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The Effect of Configuration Interaction on Atomic Scattering Factors for Transition Metals

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Abstract

Spin-only magnetic form factors and X-ray form factors for Mn, Mn^+, Co, Co^{2+}, Ni and Ni^{2+} are calculated using configuration interaction wavefunctions. The magnetic form factors for Co^{2+} are used in the analysis of polarized neutron diffraction data for Cs_3CoCl_5, to give spin populations. The inclusion of correlation functions in the wavefunction leads to changes in Hartree–Fock form factors of transition metal atoms, which maximize at $K/4\pi \sim 0{\cdot}4$ Å^{-1}, where they amount to approximately 5% of the form factor at that value of K.

Introduction

Scattering form factors for atoms and their individual orbitals calculated from Hartree–Fock (HF) level atomic wavefunctions are available for most of the elements. These provide an adequate representation of the scattering by an atom for modelling procedures employed in the analysis of experimental data for structure determination in the case of both X-ray and magnetic neutron diffraction. However, for more sensitive analysis of the experimental data in terms of the scattering density, that is the charge and spin densities, and in terms of the orbital populations, it is possible that correlation effects could sufficiently modify the atomic wavefunctions to lead to some inaccuracy in the deductions made from the experimental information.

This paper presents spin-only magnetic form factors for Mn, Mn^+, Co, Co^{2+}, Ni, Ni^{2+} evaluated using configuration interaction (CI) wavefunctions. X-ray form factors have also been calculated. These results are of immediate interest to our programme of spin and charge density analysis in transition-metal complexes, and it is hoped the set will give transition series in general. The effect of using the CI scattering curves for the analysis of the polarized neutron diffraction data for the case of $CoCl_4^{2-}$ is investigated.

Method of calculation

Radial functions

The radial functions used in the calculations are determined in an **LS** coupled representation of the atomic state. The atomic-state wave-functions are represented by the configuration interaction expansion

$$\Psi(\mathbf{LS}) = \sum_{i=1}^{N} a_i \Phi_i(\alpha_i\text{: LS}), \qquad (1)$$

where N is the total number of configurations, $\{\alpha_i\}$ specifies the angular momentum coupling scheme of the ith configuration and **L** and **S** are the total orbital and spin angular momenta. The configurational wavefunctions $\{\Phi_i\}$ are constructed from the one-electron functions (spin orbitals):

$$u(\mathbf{r}, m_s) = \frac{1}{r} P_{nl}(r) Y_l^{m_l}(\theta, \varphi) \chi(m_s). \qquad (2)$$

The radial functions are expanded in terms of Slater-type orbitals:

$$P_{nl}(r) = \sum_{j=1}^{k} C_{jnl} \phi_{jnl}(r), \qquad (3)$$

where

$$\phi_{jnl}(r) = \left(\frac{(2\zeta_{jnl})^{(2I_{jnl}+1)}}{(2I_{jnl})!} \right)^{1/2} r^{I_{jnl}} \exp(-\zeta_{jnl} r) \qquad (4)$$

and $k \geq n - l$. We also require the radial functions for a given value of l to form an orthogonal set:

$$\int_0^\infty P_{nl}(r) P_{n'l}(r)\, \mathrm{d}r = \delta_{nn'}, \qquad (l+1) \leq n' \leq n. \quad (5)$$

The coefficients $\{a_i\}$ in (1) are, for a given set of $\{\Phi_i\}$, the components of the appropriate eigenvector of the Hamiltonian matrix whose typical element is

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle. \qquad (6)$$

The corresponding eigenvalues $\{E\}$ form upper bounds to the corresponding exact energies $\{E_{\text{exact}}\}$ of the same symmetry. Because of the upper-bound property, any of the eigenvalues may be treated as variational functions to be minimized with respect to $\{\zeta_{jnl}\}$ and those coefficients $\{C_{jnl}\}$ of (3) not determined by the orthonormality conditions, *provided* configurations corresponding to lower states are included in the calculation.

