American Mineralogist, Volume 79, pages 1207–1209, 1994

SOFTWARE NOTICE

Crush: A Fortran program for the analysis of the rigid-unit mode spectrum of a framework structure

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ABSTRACT

Crush is a program designed to calculate the rigid-unit mode spectrum for any given framework structure. Release version 1.1 is now available and contains some new features compared with the prerelease version described elsewhere.

INTRODUCTION

The rigid-unit mode (RUM) model has recently been developed (Dove et al., 1991, 1992; Giddy et al., 1993) as an extension and generalization of the old observation that in silicates the SiO_4 and AlO_4 tetrahedra are the most rigid components of a framework structure, and that in displacive phase transitions in materials with framework structures, like quartz and feldspar, the structures distort in such a way as to preserve the size and shape of the tetrahedra. It has been recognized that most framework structures have some normal modes that can propagate with no distortions of the tetrahedra—these are the so-called rigid unit modes. In these modes, the tetrahedra translate and rotate as rigid units. Thus RUMs have low frequency, and hence they are natural candidates for the soft modes of displacive phase transitions. This point has been documented in some detail for quartz (Vallade et al., 1992; Tautz et al., 1991). The RUM model has been applied to the problem of structure stability in a number of particular silicates, including, besides quartz, cristobalite (Swainson and Dove, 1993) and feldspars (Hammonds et al., in preparation). The RUM model has also been generalized to show how it can explain properties such as the transition temperature (Dove et al., 1991, 1992, and in preparation), the role of critical fluctuations in framework structures (Sollich et al., 1994), the application of Landau theory (Dove et al., 1992), negative thermal expansion (Dove et al., 1991), and zeolitic catalysis (Dove et al., in preparation). Some of these ideas, and the historical background, are reviewed elsewhere (Dove et al., 1992; Hammonds et al., in preparation). The RUM spectrum can therefore provide information about the important fluctuations in a silicate. It can also provide the complete set of allowed low-energy distortions of a structure, associated either with displacive transitions or as the distortions that accompany cation ordering.

It is essential for the study of the RUM model to be able to calculate the RUM spectrum for any framework structure. In the lowest-order approximation, the RUMs are the zero-frequency solutions to the dynamical equations for a model in which the only force constants are those associated with the distortions of the structural units, for example, the SiO_4 tetrahedra. These zero-frequency solutions give an unambiguous method to determine the spectrum of these modes (Giddy et al., 1993).

The method we use to determine the RUM spectrum is the split-atom method (Dove et al., 1992; Giddy et al., 1993). In this method, we treat the atom that is shared by two structural units as two separate (i.e., split) atoms, one per unit. In principle, we have two kinds of constraints: the constraints that the units should not distort and should therefore move as rigid bodies, and the constraints that the split atoms should have the same positions in space. In our treatment of the split-atom method, we treat the rigid-body constraints as strict constraints (i.e., they are always enforced), and we treat the constraints forcing the shared corners of two neighboring tetrahedra to have identical positions as slack constraints (i.e., they are not completely enforced). The slack constraints are implemented by inventing a harmonic force between any two split atoms that is proportional to the square of the separation. This has the effect of trying to keep the two split atoms together, but if the force constant is not infinite in magnitude, the split atoms can separate. We then use the methods of molecular lattice dynamics within the harmonic approximation (Pawley, 1972) to solve the dynamical equations of this system for the normal modes of any wave vector. The rigid-unit modes are those for which both kinds of constraint are satisfied, so that in our implementation, they are the modes for which all the split atoms can move without any pairs separating. Thus, the rigid-unit modes are generated from the lattice dynamics calculation as the normal modes with zero frequency. We find that rounding errors are quite insignifi-

0003–004X/94/1112–1207$02.00

cant in these calculations, so that the zero-frequency solutions can clearly be identified from the other modes.

The split-atom method has been coded in a Fortran program called Crush, which is now available for distribution as release version 1.1. The prerelease version of Crush (version 1.0) has been described by Giddy et al. (1993). Release version 1.1 of Crush contains two new features that have not been described elsewhere.

New features in version 1.1

The first new feature implemented in Crush version 1.1 is the possibility to calculate the structure-factor component of the one-phonon cross section for inelastic scattering of neutrons or X-rays from a RUM. Calculations of cross sections are potentially useful, particularly since RUMs can be seen in measurements of diffuse scattering (Hua et al., 1988). Because the RUM solutions have frequencies $\omega = 0$, it is not possible to include the standard factor $[n(\omega) + 1]/\omega$ in the equation for the scattering cross section, where $n(\omega)$ is the Bose-Einstein factor (Dove, 1993). Thus the major term in the cross-section equation is the structure factor component for a given mode. We also assume that all atoms have the same scattering factor for all scattering vectors. This is a reasonable assumption for neutron scattering but is not appropriate for X-ray or electron scattering. However, the point is that comparisons of cross sections are usually made between a set of modes at a given scattering vector rather than between different scattering vectors for a single mode, so this assumption ought not to be a problem in practice. We also do not account for the displacement factor.

