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Synthesis and Crystal Structure Determination of the New Intermetallic Phase $Li_{13}Cu_6Ga_{21}$

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$Li_{13}Cu_6Ga_{21}$ crystallizes in a cubic structure, space group $Im3$, with $a = 13.568(2)$ Å, $Z = 4$. Diffraction data were collected on a NONIUS CAD 4 diffractometer in the range $4 \leq 2\theta \leq 50°$ (Mo$K\alpha$ radiation). The structure was solved by direct methods and refined by full-matrix least-squares to a final $R(F) = 0.033$ for 346 independent reflections with $I > 3\sigma(I)$. $Li_{13}Cu_6Ga_{21}$ presents an interesting structure composed of Samson's polyhedral clusters (104 atoms) linked to each other through smaller junction polyhedral clusters (truncated tetrahedra and hypho-13-vertex polyhedra) containing lithium atoms in their centers. © 1991 Academic Press, Inc.

Introduction

Up to now, studies of intermetallic systems of gallium with alkali metals have allowed the discovery of numerous and interesting new phases. In opposition to the naked clusters that are encountered in some Zintl phases involving the group 14 and 15 elements, and their solutions in basic polar solvents or in compounds obtained from them by cryptation techniques (*1–4*), gallium phases only display framework clusters that are interconnected in a way that depends upon different factors. For example Li_2Ga_7 (*5–7*), $RbGa_7$, and $CsGa_7$ (*8, 9*) contain only icosahedral clusters that are linked to each other within a three-dimensional network through direct interpolyhedral bonding and connection to isolated tetracoordinated gallium atoms. KGa_3 (*10*) or $RbGa_3$ (*11*) do not contain icosahedra but dodecahedra. On the other hand, K_3Ga_{13} (*12*) is composed of both icosahedra and octadecahedra. The structures become more complicated in $Na_{22}Ga_{39}$ (*13*) or Na_7Ga_{13} (*14, 15*) where the interconnection of icosahedra is not achieved by isolated gallium atoms but by a 15-vertex polyhedron spacer, displaying a largely opened geometry.

More recently, structural determinations of Li_5Ga_9 (*7, 16*) and of new ternary phases containing two kinds of alkali metal, for example $Li_9K_3Ga_{28.83}$ (*17*), $K_4Na_{13}Ga_{49.57}$ (*18*), and $Rb_{0.6}Na_{6.25}Ga_{20.02}$ (*19*), have shown that nonstoichiometry can easily occur, giving rise, sometimes, to polycondensation of icosahedra like in boron and its related phases (*20, 21*). The interpretation of these structures, according to Wade's electron-counting rules (*22*) elaborated for electron-deficient clusters, works perfectly for binary phases, but ternary phases must be examined with more circumspection. In agree-

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ment with the extended concept developed by Schäfer and co-workers (*23*), these results have contributed to bring the Zintl phases to a more general concept.

Experimental

The metals used were lithium (Cogema 99.94%), copper (Merck "powder for analysis") and Alusuisse gallium (4N). Alloys were prepared by melting together the elements in a niobium reactor which had been weld-sealed in an argon atmosphere. The mixture of composition $LiCuGa_2$ was heated at 800°C for 48 hr and then allowed to cool slowly at the rate of 12°/hr for crystal growing.

The product of the reaction appeared homogeneous and relatively brittle, it was examined under a microscope inside a glove box filled with purified argon. The material was broken into small pieces to be checked by preliminary oscillation and Weissenberg photographs for crystallinity. To avoid any contact with oxygen, nitrogen, and moisture, they were inserted into sealed Lindemann glass capillaries, thereafter the pieces that correctly displayed the expected symmetry were analyzed by conventional atomic absorption and ICP spectrometries.

The preliminary photographs indicated the crystal to have rhombohedral symmetry with parameters (hexagonal cell) $a = b = 19.20$ and $c = 11.73$ Å. This was encouraging since no such cell parameters had been encountered for compounds in the binary systems Li–Ga and Cu–Ga, and this material might be the first phase obtained in the ternary system.