The $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ and $4s$ restricted Hartree–Fock radial functions were taken from the $1s^22s^22p^63p^63d^n4s^m$ ($m = 0$, 1, 2) ground states (Clementi & Roetti, 1974). Additional correlation radial functions were calculated. For the neutral

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atoms a $4p$ correlation function was determined to describe the important $4s^2 \rightarrow 4p^2$ correlation function effect. $4d$ and $4f$ functions were determined to describe the $3d^2 \rightarrow 4l^2$ correlation (including the important $4p^2$ configurations in the optimization).

In obtaining the correlation functions we have chosen

$$k = n - l \tag{7}$$

so that the coefficients $\{C_{jnl}\}$ are determined uniquely by (5). We also choose

$$I_{jnl} = l + j, \qquad j \geq 1 \tag{8}$$

in (4), so that the freely varying parameters are the exponents $\{\zeta_{jnl}\}$. We used *CIV*3 (Hibbert, 1975; Glass & Hibbert, 1978) in the LS-coupling mode to determine the radial functions.

The atomic form factor

The quantity of interest in the scattering experiment is the free-ion form factor corresponding to the Fourier transform of the scattering density (Steinsvoll, Shirane, Nathans, Blume, Alperin & Pickert, 1967; Halpern & Johnson, 1939) for the respective scattering interactions. For the neutron case, we neglect the orbital magnetization density and consider only the spin magnetization density. The orbital component will be considered in a later publication, as a crystal-field form factor. We note that for neutrons there is also an interaction due to the short-range nuclear force. That is not considered here.

The respective form factors (Halpern & Johnson, 1939) are:

$$\langle \Psi(\mathbf{LS}) | \sum_j \exp(i\mathbf{K}.\mathbf{r}_j) | \Psi(\mathbf{LS}) \rangle \tag{9}$$

for the X-ray form factor and

$$\frac{\langle \Psi(\mathbf{LS}) | \sum_j \mathbf{s}_{z_j} \exp(i\mathbf{K}.\mathbf{r}_j) | \Psi(\mathbf{LS}) \rangle}{\langle \Psi(\mathbf{LS}) | \sum_j \mathbf{s}_{z_j} | \Psi(\mathbf{LS}) \rangle} \tag{10}$$

for the spin-only magnetic form factor.

The sum is over *all* electrons in (9), whereas (10) is only summed over the *unpaired* electrons. $\mathbf{K}$ is the scattering vector, and we note that for free atoms the form factor is *spherical*, and so is only a function of

$$|\mathbf{K}| = K = 4\pi \sin\theta/\lambda, \tag{11}$$

where θ is the Bragg scattering angle, and λ is the wavelength of the incident particle. $\Psi(\mathbf{LS})$ is the CI wavefunction, and $\mathbf{s}_j$ is the spin operator for electron j. The spin-only magnetic form factor is normalized to 1 at $\mathbf{K} = 0$.

We note that the form-factor operators are sums of one-electron-type operators. Therefore, the single excitations not important energetically in the CI wavefunction will be important in the calculation of the form factor. These, along with the energetically important double excitations, were included in the final calculation.

Results and discussion

Using the radial functions determined in the previous section CI wavefunctions (1) were determined by including in the summation for each symmetry all possible configurations with a common argon core. Note three-electron and higher excitations were not included and for the two-electron excitations only configurations with coefficients $|a_i| > 0{\cdot}001$ were included. Using these CI wavefunctions and the program *CIVFAC* (Glass, 1984) we evaluated spin-only magnetic form factors and X-ray form factors.

The spin-only magnetic form factors for the respective transition-metal atoms are illustrated in Figs. 1 to 6, where f_{HF} and f_{CI} are the curves evaluated using the HF and CI wavefunctions, respectively, and

$$\Delta f(K) = f_{\mathrm{CI}}(K) - f_{\mathrm{HF}}(K), \tag{12}$$

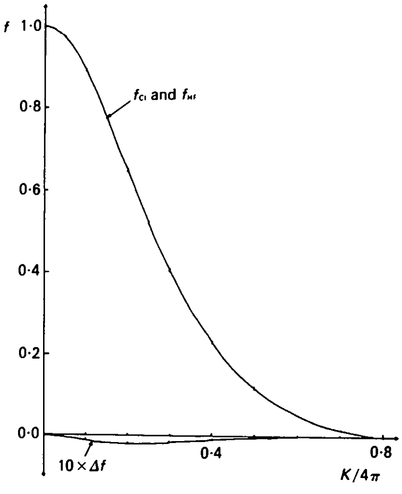

Fig. 1. Spin-only magnetic form factors for Mn.

