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Some Implications of Accurate Thermal Parameters for Beryllium

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Abstract

Authoritative values for the parameters of harmonic thermal motion have been used as criteria for various least-squares refinements of the structure model for beryllium metal. A change in the absolute scale of Brown [*Philos. Mag.* (1972), **26**, 1377–1394] improves the correspondence of the associated data with the true thermal parameters. Contraction of the core-electron distribution upon bonding is a possible implication of the rescaled data.

Introduction

In a recent report by Larsen, Lehmann & Merisalo (1980), hereafter LLM, accurate values have been given for the parameters of harmonic thermal motion in crystalline beryllium at 295 K. These values were obtained from a neutron diffraction experiment in which data were obtained at values of $\sin\theta/\lambda$ up to $2{\cdot}1$ Å^{-1}, well beyond the theoretical limit for even such short X-rays as Ag $K\alpha$ ($\lambda = 0{\cdot}56$ Å). In the present paper we use the published X-ray diffraction data of Brown (1972) in contrast to which the data of LLM extend more than twice as far in reciprocal space and are more numerous by an order of magnitude. Relative to results obtainable from Brown's data, the LLM thermal parameters may be taken as true values. Indeed it is just the point of their work, that the very careful LLM experiment should provide authoritative thermal parameters.

The work of LLM resulted in thermal parameters which significantly differed from those based on Brown's (1972) data and reported by Yang & Coppens (1978). After studying the various reports we concluded that some modeling problem probably accounted for the disparity among reported thermal parameters. We undertook to locate the problem looking first into the question of what scattering factors were used. The results of Yang & Coppens were (essentially) reproduced with the beryllium scattering-factor tabulation in *International Tables for X-ray Crystallography* (1974). Evidently there is no substantial difference (relative to this specific problem) between the scattering factor used by Yang & Coppens and that given in *International Tables for X-ray Crystallography.*

In the only other major model variation available in standard crystallographic procedures, the scale factor of $1{\cdot}0$, corresponding to Brown's (1972) absolute scale, was allowed to vary. This additional parameter in the structure model leads readily to the derivation of LLM's accurate thermal-parameter values from Brown's data. It is, of course, well known that scale and vibration parameters are highly correlated, but in this case the apparently simple effect may have masked a more significant result.

Calculations and results

The calculations are all variations of standard crystallographic least-squares refinement following the general pattern set out by Yang & Coppens (1978). The data and their observational weights are those of Brown (1972); the computer programs have been described elsewhere (Collins, Cotton & Murillo, 1976). In each refinement the scattering factor used was taken from *International Tables for X-ray Crystallography* (1974) and the iterations repeated until the parameter shifts were less than 1% of the associated e.s.d. The results are given in Table 1; structure-factor data are given in Table 2. It should be noted that correlation between the scale factor and thermal parameters is severe for the cases where low-angle data were excluded. For refinement based on all data the correlations are ~66%; when data with $\sin\theta/\lambda < 0{\cdot}5$ Å^{-1} are excluded, the correlations are ~85%; when data with $\sin\theta/\lambda < 0{\cdot}6$ Å^{-1} are excluded the correlations are ~91%.

The main result is that scale-factor variation and refinement against the entire data set leads to thermal parameters which differ from the accurate LLM values by no more than $4\sigma(U)$, where $\sigma(U)$ is the estimated standard deviation in U. This is to be contrasted with the case of a fixed unit scale factor where the computed thermal parameters differ from the LLM values by at least $6\sigma(U)$. The sequence of values arising from exclusion of low-angle data lends added authority to

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Table 1. *Comparison of the Yang & Coppens* (1978) (*YC*) *and our* (*CW*) *least-squares refinements*