The second new feature implemented in Crush version 1.1 is that we have included the option of using a force between the centers of first-neighbor rigid units. This allows the model to separate out the subset of RUMs in which the distance between these centers remains constant. The motivation for this feature is the observation that the Si-Si distance remains constant through the α-β phase transition in quartz (Grimm and Dorner, 1975). Thus the relevant soft RUM that drives the transition is one in which the Si-O-Si angle remains constant, defining a torsional mode. The feature is also useful in that with a weak force constant it becomes easy to separate degenerate RUM solutions. The feature needs to be used with care. In examples like the ideal structure of β cristobalite, where the Si-O-Si bond angle is linear, the Si-Si force constant has no physical meaning since the Si-Si distance is already at a maximum. In this case, inclusion of the Si-Si force constant has no effect on the calculated RUM frequencies. We generally find for systems with nonlinear Si-O-Si bonds that the Si-Si force constant adds a small frequency to most of the RUM solutions. In the case of quartz, the RUM that drives the phase transition is one of the few RUM solutions that retains its zero frequency when we include the Si-Si interaction, which is consistent with the observation that the structural instability caused by the softening of this RUM does not change the Si-Si distance.

The Crush program and related programs

Release version 1.1

Version 1.0 of Crush, which is a smaller and less tidy package than release version 1.1, has already been available to a few users. Version 1.1 contains two auxiliary programs. The first is called Idealiser. As reported by Giddy et al. (1993), the results of a RUM analysis may depend on whether the tetrahedra are ideal or not. Thus the Idealiser program is designed to generate atomic coordinates with ideal, rigid tetrahedra, i.e., with all tetrahedral bond angles equal to $\cos^{-1}\frac{1}{3} = 109.47°$, with equal bond lengths within any tetrahedra and with the split atoms unseparated. The bond lengths can be set by the user. The unit-cell parameters and the positions and orientations of the rigid units are adjusted to satisfy the constraints of idealization subject to the imposed space-group symmetry.

The second auxiliary program is called Analyse. This allows a group theoretical analysis of the RUM eigenvectors when used in conjunction with the group theory program of Warren and Worton (1974). Thus one can determine the irreducible representation of any RUM, which is necessary if a particular RUM is involved in the mechanism of a phase transition. The eigenvectors for the zero-frequency solutions are mixed because of the degeneracy of the eigenvalues (Giddy et al., 1993). The auxiliary program Analyse can be used to unmix the eigenvectors, but the direct eigenvectors and scattering cross sections from Crush are affected by this mixing. One tip is to provoke the unmixing by performing calculations at wave vectors slightly away from the required (usually high-symmetry) wave vector. Analyse also generates coordinates associated with the structure modulated by a zone-center RUM, which can be used in a structure-plotting program like Struplo.

Computer requirements

Crush is routinely run on both a MicroVAX 3100 under VMS and a DEC Alpha 3000/400S under OpenVMS and also under UNIX on several different platforms. A version has also been adapted to run on a Macintosh. Version 1.1 of Crush contains no system-specific calls. There are also no library calls in the actual Crush program, although there are calls to the NAG library in the auxiliary programs. Crush is written in standard Fortran77. All these features mean that it should be possible to mount Crush on any platform.

The size of the memory requirements of the program is controlled by one dimension parameter, which specifies the maximum number of rigid units. This can be globally changed with no problem—we have ensured that any implications of the change in this parameter will be taken account of automatically. With a structure having 32 rigid units in one unit cell, for example, as in $P\bar{1}$ anorthite, the memory requirement is 4 Mbytes, and on the DEC Alpha 3000/400S the cpu time is 90 s for one wave vector. The memory required scales as the square of the number of rigid units, and the cpu time roughly scales as

the cube of the number of rigid units. Thus a calculation for quartz executes virtually instantaneously. Another interesting comparison is that to calculate the RUM spectrum for a single wave vector in leucite, which has 24 rigid units in one unit cell, takes 19 s on the DEC Alpha 3000/400S and about 10.5 min on a Macintosh Quadra 610. Thus it is quite feasible to run Crush on a personal computer as well as on a work station or main-frame computer.

Licensing and availability

It is our intention neither to charge for academic use of our suite of programs nor to restrict usage, although with the changing times and funding climate, it may not be possible to retain our policy. The complete Crush package includes the Fortran source code for Crush and the auxiliary programs, a VMS command file for assigning files to Fortran channels and running Crush, and two sample input and output files (for β quartz and cubic leucite). It also contains a user manual prepared in LaTeX (a hard copy is available on request), which describes in detail the input and output files and provides some practical information. The package is most easily distributed by electronic mail or anonymous FTP and can be requested by electronic mail to martin@minp.esc.cam.ac.uk. In addition, arrangements can be made to distribute the package on floppy disks. Updates will be distributed automatically to all registered users.

Acknowledgments

We are grateful to Stuart Pawley (Edinburgh), who has kindly allowed us to use his molecular lattice-dynamics program as the basis of Crush, to David Palmer (Cambridge), for compiling Crush on a Macintosh, and to Eric Browne (Cambridge), for providing support for the distribution of the Crush package by anonymous FTP. This work has been supported by NERC (U.K.) and the Royal Society (U.K.).

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Manuscript received March 17, 1994
Manuscript accepted July 1, 1994