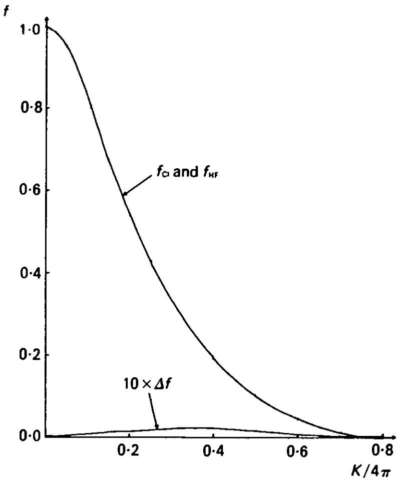

Fig. 2. Spin-only magnetic form factors for Mn^{2+}.

Table 1. *Spin-only magnetic form factors as a function of the scattering vector*

The amount by which the function differs from the HF form factor, Δf, is also given

$K/4\pi$	Mn		Mn^+		Co		Co^{2+}		Ni		Ni^{2+}	
($Å^{-1}$)	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$
0·00	1·0000	0·00	1·0000	0·00	1·0000	0·00	1·0000	0·00	1·0000	0·00	1·0000	0·00
0·05	0·9701	−0·34	0·9487	0·12	0·9764	0·65	0·9785	1·08	0·9790	0·97	0·9800	0·77
0·10	0·8880	−1·06	0·8230	0·46	0·9105	2·45	0·9178	3·98	0·9199	3·60	0·9234	2·86
0·15	0·7721	−1·65	0·6758	0·90	0·8150	4·90	0·8278	7·86	0·8332	7·10	0·8391	5·70
0·20	0·6429	−1·92	0·5413	1·36	0·7046	7·33	0·7213	11·71	0·7312	10·54	0·7385	8·60
0·25	0·5166	−1·88	0·4282	1·76	0·5919	9·21	0·6101	14·78	0·6248	13·20	0·6323	11·01
0·30	0·4031	−1·63	0·3348	2·03	0·4853	10·29	0·5032	16·62	0·5221	14·73	0·5289	12·60
0·40	0·2274	−0·94	0·1944	2·06	0·3073	10·21	0·3216	16·69	0·3450	14·63	0·3495	13·16
0·50	0·1159	−0·38	0·1025	1·58	0·1810	8·30	0·1910	13·64	0·2135	11·94	0·2164	11·26
0·60	0·0508	−0·07	0·0463	0·95	0·0980	5·87	0·1044	9·67	0·1231	8·52	0·1252	8·41
0·70	0·0154	0·07	0·0146	0·43	0·0465	3·70	0·0501	6·08	0·0643	5·43	0·0657	5·64
0·80	−0·0024	0·12	−0·0018	0·12	0·0162	2·03	0·0177	3·31	0·0278	3·04	0·0286	3·38
0·90	−0·0102	0·11	−0·0091	−0·01	−0·0007	0·88	−0·0043	1·41	0·0062	1·38	0·0066	1·72
1·10	−0·0126	0·06	−0·0109	0·03	−0·0127	−0·27	−0·0134	−0·44	−0·0114	−0·32	−0·0115	0·09

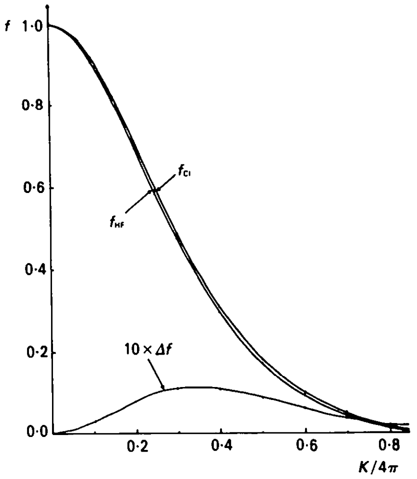

Fig. 3. Spin-only magnetic form factors for Co.