Analysis gave a Li/Cu/Ga atomic ratio of 1/0.473/1.526.The best diffracting crystal of dimensions 0.30 × 0.28 × 0.05 mm was selected and mounted on an Enraf-Nonius CAD 4 automatic diffractometer. Accurate lattice parameters were determined by least-squares refinement of the angular positions of 25 reflections collected and automatically centered on the diffractometer (rhombohedral axes $a = b = c = 11.747(3)$ Å, $\alpha = 109.47(2)$, hexagonal axes $a = b = 19.185(3)$, $c = 11.753(1)$ Å).

Integrated diffraction intensities were collected at room temperature in the range $4 \leq 2\theta \leq 50°$ within the octants hkl, $-hkl$, $h\ -kl$, $-h\ -kl$ and $hk\ -\ l$ using graphite monochromated Mo$K\alpha$ radiation.

The profile analysis of a few angle reflections indicated that an $\omega - \frac{1}{3}\theta$ method was the most appropriate for data collection. Scan ranges were calculated from the formula $Sr = A + B \tan \theta$, where A depends upon the mosaic spread of the crystal and B allows for increasing peak width due to $K\alpha_1$ and $K\alpha_2$ splitting; A and B were taken as 1.2 and 0.35°, respectively. Maximum scan times of 60 seconds were programmed.

During data collection, the intensities of three standard reflections were checked after every 50 reflections and no significant loss in intensities was observed. The data were corrected for background and Lorentz-polarization effects. Once the composition of the crystal was determined, the data were corrected for the absorption effect ($\mu = 266\ cm^{-1}$, transmission factors varying from 0.015 to 0.289) and equivalent data were averaged using SHELX facilities (*24*). It rapidly appeared that the cell had the higher cubic symmetry, and the reflections were indexed in a body-centered cubic cell ($a = 13.568(2)$ Å). The best average (Rint $= [\Sigma(F^2 - \bar{F}^2)^2/\Sigma F^4]^{1/2} = 3.6\%$) was obtained for the space group $Im3$ (No. 204). The final data set consisted of 346 independent reflections with $I > 3\sigma(I)$.

Structure Solution and Refinement

The structure was solved by the direct methods provided by SHELX86 (*25*), in the space group $Im3$. The output of the Fourier step contained four peaks of high weight which were initially attributed to gallium atoms. After a few cycles of positional and

TABLE I

FINAL ATOMIC POSITIONS AND THERMAL PARAMETERS FOR ATOMS IN $Li_{13}Cu_6Ga_{21}$

Atom	Position	x	y	z	B_{eq}	$U_{eq}U_{iso}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ga(1)	48(h)	0.1903(1)	0.4055(1)	0.1581(1)	0.99(5)	0.013(1)	0.0167(6)	0.0106(6)	0.0102(6)	−0.0017(3)	0.0029(3)	0.0003(3)
Ga(2)	24(g)	0.0956(1)	0.1565(1)	0.0	0.87(6)	0.011(1)	0.0105(7)	0.0118(8)	0.0107(7)	0.0053(4)	0.0	0.0
Ga(3)	12(e)	0.0932(1)	0.5	0.0	0.95(7)	0.012(1)	0.0079(9)	0.0165(9)	0.0116(9)	0.0	0.0	0.0
Cu	24(g)	0.1779(1)	0.3144(1)	0.0	0.78(6)	0.010(1)	0.0095(7)	0.0126(8)	0.0076(7)	0.0038(4)	0.0	0.0
Li(1)	24(g)	0.884(2)	0.0	0.303(2)	2.4(5)	0.030(6)						
Li(2)	16(g)	0.314(1)	0.314(1)	0.314(1)	2.4(5)	0.031(7)						
Li(3)	12(e)	0.5	0.0	0.706(3)	2.7(7)	0.034(9)						

Note. $B_{eq} = 8\pi^2 U_{eq} = 8\pi^2/3 \sum\sum U_{ij} a_i^* a_j^* \vec{a}_i . \vec{a}_j$ (Å^2).

isotropic thermal parameter refinement, a Fourier synthesis revealed the presence of three peaks which were assigned to lithium atoms.

