices can be found in a paper soon to be published by the author. See also (a) A. D. LIEHR and C. J. BALLHAUSEN, Ann. Physics **6**, 134 [1959].

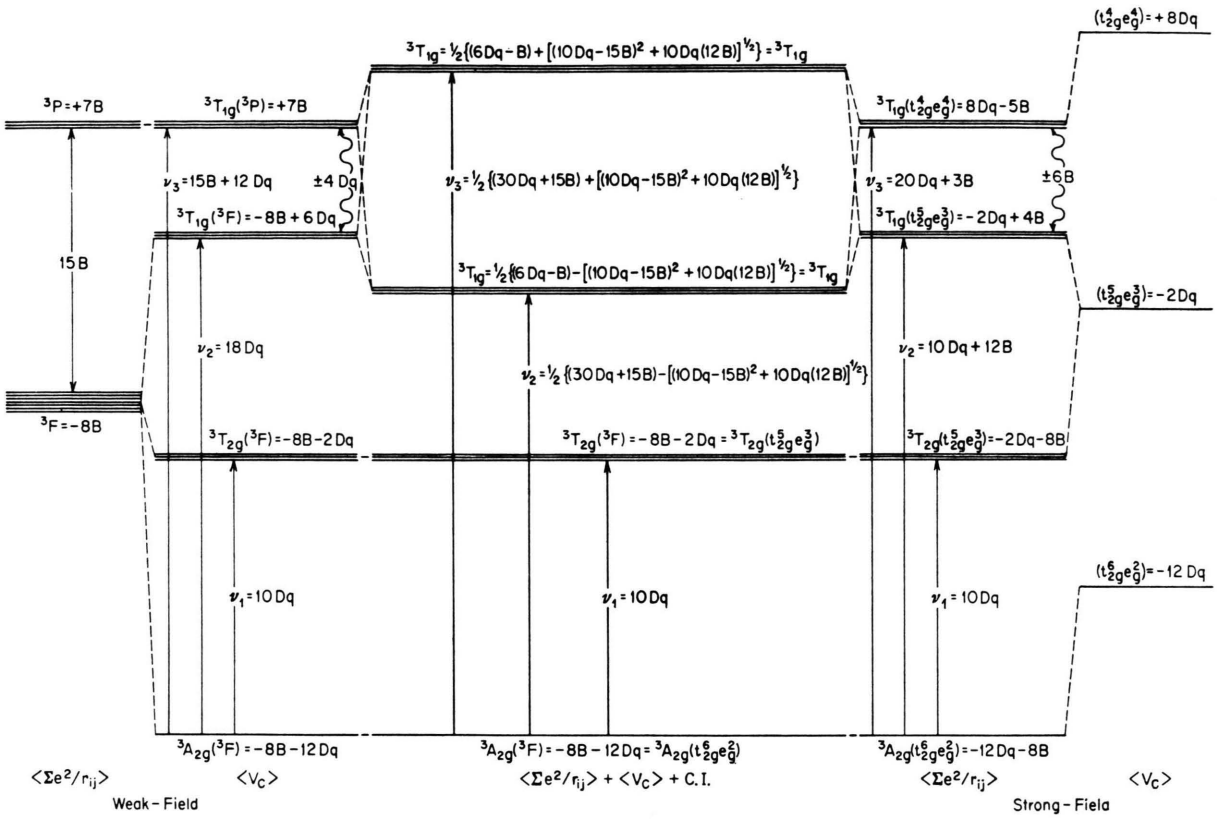

Fig. 1. Schematic energy level diagram for d^8 configuration in octahedral fields.

In Fig. 1 are shown a schematic representation of the energy levels for the d^8 configuration in octahedral fields in both the weak-field and strong-field schemes and also the effects of configuration interaction in both these schemes. Since the $^3T_{2g}$ is the only state of this symmetry designation, it should be noted that the transition energy $^3A_{2g} \rightarrow {}^3T_{2g}$ is not subject to perturbation by the other states [6]. It is the two $^3T_{1g}$ states that are perturbed by each other by configuration interaction [7]. We now present a procedure based on equation (3) for the fitting of experimental data.

Fitting of the Experimental Data

As shown above, three spin-allowed transitions are expected in the spectra of octahedral complexes of nickel (II) [8]. The transition energies of the three predicted bands given by equation (3) contain two parameters Dq and B. A value for B can be obtained from the free-ion spectrum. However, the B value of a complex has been found to be usually less than that of the corresponding free-ion [9], so we shall treat B as an unknown parameter in addition to Dq. The value of Dq is given by the lowest energy spin-alowed band (ν_1). The B value can then be evalu-

[6] For spin-orbit perturbation effects, read ref. [5(a)].