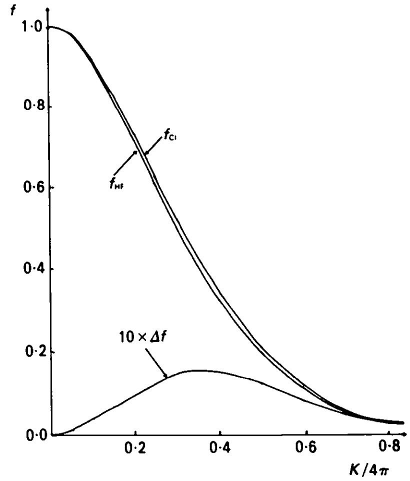

Fig. 5. Spin-only form factors for Ni.

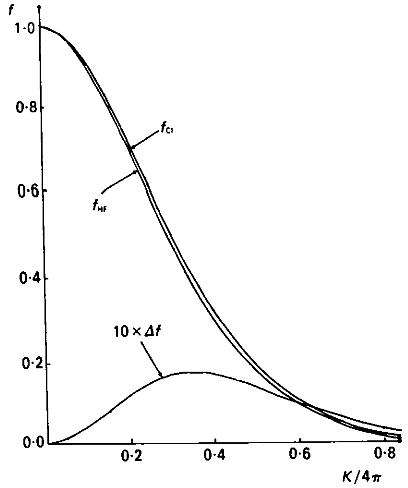

Fig. 4. Spin-only magnetic form factors for Co^{2+}.

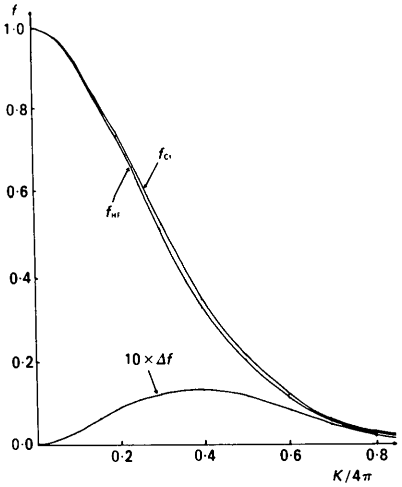

Fig. 6. Spin-only form factors for Ni^{2+}.

Table 2. *X-ray form factors as a function of the scattering vector*

The amount by which the function differs from HF form factor, Δf, is also given.

$K/4\pi$ (Å^{-1})	Mn		Mn^+		Co		Co^{2+}		Ni		Ni^{2+}	
	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$	f_{CI}	$10^3\Delta f$
0·00	25·000	0·00	24·000	0·00	27·000	0·00	25·000	0·00	28·000	0·00	26·000	0·00
0·05	24·267	−1·38	23·540	−1·00	26·321	−1·51	24·720	2·17	27·345	−2·47	25·721	−0·84
0·10	22·600	−6·84	22·344	−3·68	24·722	−6·81	23·917	8·07	25·780	−10·11	24·920	−3·05
0·15	20·769	−12·13	20·774	−7·08	22·879	−12·94	22·695	16·11	23·940	−19·51	23·698	−5·82
0·20	19·034	−12·30	19·094	−10·09	21·079	−15·41	21·189	24·41	22·118	−25·55	22·187	−8·26
0·25	17·390	−9·37	17·431	−11·86	19·354	−14·26	19·536	31·38	20·360	−27·07	20·521	−9·68
0·30	15·825	−6·57	15·839	−12·14	17·698	−11·77	17·852	36·11	18·664	−25·70	18·816	−9·84
0·40	13·021	−3·58	13·013	−9·48	14·669	−7·08	14·711	38·17	15·534	−19·69	15·601	−7·24
0·50	10·808	−1·85	10·801	−5·27	12·170	−3·49	12·133	32·93	12·905	−12·98	12·918	−3·32
0·60	9·206	−0·58	9·202	−1·79	10·264	−1·01	10·184	24·61	10·855	−7·42	10·851	−0·31
0·70	8·099	0·17	8·098	0·26	8·886	0·37	8·783	16·31	9·340	−3·57	9·334	1·28
0·80	7·333	0·50	7·333	1·04	7·913	0·94	7·800	9·49	8·252	−1·21	8·249	1·77
0·90	6·774	0·56	6·774	0·99	7·219	1·03	7·105	4·50	7·475	0·08	7·473	1·65
1·10	5·928	0·36	5·927	−0·07	6·280	0·67	6·190	−0·78	6·454	0·89	6·454	0·87