The structure was refined with the program SHELX (*24*) using isotropic thermal parameters for all atoms; at this stage the reliability factor $R(F) = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ was 0.043. The value of the isotropic temperature factor of one of the heavy atoms was found to be 1.5 times that of the other atoms, and the computed interatomic distances around this atom were clearly found shorter, thus it was considered to be a copper atom[1] and consequently refined, with its isotropic temperature factor reaching a correct value.

Actually the stoichiometry determined crystallographically (Li/Cu/Ga: 1/0.46/1.61) is in relatively good agreement with that determined by chemical analysis (1/0.47(1)/1.54(3)).

[1] An EXAFS (Extended X-Ray Absorption for Fine Structure) experiment was performed on the finely ground sample. Copper K-edge absorption spectra were recorded with an Exafs I setup, using the synchrotron radiation source DCI at LURE (LURE Laboratoire d'Utilisation du Rayonnement Electromagnétique, 91405 Orsay, France). Data analysis, using the well known procedure thoroughly described (B. K. Teo, "EXAFS: Basic principles and data analysis," Springer Verlag, Berlin, 1985.), showed that the mean Cu–Ga distance was 2.52 Å with 6-coordination for copper atoms; this distance agrees with the mean cristallographic Cu–Ga distance of 2.55 Å.

Finally, all atomic positional parameters, anisotropic temperature factors for gallium and copper atoms, and isotropic temperature factors for lithium atoms were refined, minimizing the function $\omega(|F_0| - |F_c|)^2$ with $\omega = 2.074/\sigma^2(F) + 0.024\,F^2$), and the final agreement factors were $R(F) = 0.033$ and $R\omega(F) = 0.035$. The last Fourier difference map was flat except for a residual peak of density 1.9 e$^-$/Å^3 on (0, 0 ,0) at the center of the icosahedron that might correspond to an encapsulated lithium cation with 100% occupancy or a copper atom at nearly 6.5% occupancy; this will be discussed below.

Results and Discussion

The final positional and thermal parameters are listed in Table I, and main bond distances are given in Table II. The unit cell contains four formula units of $Li_{13}Cu_6Ga_{21}$.

Atom Ga(2) lies on the special position 24(g) and forms the icosahedron centered at (0, 0, 0) on the 2(a) position with $m3$ symmetry. Twenty lithium atoms sit in front of the triangular faces of the icosahedron and constitute a pentagonal dodecahedron (Fig. 1); each of these lithium atoms is encapsulated in a 12-vertex polyhedron (truncated tetrahedron) composed of 9 gallium and 3 copper atoms (Fig. 2) with the copper atoms lying on the five-fold axes of the icosahedron. Actually this type of coordination around the central isosahedron constitutes