[7] Based on the assumption that the $^3T_{2g}$ state is perturbed by the higher energy states, some "modified" equations and a procedure for fitting experimental data have been suggested by (a) V. S. Sharma, H. B. Mathur, and A. B. Biswas, Indian J. Chem. **2**, 5 [1964]. These habe been copied and employed without comment by (b) G. N. Rao and N. C. Li, Can. J. Chem. **44**, 1637 [1966]. Since this assumption is improper, the equations and procedure based on it are of no significance.

[8] The visible spectra of octahedral nickel (II) complexes show actually four bands, fourth one around 12000—13000 cm^{-1} as a low intensity absorption tailing the second spin-allowed band. This low intense band has been attributed to either a spin-orbit component of the second triplet transition or to the spin-forbidden ^1E_g transition. A discussion of these alternate assignments can be found in reference (5a) and also (a) C. K. Jørgensen, Acta chem. scand. **9**, 1362 [1955].

[9] C. K. Jørgensen, Acta chem. scand. **10**, 887 [1956].

ated either by fitting the second spin-allowed band (ν_2) or by fitting the highest energy spin-allowed band (ν_3). In either case, by fitting one of the two bands, the frequency of the other band can then be calculated using the derived values of Dq and B and compared with the observed value. Here it may be pointed out that as the observed absorption bands in the solution spectra are usually broad and do not exhibit sharp maxima, the error involved in the estimation of the absorption maxima of both the second and the third bands may be of comparable magnitude. As there is no reason why the estimation of the frequency maximum of one of them is more exact than that of the other, we may fit both the bands allowing a reasonable error by varying the B value. In place of the "trial and error" method, a simpler approach would be to derive the B value by two independent means, one by adding the frequency maxima of the two high energy spin-allowed transitions, or alternatively by taking their difference. The actual B value of the complex would, of course, be in the range of these two values. Formulae for the evaluation of the B value are given below [10]:

$$B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1) \quad \text{(fitting the second band)},$$

$$B = (2\nu_1^2 + \nu_3^2 - 3\nu_1\nu_3)/(15\nu_3 - 27\nu_1) \quad \text{(fitting the third band)},$$

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15 \quad \text{(fitting the sum of the second and the third band maxima)},$$

$$B = 1/75\ \{3\nu_1 + [25(\nu_3 - \nu_2)^2 - 16\nu_1^2]^{1/2}\} \quad \text{(fitting the difference of the third and the second band maxima)}. \qquad (6)$$

By the use of these four equations, we have calculated the B values for a few typical octahedral complexes of nickel (II) listed in reference 1c. These are given in Table I where the observed and the calculated frequency maxima are also included [11]. If the B value obtained by fitting the second band is used, the agreement between the observed and the calculated values of the third band maximum is not good. On the other hand, the B value obtained by fitting the third band gives very good agreement between the observed and the calculated energy of the second band maximum. The B values obtained by fitting

Complex	ν_1, cm^{-1} $^3A_{2g} \rightarrow {}^3T_{2g}$	ν_2, cm^{-1} $^3A_{2g} \rightarrow {}^3T_{1g}$	ν_3, cm^{-1} $^3A_{2g} \rightarrow {}^3T_{1g}$	B, cm^{-1}	$\frac{B_{complex}}{B_{free-ion}} \times 100$
$Ni(H_2O)_6^{2\oplus}$	8500	13500	25300	Observed	
	Fitted	Fitted	21722	648.1	62.2
	Fitted	14144	Fitted	929.6	89.2
	Fitted	14074	24727	886.7	85.1
	Fitted	14222	26022	982.9	94.3
$Ni(NH_3)_6^{2\oplus}$	10750	17500	28200	Observed	
	Fitted	Fitted	29344	972.9	93.4
	Fitted	17261	Fitted	880.7	84.5
	Fitted	17306	28395	896.7	86.1
	Fitted	17183	27883	854.4	82.0
$Ni(en)_3^{2\oplus}$	11200	18350	29000	Observed	
	Fitted	Fitted	32249	1066.6	102.4
	Fitted	17890	Fitted	886.0	85.0
	Fitted	17981	29370	916.7	88.0
	Fitted	17714	28364	831.8	79.8
$Ni(gly)_3^{\ominus}$	10100	16600	27600	Observed	
	Fitted	Fitted	28510	987.3	94.8
	Fitted	16448	Fitted	916.5	88.0
	Fitted	16471	27730	926.7	88.9
	Fitted	16412	27412	901.6	86.5

Table I. Observed and Calculated Frequency Maxima of the Spectra of Some Octahedral Complexes of Nickel (II).

[10] These equations as well as the entire discussion of this section are also applicable to the d^3 configuration in O_h, if the triple spin-degeneracy of the states is replaced by quadruple spin-degeneracy.