where $\Delta f(K)$ represents the change in the form factor through correlation effects. In Tables 1 and 2 we present our results for the spin-only magnetic form factors and the X-ray form factors, respectively, evaluated using CI wavefunctions.

The effect of CI on the HF spin-only magnetic form factor is small in every case, and only has a probability of being large enough to be significant in the analysis of neutron diffraction for the cases of Co, Co^{2+}, Ni and Ni^{2+}. Co^{2+} (Fig. 4) shows the largest effect, where there is a maximum change amounting to approximately 1·7% of $f(0)$, and to ~5% of $f(K)$ where this maximum occurs. In Ni (Fig. 5) correlation causes a change of 1·5% of $f(0)$ and over 4% of $f(K)$ at the maximum value. For Ni^{2+} (Fig. 6) corresponding changes are 1·3% of $f(0)$ and less than 4% of $f(K)$ at the maximum value. Both Mn and Mn^+ (Fig. 1 and 2) show very small corrections to the HF spin-only magnetic form factor; the changes being substantially less than 1% of $f(0)$ and of $f(K)$ at its maximum value. These changes in the Mn and Mn^+ magnetic form factors are not expected to be of importance in the evaluation of spin-only magnetic form factors.

Table 2 contains the X-ray form factors from the CI wavefunctions as a function of the scattering vector, and also the amount by which the function differs from the HF form factor. The relative change brought about by including correlation is roughly an order of magnitude smaller in the cases examined than occurs for the spin-only magnetic form factors. As with the spin-only magnetic form factors the largest corrections occur in Co^{2+} and Ni. All other cases, even Co and Ni^{2+}, show significantly smaller effects. One further interesting difference between the two sets of form factors is that for the X-ray scattering factor the CI corrections, except for Co^{2+}, indicate that expansion of the charge density occurs when the charge, not close to the nucleus, is being sampled. For the spin-only magnetic form factor the changes, except for Mn, indicate a contraction in the spin-only function.

Table 3. *Comparison of the spin populations in the* $CoCl_4^{2-}$ *ion deduced from the polarized neutron diffraction data employing* (i) *the HF form factors*; (ii) *the CI form factors for the* Co^{2+} *3d orbitals*

	Spin populations	HF	CI
Cobalt	$3d_{xy}$	0·86 (2)	0·85 (2)
	$3d_{xz}=3d_{yz}$	0·99 (3)	0·96 (2)
	$3d_{z^2}$	−0·20 (4)	−0·15 (4)
	$3d_{x^2}=3d_{y^2}$	0·00 (2)	0·02 (2)
	$4p_x=4p_y$	−0·11 (3)	−0·10 (3)
	$4p_z$	0·15 (5)	0·15 (5)
	$3d$–$4p$ mixing	1·62 (12)	1·60 (12)
Chlorine	$3(sp_x)_1$	0·049 (9)	0·049 (9)
	$3(sp_x)_2$	0·039 (5)	0·039 (5)
	$3p_y$	0·004 (7)	0·004 (7)
	$3p_z$	0·015 (4)	0·015 (4)
Radial parameters			
	χ^{3d-3d}(Co)	0·963 (5)	0·995 (5)
	$\chi^{3s(p)-3s(p)}$(Cl)	1·01 (3)	1·00 (3)

Note that χ^{3d-4p}(Co) was fixed at 1·000 owing to a high apparent correlation coefficient observed between this parameter and the $3d$–$4p$ spin population in the refining procedure with the CI form factor. This apparent change from HF results is thought to be due to the non-linear model and use of a linearly based refining procedure.