TABLE II

PRINCIPAL DISTANCES LESS THAN 4 Å IN $Li_{13}Cu_6Ga_{21}$

Ga(1)		Cu	2.481(2)	Li(1)	2×	Ga(2)	2.86(2)
		Ga(1)	2.565(3)			Ga(2)	2.87(2)
		Cu	2.570(2)		2×	Cu	2.89(1)
	2×	Ga(1)	2.582(1)			Li(3)	2.93(3)
		Ga(3)	2.825(2)		2×	Ga(1)	2.96(2)
		Li(3)	2.87(2)		2×	Ga(1)	2.98(1)
		Li(3)	2.95(1)		2×	Li(2)	3.13(2)
		Li(1)	2.96(2)			Li(1)	3.16(5)
		Li(2)	2.98(1)			Cu	3.18(2)
		Li(1)	2.98(1)		2×	Ga(3)	3.35(2)
		Li(2)	3.01(2)				
				Li(2)	3×	Ga(2)	2.83(3)
Ga(2)		Cu	2.416(2)		3×	Ga(1)	2.98(1)
		Ga(2)	2.596(3)		3×	Ga(1)	3.01(2)
	4×	Ga(2)	2.622(2)			Li(2)	3.03(5)
	2×	Li(2)	2.83(3)		3×	Cu	3.07(1)
	2×	Li(1)	2.86(2)		3×	Li(1)	3.13(2)
		Li(1)	2.87(2)				
				Li(3)		Ga(3)	2.72(4)
Ga(3)		Ga(3)	2.529(3)		4×	Ga(1)	2.87(2)
		Li(3)	2.72(4)		2×	Li(1)	2.93(3)
	2×	Cu	2.767(2)		4×	Ga(1)	2.95(1)
	4×	Ga(1)	2.825(2)		2×	Cu	2.97(2)
	2×	Li(3)	3.07(3)		2×	Ga(3)	3.07(3)
	4×	Li(1)	3.35(2)				
Cu		Ga(2)	2.416(2)	Cu	2×	Li(1)	2.89(1)
	2×	Ga(1)	2.481(2)			Li(3)	2.97(2)
	2×	Ga(1)	2.570(2)		2×	Li(2)	3.07(1)
		Ga(3)	2.767(2)			Li(1)	3.18(2)

the so-called "Samson's complex." As shown in Figs. 1 and 3, the first shell around the icosahedron is constituted by the pentagonal dodecahedron of lithium (20 atoms), the second shell by the 12 copper atoms with

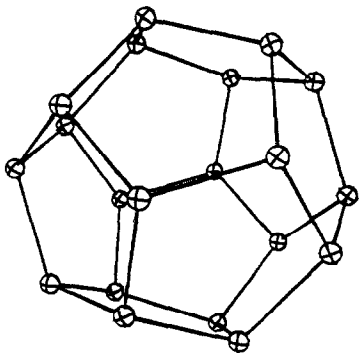

FIG. 1. The lithium (Li(1) and Li(2)) pentagonal dodecahedron arrangement.

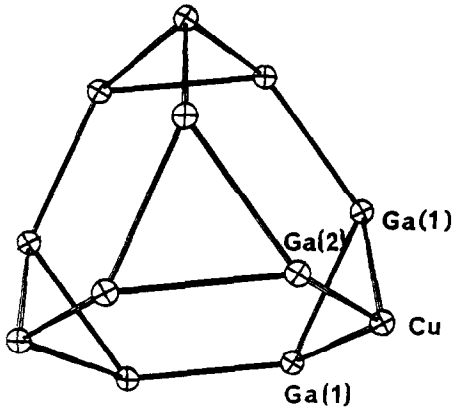

FIG. 2. The lithium encapsulating truncated tetrahedron.

an icosahedral arrangement, and the outer shell by a truncated icosahedron of gallium (30 atoms arranged like a "soccer ball" on hexagons and pentagons), a structure which is very appropriate for the Mondiale. This Samson's complex (Fig. 3) has already been encountered in phases of boron (*20*) and in LiCuAl compounds (*26, 27*).

Owing to the nonexistence of fivefold axes, the packing of only Samson polyhedra

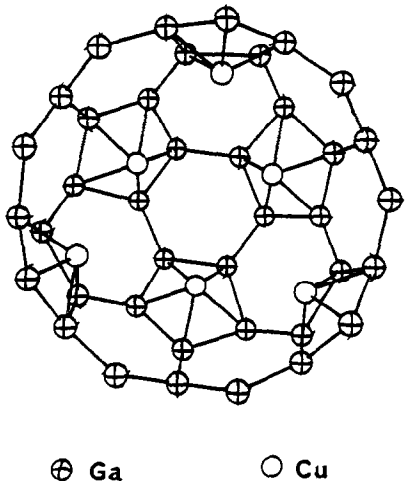

FIG. 3. Representation of the outer shells (Cu and Ga) of the Samson complex.

