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Electronic charge distribution in crystalline germanium

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We use a recently published set of high-accuracy structure factors, based on p-ray measurements [Dewey et al., Phys. Rev. B 50, 2800 (1994)]to derive the charge density distribution in crystalline
germanium with a millielectron-level resolution. We use a multipole expansion model of the charge
densities represented as a superposition of orbital-dependent, nonspherical atomic charge densities.
We include in the model anharmonic and nonrigid atomic thermal motions. This model is then 6t to
the measured structure factors. We find (i) a considerable improvement in the fit residuals (especially
for the low-order structure factors) relative to our previous analysis, based on earlier measurements;
(ii) a factor-of-2 improvement in the agreement between experiment and our earlier ab initio density-functional calculated structure factors; (iii) the evidence for the existence of nonrigid atomic thermal motion is marginal; (iv) a cle,

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by orbital nl and (At, At, () are fitting parameters.

The static structure factor

p g,~(C) at the reciprocal
lattice vector

G is obtained from Eq. (1) by Fourier
transforming

p q,~(r). The dynamic structure factor F (G) is then

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This is about twice the R, = 0.19%%uo value in

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TABLE II. Comparison of the "best estimate" experimental and fitted 8tatic structure fac-

tors p(G) for Ge units of e/atom. R, is the fit vs. experiment R factor [Eq. (3)]. bp(G) is p,„~(G)—psq(G), thirteen values of p(G) are used to evaluate R values. The fit vs experiment R in this table was calculated using static structure factors p(G) instead of dynamic structure factors F(G) as in Table I, hence there are slight difFerences. Note that the R, for LZD is very different from Table I, since we are now comparing with the current "best estimate" data instead of with the old experimental data.

G

hkl ill
220
311
222
400
331
422
333
440
444
660
555
777
R /0

exp
pexp (Cr)
27.450
23.581
22.181
0.120
20.257
19.606
18.059
17.345
16.173
13.528
11.006
10.669
7.531

LZD

p(~)
27.894
23.766
22 ~ 142
0.152
20.235
19.482
18.040
17.300
16.198
13.498

~p(C) —0.444 —0.185
0.039 —0.032
0.022
0.124
0.019

0.045 —0.025
0.030

10.680 —0.011
7.547 —0.016
0.51

Fit A

p(&) ~p(&)
27.468 —0.018
23.639 —0.058
22.128 0.053
0.135 —0.

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Exp vs Fit
LDA vs Fit

I

LZD fit

C. Valence shell contraction/expansion

4 -(b);
2

()
-2—

Fit D

4 -(c),
2-

0
-2—
-4
I I I I

0.0 0.2 0.4 0.6 0.8

sinB]g (A')

I

Fit B

1.0 1.

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TABLE V. Values of the total deformation density b, p(; t(R) (in units of e/A.)

and ~R~ (in units

o ~3a) at the same points as in Table V along the (111)direction as indicated in Fig. 4(a).

LZD Fit
LDA
Fit B
Fit D

Pval —0.01 —0.05 —0.16 —0.13

IRI
0.068
0.076
0.069
0.069

Pval

0.09 —0.06 —0.08 —0.02

IRI
0.057
0.051
0.062
0.062

Pval

0.25
0.13
0.17
0.18

IRI
0.125
0.125
0.125
0.125

Pval —0.05 —0.02 —0.02 —0.00

IRI

0.50
0.50
0.50
0.50

E. Forbidden reflections

The nonzero values of the "forbidden" structure factors

are contributed solely by the antisymmetric component of the bonding charge, B3K3, and the anharmonic force
constant P seen by the centrosymmetric charge compo-
nents B0 and B4K4. A comparison of the ab initio cal-culated, and the multipole expansion, values with the

~ ~

COI

0
I

CO
CO

O

- Theory:
LDA

0.1——————--—III 00 ~

~ ~

-0.1—

0 2

(I
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LZD Fit

I

0.1— I' I I I I

(I

Q Q

(II I
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~ ~ Il

-0.1—

I -02 I
Fit D

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this means that there is no support for a 6nite, nonzero P, it also does not exclude one as long as it is small, as
discussed above. This conclusion is also supported by
the recent powder study of Saravanan, Mohanlal, and Nethaj1

measured ones provides therefore important tests for the quality of the calculation and the 6tted models. Due to their small magnitude, only the three lowest-order such factors were ever measured for Ge: E222, E442, and E622. The values obtained for these in the

22.