	Isotropic		Anisotropic					
	YC	CW	YC	CW	YC	CW	YC	CW
sin θ/λ (Å^{-1})	0·05–0·90		0·00–0·90		0·50–0·90		0·60–0·90	
U_{11} (Å^2) [= 0·00594 (3)*]	0·00743 (7)	0·00663 (17)	0·0080 (3)	0·0064 (3)	0·00768 (13)	0·00700 (21)	0·00759 (12)	0·00747 (26)
U_{33} (Å^2) [= 0·00537 (3)*]			0·0071 (3)	0·0062 (2)	0·00689 (12)	0·00655 (15)	0·00686 (10)	0·00689 (20)
Number of observations	18	21	27	27	18	21	13	16
Number of variables	1	2	2	3	2	3	2	3
$R(F)$ (%)	1·5	1·2	3·2	1·7	1·3	1·1	1·0	1·0
$R_w(F)$ (%)	1·3	1·0	3·2	1·8	1·2	0·9	0·8	0·8
Scale factor†	1·0	0·959 (7)	1·0	0·944 (7)	1·0	0·966 (10)	1·0	0·987 (11)

* Neutron scattering data thermal parameters (LLM) are given in square brackets.
† $F_o \simeq kF_c$.

Table 2. *Structure-factor data for beryllium*

h k l	$\lvert F_o\rvert$	F_c*	$\lvert\Delta F\rvert$ ($\times10^3$)	sin θ/λ (Å^{-1})
1 0 0	1·817	−1·716	56	0·253
1 1 0	2·651	2·654	3	0·438
2 0 0	1·196	−1·188	9	0·505
2 1 0	0·867	−0·862	5	0·668
2 2 0	1·058	1·050	8	0·875
3 0 0	1·384	1·406	22	0·758
1 0 1	2·761	2·857	96	0·289
2 0 1	2·002	−1·990	11	0·524
2 1 1	1·449	1·448	1	0·683
0 0 2	3·156	−3·358	203	0·279
1 0 2	1·487	1·454	33	0·376
1 1 2	2·322	−2·322	0	0·519
2 0 2	1·056	1·042	14	0·577
2 1 2	0·752	0·762	9	0·724
3 0 2	1·234	−1·248	14	0·807
1 0 3	2·139	−2·123	17	0·489
2 0 3	1·571	1·539	32	0·656
2 1 3	1·144	−1·135	9	0·788
0 0 4	2·162	2·172	10	9·558
1 0 4	0·999	−0·976	23	0·612
1 1 4	1·614	1·584	30	0·709
2 0 4	0·719	−0·716	4	0·753
2 1 4	0·545	−0·534	11	0·871
1 0 5	1·305	1·276	29	0·742
2 0 5	0·946	−0·951	5	0·861
0 0 6	1·143	−1·173	30	0·837
1 0 6	0·537	0·533	4	0·874

* F_c is based on the anisotropic structure model determined for all (27) observations.

the variations in thermal parameters as significant. Fig. 1 shows the monotonic tendency of the two structure models to yield the same thermal-parameter values as low-angle data are excluded from the refinement. It is evident that the trends are intimately related to scale variation for when the thermal parameters from the two structure models become effectively equal, the scale factors are effectively equal also (see Table 1).

Discussion

Our observations hinge on scale-factor variation and the validity of its computed value. It increases the scale of Brown's (1972) observations by 6·0% when the full range of data is used. It is, of course, perfectly clear that more data, especially from a wider range of scattering angles, quite generally will provide more authoritative results for scale factors and thermal parameters. This point is made empirically by the correlations reported in the preceeding section. There is, nevertheless, a widespread suspicion of the lowest-order diffraction data as predjudicially unsuitable for least-squares calculations in which electronic features of bonding are the ultimate goal.

Whatever merit such an idea may have, it lacks force in the case of beryllium metal, a simple h.c.p. structure. A result of the structural simplicity is that reciprocal space is only coarsely sampled by the lattice and the structure factor of lowest scattering angle is F_{100} at sin $\theta/\lambda \sim 0{\cdot}25$ Å^{-1} (see Table 2). Inspection of any tabulation of scattering factors makes clear that at such values of sin θ/λ scattering factors are only marginally dependent on valence-electron effects. Moreover, it is quite generally true for sin $\theta/\lambda > 0{\cdot}30$ Å^{-1} that a scattering-factor effect does not follow directly upon a valence-shell effect. For example, at sin $\theta/\lambda = 0{\cdot}30$ Å^{-1} the order of scattering-factor magnitudes for Be, Be^{1+},