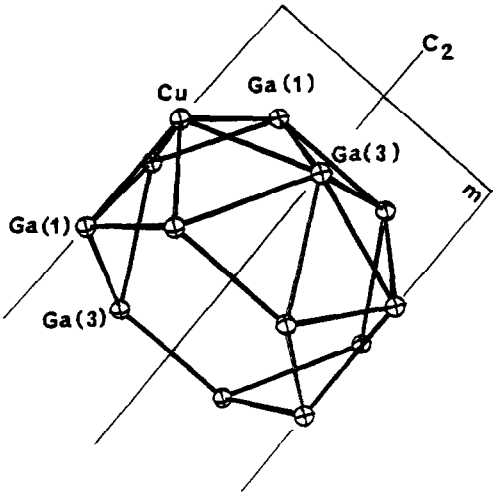

FIG. 4. The junction polyhedron: the 13-vertex spacer.

cannot form a stable structure. The constitution of a crystalline network requires their combination with other junction polyhedra which fill the residual space.

In the present structure, the Samson polyhedra are linked to eight homologues by sharing a common hexagonal face. The junction polyhedra or spacers (13-vertex polyhedra) described in Fig. 4 result from the interstitial space between four Samson polyhedra and contain two pentagonal faces capped with copper atoms and two hexagonal faces; the two pentagonal faces share one gallium atom yielding 14 triangular faces. The spacer displays a cuneane geometry with the *mm* symmetry. The stacking of Samson polyhedra and spacers in the unit cell is schematically represented on Fig. 5.

In this anionic lattice, all atoms except Ga(3), which is seven-coordinated, gallium as well as copper, display the six-coordination. Lithium atoms sit in the cavities inside the anionic network. Li(1) and Li(2) lie at the center of the truncated tetrahedra (Fig. 2) respectively at the 24(g) and 16(f) positions, and Li(3) sits on the special 12(e) position inside the 13-vertex spacer.

The residual of $1.9e^-/Å^3$ found at the center of the icosahedron might correspond to an encapsulated lithium atom. The alternative stoichiometry would be in better agreement for Li/Ga but not for Li/Cu ratios. On the other hand, distances from the center to the gallium atoms on the icosahedron are very short (2.488 Å) com-

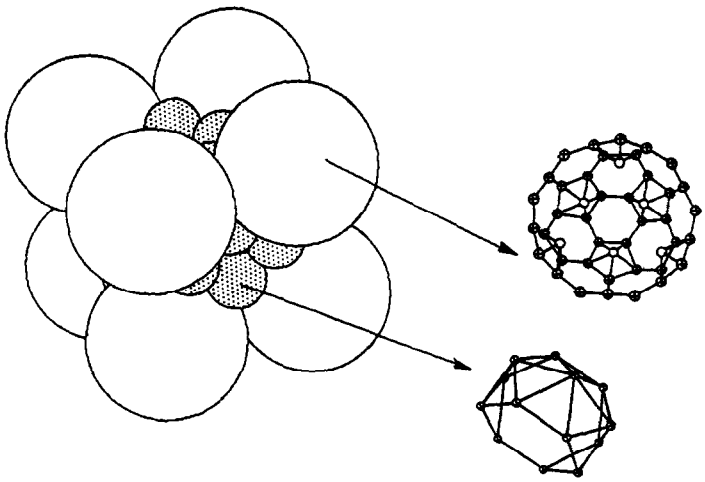

FIG. 5. Stacking of Samson polyhedra displaying the three dimensional interstitial 13-vertex spacer.

pared to generally observed Li–Ga distances in related structures. This puzzling electron density probably arises from the inner molecular orbital (*Ag*) resulting from the combination of the individual inward-pointing gallium atomic orbitals on the icosahedron.