Application to $CoCl_4^{2-}$

An analysis of the polarized neutron diffraction results for the $CoCl_4^{2-}$ ion in Cs_3CoCl_5 in terms of spin populations in the various valence orbitals of the cobalt and chlorine atoms has been carried out previously (Figgis, Reynolds, Williams, Mason, Smith & Varghese, 1980; Figgis, Reynolds & Williams, 1980). The analysis was repeated in this work using the CI form factors for the Co^{2+} ion. The results of the two analyses are compared in Table 3. Parameters and axes are defined as previously (Chandler, Figgis, Phillips, Reynolds, Mason & Williams, 1982). It is seen that the corrected curves alter the spin populations by amounts which are small compared with the experimental errors quoted in Table 3. Interestingly, the radial parameter χ^{3d-3d} moves much closer to the free-ion value of unity. This parameter was introduced (Figgis, Reynolds & Williams, 1980) to allow sufficient radial flexibility in the form factor when moving from the free ion to the molecule. However, these results indicate that the expansion of the form factor in reciprocal space, owing to the inclusion of correlation effects, corresponding to a contraction of the orbitals in real space, has virtually eliminated the need for the radial parameter χ^{3d-3d}. Thus it seems the radial parameter was, in this case, accounting for small inadequacies owing to the use of free-ion form factors in the crystal.

Summary

The inclusion of the more important double excitation configurations and all single configurations leads to changes in the single valence orbital HF form factors of transition-metal atoms which maximize at $K/4\pi \sim 0{\cdot}4$ Å^{-1}, where they amount to ~5% of the form factor at that value of K. The curves are, with one exception, expanded in reciprocal space, corresponding to a contraction of the spin density distribution in real space. For the ions with high-spin ground states the effects are much smaller. The changes in these form factors seem to be of relatively small importance in the analysis of spin density distributions, at the present level of accuracy of the experimental measurement. Further examples may be considered in the future using the CI form factors in the refining procedure.

The X-ray form factors are contracted in reciprocal space by about the same absolute amount (Table 2) as the spin-only magnetic form factors are expanded.

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Les Sous-Groupes Isomorphes d'un Groupe d'Espace de Type *p*4. I. Détermination Univoque*

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Abstract

From a given standard setting (O, $\mathbf{A}$, $\mathbf{B}$) (conventional unit-cell origin and vectors) of a two-dimensional space group $G(p4)$, it is possible, for each isomorphic subgroup $g(p4)$, to select exactly *one* standard setting (o, $\mathbf{a}$, $\mathbf{b}$) subject to the following conditions. (1) *Vector conditions*: $\mathbf{a}=p_1\mathbf{A}+p_2\mathbf{B}$, $\mathbf{b}=-p_2\mathbf{A}+p_1\mathbf{B}$, $p_1>0$, $p_2\geq 0$ ($p_1, p_2\in\mathbb{Z}$). (2) *Origin conditions*: (a) if (p_1+p_2) is odd, then the coordinates X, Y of o, with respect to (O, $\mathbf{A}$, $\mathbf{B}$), obey the next conditions: X, Y integers, $0\leq X<\mathrm{GCD}(p_1,p_2)$, $0\leq Y<(p_1^2+p_2^2)/\mathrm{GCD}(p_1,p_2)$, GCD = greatest common divisor; (b) if $(p_1+p_2)/\mathrm{GCD}(p_1,p_2)$ is even, then $2X$ and $2Y$ are both even or odd, $0\leq X<\mathrm{GCD}(p_1,p_2)$, $0\leq Y<(p_1^2+p_2^2)/2\mathrm{GCD}(p_1,p_2)$; ($c$) if p_1, p_2 are even and $(p_1+p_2)/\mathrm{GCD}(p_1,p_2)$ is odd then $2X$ and $2Y$ are both even or odd, $0\leq X<\mathrm{GCD}(p_1,p_2)/2$ and $0\leq Y<(p_1^2+p_2^2)/\mathrm{GCD}(p_1,p_2)$. In any case there are exactly $(p_1^2+p_2^2)$ subgroups relevant to the same vector conditions. Tables of isomorphic subgroups $p(4)$ are given for indices up to 25.

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* English translations, 'not refereed', may be obtained from the authors upon request.

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