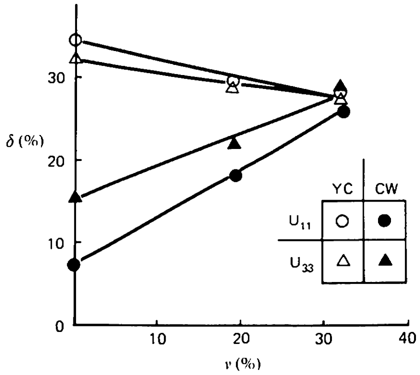

Fig. 1. Trends of thermal parameters from Table 1. The coordinates are δ, the percent difference from reference (LLM) values, and $\nu = 100\% \times \sin^3\theta_{\rm min}/\sin^3\theta_{\rm max}$, which measures the portion of data excluded from a refinement.

Be^{2+} is the exact inverse of the order given by the number of electrons; at $\sin\theta/\lambda = 0{\cdot}60$ Å^{-1} the order of scattering-factor magnitudes is again the same as the order given by the number of electrons.

Since in the range of observations for beryllium metal the scattering factors do not directly follow valence-shell effects, and since a unit change in the number of electrons results in scattering-factor changes of only ~1%, it is entirely improbable that valence-shell effects could seriously skew the results of structure refinement whether or not all observed data are employed. But use of all observed data does relieve the problem of correlation between scale factor and thermal parameters in the present case. Confidence in our scale in contrast to that of Brown (1972) is finally established by the essential agreement between the corresponding thermal parameters and the authoritative values of LLM. It seems probable that Stewart's (1977) persistent high-angle residuals could have been substantially reduced through use of our scale for the observed data.

The 6·0% increase of scale for the observations produces a variety of changes in deformation density. Nor are the causes of change limited to scale effects, for corresponding changes in thermal parameters, however small, also affect deformation density. Nevertheless, our deformation density maps are not substantially different from those of Yang & Coppens (1978) except possibly near the nuclei.

Stevens & Coppens (1976) show in their analysis of errors in deformation density that errors near nuclear positions are very large. For the very same reasons of functional form, any small percentage change in scale factor is expected to leave the pattern of a deformation density largely unchanged except possibly near nuclear positions. This corresponds exactly to what we find in comparison with the result of Yang & Coppens (1978) and we ascribe the differences which do exist near the Be positions to the change in scale. The maximum density is 0·03 (30) e Å^{-3} at the nuclear position; the error estimate is that of Yang & Coppens. Our purpose in reporting a positive deformation density at the Be position, notwithstanding the associated error, is to emphasize that use of a suitable scale changes the density from a large negative value shown by Yang & Coppens to a positive value. While the absolute significance of either value is probably not great, the magnitude of change, one e.s.d., is such as to permit an opposite interpretation of bonding effects upon charge density in the nuclear region.

Conclusion

The very large relative errors in deformation density near nuclear positions destroy the quantitative significance of experimental results in the core-electron region for most crystal structures. This quite naturally results in scant attention to density details near nuclei, even in cases such as beryllium metal for which the errors may eventually be made acceptably small. Moreover, the directedness of chemical bonding emphasizes electronic bonding effects between atoms and at substantial distances from nuclear positions.

Feinberg & Ruedenberg (1971), on the other hand, have emphasized that charge-density accumulation in an internuclear region may be only secondary in chemical binding. Such accumulation allows for contraction or concentration of the electron clouds near their respective nuclei which would then be the primary cause for binding through lowering of potential energy. It is problematic that this effect could ever be established with authority by X-ray diffraction experiments in view of the error in nuclear regions. Beryllium metal may be one of the few materials for which pertinent authoritative results could be derived on the basis of current methodology. Accurate thermal parameters from the work of Larsen, Lehmann & Merisalo (1980) have made it possible for us to determine that Brown's (1972) data, while not establishing the effect of Feinberg & Ruedenberg for beryllium metal, are at least in agreement with it.

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