To resolve the problem, a Fourier difference was performed using reflections with $\sin\theta/\lambda$ less than 0.3 to emphasize the core electron contribution. The overall difference electron density was less than $1e^-/Å^3$ and no electron density was found at the center of the icosahedron.

Due to the fact that the polyhedra are much more imbricated than in previously described structures, interpretation of this phase on the basis of Wade's electron counting scheme (*22*) is not easy. Nevertheless, stabilization of the icosahedron needs 26 electrons and each Cu–Ga(2) short bond must be considered as a two-center two-electron bond.

The Cu-icosahedron bond has been found to be 0.08 Å shorter than the mean *2c–2e* direct interpolyhedral Ga–Ga bond observed in similar structures (*5, 10, 12*). This shortening is in good agreement with the difference in covalent radii of the elements.

There are two icosahedra in the unit cell that need 52 skeletal bonding electrons, and 24 two-center two-electron Ga–Cu bonds that require 48 electrons. Since lithium atoms are completely ionized, as demonstrated by NMR for Li_2Ga_7 (*28*), from a total of 328 valence electrons (four $Li_{13}Cu_6Ga_{21}$ units) in the unit cell, 228 electrons remain on the spacer three-dimensional network. In a simplified view of the matter, there are two electron-deficient zones (icosahedra and spacer network with, respectively, 0.866 and 0.926 e^-/bond) which are separated by the more electron rich area containing the two-center two-electron Ga–Cu bonds.

Appendix

h k l	F_0 (×10)	F_c (×10)	*h k l*	F_0 (×10)	F_c (×10)	*h k l*	F_0 (×10)	F_c (×10)
0 1 1	323	250	0 0 2	857	764	1 1 2	2199	2159
0 2 2	846	863	2 2 2	4222	4143	1 0 3	4910	5026
0 1 3	3347	3408	2 1 3	3172	3250	1 2 3	4009	4074
0 3 3	2822	2822	0 0 4	3425	3565	2 0 4	2792	2747
1 1 4	447	447	3 1 4	1157	1077	0 2 4	2748	2733
2 2 4	966	884	3 3 4	1425	1420	0 4 4	1113	1151
2 4 4	732	755	4 4 4	1350	1260	1 0 5	440	425
3 0 5	4274	4361	0 1 5	758	722	2 1 5	1257	1244
4 1 5	2911	2966	1 2 5	439	405	3 2 5	7824	8395
0 3 5	7365	8178	2 3 5	1638	1630	4 3 5	7350	7657
1 4 5	1550	1479	3 4 5	4488	4539	0 5 5	998	1017
2 5 5	2510	2512	4 5 5	1996	2013	0 0 6	9276	10541
2 0 6	1935	1917	4 0 6	2482	2448	1 1 6	858	903
3 1 6	9659	10907	5 1 6	529	545	0 2 6	1109	1068
2 2 6	2510	2516	4 2 6	485	346	1 3 6	455	241
3 3 6	2717	2751	5 3 6	492	335	0 4 6	7066	7406
2 4 6	1987	1965	4 4 6	526	514	1 5 6	3689	3705
3 5 6	3277	3273	0 6 6	945	986	2 6 6	1304	1242