558 Td (powder)Tj ET B

w as()Tj ETj ET BT /Xi5 8.9 Tf7 Tf 43353.33 Td92.he

''/ (A /—

—

—

C46 (ll)wedT /Xi5 9.85 Tf 91049..22 d (-)Tj4three

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(8IXl 8/ A)rrissx (A-')

0.4
0.6
0.8
0.9
1.0
1.2
1.4
1.6
1.8
2.0
2.1

8
18
35
46
59
96
139
198
271
357
411

(1 —m„ 1 } x 100
(%)
- 7.5
-4.5
-4.0
-3.0
-2.5
-2.0
-2.0
- 1.5
- 1.5
- 1.5
- 1.5

TABLE VI. The valence shell expansion/contraction pa-

rameter ~ ~ obtained by fitting the LDA-calculated static structure factors pi,DA(G) by the multipole model in Eqs. (1) and (2) for lattice vectors up to the indicated G „[denoted
by the corresponding (sin 8/A) „].iV is the number of struc-

ture factors within this limit. Negative values indicate expan-sion. The fit to 13 measured structure factors yields values of
- 10'%% to -17%, as shown in Table I.

Ab initio theory
Multipole model fit

Experiment

LDA
LZD ht
Fit A
Fit B
Fit C
Fit D
MKb
MB
TB2d

0.1135
0.1466
0.1304
0.1314
0.1469
0.1485
0.1330

+442
0.0026
0.0116
0.0098
0.0078
0.0111
0.0097

0.0079
0.0123

+e22
0.0020
0.0056
0.0047
0.0032
0.0041
0.0027

0.0070
0.0083

Reference 3.

Reference 7.

'Reference 26.

Reference 28.

TABLE VII. Multipole fit and LAPW-calculated dynamic

structure factors E(G) (using B = 0.5654 A.)

for the "for-

bidden" re8ections h + k + l = 4n + 2 in electron units. The

model fits are defined in Table I.

V. SUMMARY

The analysis based on the new p-ray measurements of Dewey et al.s

shows the following: (i) The experi-
ment versus model R factor B, is essentially the same as the LZD 6t to the older data, but the fit residu-als for the lowest-order structure factors are consider-

ably smaller here, indicating a better fit. (ii) The static density p g ~(r) obtained from the fit shows a factor of two improvement in the agreement with the ab initio I DA calculations, bringing B and Rz into equality. Fur-thermore, the unphysical negative valence densities found

previously by LZD in the interstitial region of the valence density of p ~,~(r) have now disappeared, and the agree-ment with theory in the bond region is improved. (iii) No support is obtained for a nonrigid thermal motion, in line with the conclusions of

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F. Sacchetti, Phys. Rev. B 36, 3147 (1987).
D. Y. Smith, Phys. Rev. A 35, 3381 (1987).
J.B.Roberto, B.W. Batterman, and D. T. Keating, Phys.
Rev. B 9, 2590 (1974).
M. O'Keeffe and J. C. H. Spence, Acta Crystallogr. Sect.
A 50, 33 (1994).
R. Saravanan, S. K. Mohanlal, and M. Nethaji, Phys. Sta-tus Solidi A 183, 359 (1994).
P. J. E. Aldred and M. Hart, Proc. R. Soc. London Ser. A

332, 223 (1973); S. Cummings and M. Hart, Aust. J. Phys. 41, 423 (1988).
D. Mills and B. W. Batterman, Phys. Rev. B 22, 2887 (1979).
P. Trucano and B. W. Batterman, Phys. Rev. 8 6, 3659 (1972).
J. Z. Tischler and B.W. Batterman, Phys. Rev. B 30, 7060 (1984).