[11] The free-ion B value used in Table I is 1042 cm^{-1} taken from (a) A. D. Liehr, J. physic. Chem. **67**, 1314 [1963]. The B value of 1042 cm^{-1} has been obtained by fitting all the individual J levels of the free-ion terms as exact as possible. Such a fitting depends also on the spin-orbit interaction parameter, ζ, and modifies the B value somewhat from that obtained by a simple fitting of the baricenter energies of ^3F and ^3P. According to the latter procedure, 15 B equals 17,000 cm^{-1} and $B = 1133.3$ cm^{-1}.

the sum as well as the difference of the second and the third band maxima usually are nearer to the B value derived by fitting the third band maximum and also give rise to good agreement between the observed and the calculated energies of the second and the third band maxima [12].

[12] Note that the B values derived by different ways differ much from each other, particularly the first two procedures where the positions of the second and the third spin-allowed transitions are used directly in turn. (This is true not only in the case of the complexes quoted in the Table but in forty other octahedral complexes of nickel (II) for which such a fitting has been made. These are not listed here because of space limitations.) In some systems all of the three bands are not uncovered. For instance, most of the chromium (III) octahedral complexes show only two spin-allowed bands and the third is usually buried under intense higher energy charge transfer absorption. This means that no independent check is available on the B values obtained in these systems. So, one has to be cautious in the discussion of covalency (such as nephelauxetic effect) if it has to be based on the derived B value of the complex and its reduction from the free-ion B value in such cases.

Untersuchungen der kernmagnetischen Resonanz von Phosphorverbindungen, XVII

^{31}P- und ^{1}H-Kernresonanzuntersuchungen an Trimethylsilylphosphinen. Isotopeneffekt in der ^{31}P-Kernresonanzspektroskopie

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Die kernmagnetischen ^{31}P- und ^{1}H-Resonanzspektren der primären, sekundären und tertiären Trimethylsilylphosphine und ihrer am Phosphor deuterierten Analoga werden beschrieben und diskutiert. Die deuterierten Verbindungen zeigen eine Isotopenverschiebung der ^{31}P-Resonanzlinien.

Nach den bisherigen Erfahrungen lassen sich die chemischen Verschiebungen von Verbindungen, in denen Phosphor die Koordinationszahl 3 hat, durch Addition von Inkrementen [1] oder unter Verwendung sog. σ^{P}-Werte nach bestimmten Gleichungen [2] in guter Annäherung an die beobachteten Werte berechnen. Ein abweichendes Verhalten zeigten bisher im wesentlichen nur fluorhaltige Phosphor(III)-Verbindungen [3]. Nach dem Ergebnis neuer Untersuchungen an Organozinn- und Organogermanium-Verbindungen [4] sowie an den hier behandelten Trimethylsilylphosphinen machen jedoch auch diese Verbindungsklassen eine Ausnahme. Offensichtlich können den Liganden in der Reihe der Stannylphosphine $[(C_6H_5)_3Sn]_3P$ (δ = 323 ppm), $[(C_6H_5)_3Sn]_2P(C_6H_5)$ (δ = 163 ppm) und $[(C_6H_5)_3Sn]P(C_6H_5)_2$ (δ = 56 ppm), die von ENGELHARDT et al. [4] vermessen wurden, keine konstanten Inkremente mehr zugeordnet werden.

In den Trimethylsilylphosphinen tritt dieser Effekt allerdings weniger deutlich zutage, da sich $[(CH_3)_3Si]_3P$ und PH_3, die Endglieder der homologen Reihe, in ihren chemischen Verschiebungen nur um etwa 10 ppm unterscheiden. Die chemischen Verschiebungen δ^{31}_{P} und die Kopplungskonstanten J_{HP} dieser Trimethylsilylphosphine sind in Tab. 1

[1] E. FLUCK, Die kernmagnetische Resonanz und ihre Anwendung in der anorganischen Chemie, Springer-Verlag, Heidelberg 1963, S. 171 ff; E. FLUCK, Z. Naturforschg. **19 b**, 869 [1964]; Chem. Ber. **98**, 2674 [1965].

[2] E. FLUCK u. J. LORENZ, Z. Naturforschg., im Druck; S. O. GRIM u. W. MCFARLANE, Nature [London] **208**, 995 [1965]; S. O. GRIM, W. MCFARLANE, E. F. DAVIDOFF u. T. J. MARKS, J. physic. Chem. **70**, 581 [1966]; L. MAIER, Helv. chim. Acta **49**, 1718 [1966].

[3] J. R. VAN WAZER, C. F. CALLIS, J. N. SHOOLERY u. R. C. JONES, J. Amer. chem. Soc. **78**, 5715 [1956]; E. FLUCK, Z. Naturforschg. **19 b**, 869 [1964].

[4] G. ENGELHARDT, P. REICH u. H. SCHUMANN, Z. Naturforschg., im Druck; wir danken den Autoren für die Überlassung des Manuskriptes dieser Arbeit.