Appendix—*Continued*

h k l	F_0 (×10)	F_c (×10)	h k l	F_0 (×10)	F_c (×10)	h k l	F_0 (×10)	F_c (×10)
4 6 6	2803	2833	6 6 6	6459	6838	1 0 7	6965	7300
3 0 7	3951	4098	5 0 7	1005	949	0 1 7	3436	3535
2 1 7	1980	1952	4 1 7	826	786	6 1 7	932	961
1 2 7	1300	1312	3 2 7	2733	2676	0 3 7	2246	2260
2 3 7	1697	1701	4 3 7	782	761	6 3 7	643	667
1 4 7	2185	2252	3 4 7	2474	2408	5 4 7	589	644
2 5 7	1980	2044	6 5 7	1188	1085	1 6 7	3059	3022
3 6 7	466	342	5 6 7	3768	3904	0 7 7	833	769
2 7 7	1345	1317	4 7 7	648	625	0 0 8	1284	1254
2 0 8	763	784	4 0 8	583	558	6 0 8	496	394
1 1 8	1850	1794	3 1 8	1267	1278	5 1 8	631	667
7 1 8	1109	1074	2 2 8	3035	2995	4 2 8	585	338
6 2 8	1735	1755	1 3 8	1718	1769	5 3 8	7879	8035
7 3 8	3107	3071	0 4 8	488	387	2 4 8	1172	1129
4 4 8	1101	1118	6 4 8	2099	2130	1 5 8	1662	1634
3 5 8	1607	1643	5 5 8	1785	1828	7 5 8	1565	1551
0 6 8	2264	2238	2 6 8	1968	1955	4 6 8	1453	1443
6 6 8	894	891	1 7 8	2371	2303	3 7 8	2128	2138
5 7 8	1211	1303	7 7 8	1439	1413	0 8 8	637	400
2 8 8	2422	2413	4 8 8	721	607	6 8 8	1318	1347
8 8 8	2147	2265	1 0 9	487	352	3 0 9	1300	1284
5 0 9	4856	4913	7 0 9	2085	2123	0 1 9	476	450
2 1 9	1624	1668	4 1 9	579	620	8 1 9	1054	1058
1 2 9	680	696	3 2 9	2733	2795	5 2 9	1370	1396
7 2 9	615	294	0 3 9	849	777	2 3 9	961	957
4 3 9	624	663	6 3 9	3394	3412	1 4 9	1735	1703
3 4 9	2244	2244	5 4 9	3985	3955	7 4 9	597	500
0 5 9	3330	3303	2 5 9	5726	5791	4 5 9	3125	3128
6 5 9	868	842	8 5 9	5453	5567	1 6 9	5146	5142
3 6 9	2162	2168	5 6 9	2564	2588	7 6 9	630	659
0 7 9	948	898	2 7 9	1867	1761	6 7 9	1448	1442
8 7 9	2157	2198	1 8 9	597	593	3 8 9	2519	2565
5 8 9	950	989	2 9 9	2335	2325	4 9 9	897	851
6 9 9	1297	1314	8 9 9	1443	1449	0 0 10	8333	8492
2 0 10	1547	1536	4 0 10	4796	5004	6 0 10	684	595
8 0 10	1284	1283	3 1 10	3873	3943	5 1 10	1737	1756
7 1 10	708	661	9 1 10	2506	2416	0 2 10	2829	2841
2 2 10	1045	1009	4 2 10	915	860	6 2 10	1145	1116
8 2 10	1222	1193	1 3 10	1314	1330	3 3 10	729	701
5 3 10	1244	1195	7 3 10	1285	1336	9 3 10	609	600
0 4 10	2644	2587	2 4 10	1416	1448	4 4 10	1180	1089
6 4 10	4182	4173	8 4 10	739	738	5 5 10	714	741
7 5 10	3816	3857	9 5 10	1161	1132	0 6 10	10424	10820
4 6 10	2582	2633	6 6 10	2643	2669	8 6 10	881	878
1 7 10	1349	1347	3 7 10	632	599	5 7 10	585	403
7 7 10	880	876	0 8 10	1568	1548	2 8 10	862	864
4 8 10	530	422	6 8 10	1892	1926	8 8 10	647	592
1 9 10	602	392	3 9 10	2891	2971	7 9 10	979	1083
2 10 10	704	715	6 10 10	3143	3129	1 0 11	3302	3346

