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TEMPERATURE DEPENDENCE OF THE EXAFS DEBYE-WALLER FACTORS OF AgI

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Abstract

The EXAFS Debye-Waller factors of the first and second coordination shells of iodine in AgI have been measured as a function of temperature in the 50–292 K range. A very different behaviour has been found for the two shells; the difference is explained in terms of correlation of atomic motion induced by low frequency optical modes. The peculiar sensitivity of the EXAFS Debye-Waller factors to the phase relationships between thermal displacements is evidenced and its relevance in testing the eigenvectors from different force constant models is discussed.

Since the first developments of EXAFS it was recognized that the temperature dependence of its amplitude can give information on the vibrational excitations in solids. In the single electron, single scattering treatment of EXAFS signals, both static and thermal disorder of each coordination shell around the absorbing atom are accounted for by a damping term $exp(-2k^2\sigma^2)$, where σ^2 is the EXAFS Debye-Waller (DW) factor. The dependence of σ^2 on temperature is in general correlated only with thermal motion. In harmonic approximation the Mean Square Relative Displacement (MSRD) with respect to an equilibrium interatomic distance $\vec{R}_j^0$ is $\sigma_j^2 = \langle(\vec{u}_0 \cdot \hat{R}_j^0)^2\rangle + \langle(\vec{u}_j \cdot \hat{R}_j^0)^2\rangle - 2\langle(\vec{u}_0 \cdot \hat{R}_j^0)(\vec{u}_j \cdot \hat{R}_j^0)\rangle$; the first two terms on the right hand are the Mean Square Displacements (MSD) of the two atoms (absorber and backscatterer, respectively, in the case of EXAFS) while the third term is the Displacement Correlation Function (DCF); $\hat{R}_j^0 = \vec{R}_j^0/R_j^0$ and $\vec{u}_0$ and $\vec{u}_j$ are the thermal atomic displacements.[1] If eigenfrequencies and eigenvectors of the dynamical matrix are known with sufficient accuracy, the MSRD can be calculated as a function of temperature.[2]

The knowledge of the MSRD for each pair of atoms in a crystal allows to obtain the DW factors of both EXAFS and X-Ray Diffraction (XRD). XRD patterns are built up from the contributions of all the atomic pairs: the XRD DW factor, which determines the thermal damping of Bragg peaks, depends only on the uncorrelated

MSD; the correlation of atomic motion is smeared out by long range averaging, and the DCF determines the characteristics of thermal diffuse scattering. EXAFS is instead sensitive only to short range order; the contribution of the DCF term to the EXAFS DW factor of one coordination shell is in general far from negligible. DCF strongly depends on the phase relationships between the thermal displacement vectors of absorber and backscatterer atoms, which can be quite complex in non monatomic crystals. It is well known that different ab initio and model calculations can satisfactorily reproduce the phonon dispersion curves measured by inelastic neutron scattering though giving very different eigenvectors.[3] The reproduction of the temperature dependence of the EXAFS DW factor is in principle a relatively simple way to check the phase relationships between eigenvectors obtained from different force constant models or from ab initio calculations.

The temperature dependence of the EXAFS DW factor has been extensively studied only for high symmetry Bravais lattices. For polyatomic crystals a systematic work exploring the potentiality of EXAFS as probe of phonon polarisation properties and testing the validity of different approximate models is still lacking.

EXAFS measurements have been done at the edge L_3 of iodine in AgI at the PULS beam line of the Frascati National Laboratories. The spectra were collected at various temperatures in the range 50 to 292 K. The measured sample was obtained by finely powdering single crystals of hexagonal β-AgI; this procedure produced a slight contamination due to the cubic γ phase. From the EXAFS point of view, the two phases are structurally equivalent within the first two coordination shells of iodine; also the phonon densities of states are very similar.[4]

By a standard analysis within the framework of the single electron, single scattering approximation we obtained the temperature variation of the EXAFS DW factors for the first and second coordination shells of iodine (4 Ag at 2.82 Å and 12 I at 4.59 Å, respectively) with respect to a reference temperature.[5] In the temperature range $50 \div 292$ K the slope of $\sigma^2(T)$ is much stronger for the second than for the first coordination shell of iodine (respectively triangles and circles in Fig. 1, where the experimental points have been upward shifted to match the calculated absolute values at 50 K.) This behaviour has been compared with the known vibrational properties of AgI by means of different interpretation schemes.

An uncorrelated Einstein model was fitted to the experimental data (Fig. 1a); the Einstein frequencies correspond to effective bond stretching force constants $f_1 = 26.9 Nm^{-1}$ and $f_2 = 7.5 Nm^{-1}$ for the I–Ag and I–I bonds, respectively. Bührer et al [4] obtained the best fit to phonon dispersion curves from neutron scattering by a valence shell model with bond stretching force constants $\lambda = 37 Nm^{-1}$ and $\mu = 4.5 Nm^{-1}$ for the I–Ag and I–I bonds, respectively. The discrepancy with EXAFS results can be attributed to the presence of long range Coulomb forces which are taken into account by additional parameters in the valence shell model.