Appendix—*Continued*

h k l	F_0 (×10)	F_c (×10)	*h k l*	F_0 (×10)	F_c (×10)	*h k l*	F_0 (×10)	F_c (×10)
3 0 11	1244	1261	5 0 11	2757	2815	7 0 11	2528	2615
9 0 11	1316	1322	0 1 11	1852	1819	2 1 11	745	796
4 1 11	1434	1452	6 1 11	581	554	8 1 11	1007	1009
10 1 11	744	658	1 2 11	1229	1222	3 2 11	1242	1250
5 2 11	2013	2013	7 2 11	1708	1650	9 2 11	820	792
0 3 11	3336	3376	2 3 11	2172	2158	4 3 11	1851	1788
6 3 11	8353	8726	10 3 11	2807	2791	1 4 11	1195	1144
5 4 11	1411	1398	7 4 11	708	602	2 5 11	1017	1003
4 5 11	1362	1321	6 5 11	611	600	8 5 11	725	632
10 5 11	1356	1340	1 6 11	954	932	5 6 11	811	809
7 6 11	629	555	9 6 11	688	692	0 7 11	5608	5621
4 7 11	1699	1715	6 7 11	1783	1845	1 8 11	1510	1459
3 8 11	742	768	5 8 11	1089	1106	7 8 11	2168	2154
0 9 11	904	855	2 9 11	1418	1457	4 9 11	1514	1474
6 9 11	4720	4797	1 10 11	831	854	5 10 11	2287	2358
0 11 11	1772	1773	2 11 11	1016	1053	0 0 12	8976	9256
2 0 12	1059	1119	4 0 12	694	643	6 0 12	4833	4870
8 0 12	1291	1313	10 0 12	2362	2359	1 1 12	646	658
3 1 12	1946	1886	5 1 12	1488	1520	7 1 12	2243	2272
9 1 12	776	675	0 2 12	1399	1355	2 2 12	654	596
4 2 12	1107	1095	10 2 12	1623	1659	1 3 12	2607	2643
3 3 12	534	429	5 3 12	1555	1520	9 3 12	1490	1564
0 4 12	620	530	4 4 12	1119	1107	10 4 12	1125	1416
1 5 12	598	555	3 5 12	3401	3390	9 5 12	1890	1916
0 6 12	1785	1744	2 6 12	589	581	4 6 12	2551	2580
3 7 12	1331	1413	5 7 12	932	1029	7 7 12	1199	1234
2 8 12	860	780	4 8 12	642	517	6 8 12	876	977
1 9 12	1258	1273	3 9 12	1198	1160	5 9 12	755	694
0 10 12	4624	4734	2 10 12	1001	951	1 0 13	5099	5169
3 0 13	2318	2377	7 0 13	1578	1549	9 0 13	1582	1522
0 1 13	2462	2485	2 1 13	2356	2300	4 1 13	1568	1553
8 1 13	2747	2698	1 2 13	609	603	3 2 13	885	849
5 2 13	739	704	9 2 13	645	629	0 3 13	862	792
2 3 13	1320	1389	4 3 13	1414	1394	8 3 13	1253	1318
1 4 13	2231	2233	4 5 13	1121	1136	6 5 13	812	711
8 5 13	634	302	1 6 13	2265	2262	5 6 13	3308	3317
7 6 13	790	703	2 7 13	1142	1115	6 7 13	1374	1364
5 8 13	996	1017	2 9 13	707	589	6 0 14	1206	1256
1 1 14	599	527	3 1 14	1041	1077	2 2 14	1479	1456
6 2 14	684	695	3 3 14	901	895	5 3 14	4162	4192
7 3 14	1469	1429	0 4 14	1767	1857	2 4 14	717	662
6 4 14	2006	2081	1 5 14	1564	1639	5 5 14	714	706
0 6 14	2360	2402	4 6 14	1059	1085	1 7 14	980	979
3 7 14	1540	1534	3 0 15	1448	1509	5 0 15	951	911
0 1 15	577	612	2 1 15	1187	1177	4 1 15	1075	1109
1 2 15	740	761	3 2 15	2554	2535	5 2 15	1183	1188
0 3 15	4328	4333	4 3 15	2634	2654	1 4 15	1405	1372
0 5 15	1298	1306	2 5 15	1632	1625	1 1 16	770	741

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