The EXAFS DW factors are (neglecting higher order terms due to anisotropy) the average MSRDs over each coordination shell. In Table I we compare their temperature dependence with that of the MSDs calculated on the basis of the valence shell model,[4] (the calculated MSDs were in agreement at room temperature with XRD measurements). The MSDs terms alone give, for both I–Ag and I–I distances, a stronger slope than that found experimentally by EXAFS for I–I. The correlation term DCF= MSRD–MSD, negative for both distances, has a much larger influence

on the I–Ag than on the I–I bond.

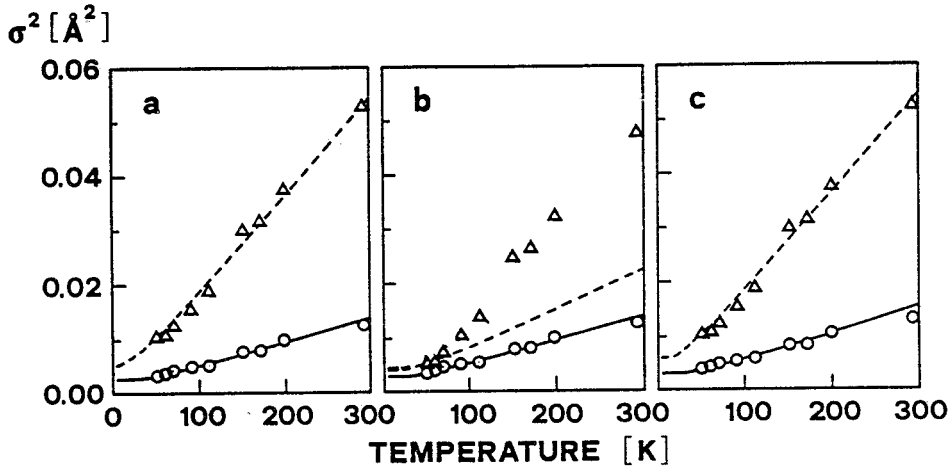

Figure 1

A Debye correlated model[1], based on the Debye temperature best fitting the specific heat above 50 K,[4] satisfactorily reproduces the experimental slope for the I–Ag DW but underestimates that for I–I (Fig.1b: continuous and dashed lines, respectively). The phonon spectrum of β-AgI is characterized by two nearly dispersionless low frequency ($\simeq$ 0.5 THz) optical branches[4] which are responsible for the high absolute values of MSDs but cannot be adequately accounted for by the Debye model. The result of Fig.1b suggests that the effect of the low frequency branches on the 1st shell DW is negligible due to a strong correlation of atomic motion.

To attempt a crude estimate of the influence of correlation on the EXAFS DW factors of AgI, we considered the eigenvectors of the 0.5 THz optical modes calculated at the centre of BZ for the β phase[6]. The corresponding atomic displacements of iodine and silver nearest neighbours are either in phase or perpendicular to the interatomic distances (Fig.2, left): the DCF cancels out the MSDs and the resulting MSRD is negligible. For the I–I distances the correlation of atomic motion is much less effective and correspondingly the MSRD is large (Fig. 2, right). By adding the contribution of the 0.5 THz optical modes to that of the Debye correlated model a good agreement with the experimental data was found (Fig.1c).

The above results show the possible dramatic effects of the correlation of ionic motion on the EXAFS DW factors. These effects can be directly evidenced by comparison with the XRD DW factors. The EXAFS DW factors carry peculiar information on average local polarization of vibrational modes. Their direct calculation from eigenvalues and eigenvectors of the dynamical matrix is sensitive to phase relationships between eigenvectors, and should help in discriminating between

different force constant models.

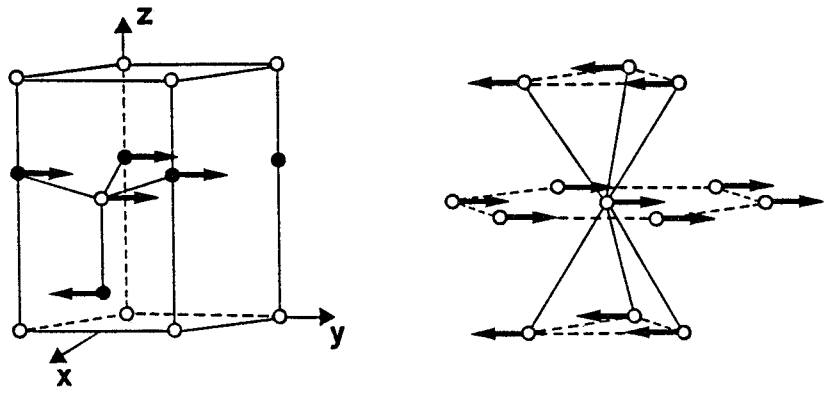

Figure 2

TABLE I: *Differences in $\AA^2$ between the values at 292K and the values at 50K:*

	I–Ag	I–I
MSRD from EXAFS	0.010	0.043
MSD from valence shell model	0.115	0.090

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