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[9] This is one order of magnitude smaller than the observed width of the *R* lines. The calculated ratio of the *R* lines. The calculated ratio of the broadening due to random crystal fields between $2\bar{A} \leftrightarrow \bar{E}$ and the *R* lines is ~ 0.1 (V. M. Hol and H. W. de Wijn, unpublished calculations), in agreement with our findings.

[10] At the highest excited-state populations reached in our experiments the interruption rate of a phonon $\sigma/T_{LB} \approx 10^4/10^{-6} = 10^{10}$ Hz is comparable with the resonance linewidth of 0.02 cm^{-1}, so that the reactive coupling (Ref. 4) between the phonons and the spins is beginning to play a part. In our case the effects are small, but in more concentrated ruby the coupling may be observable.

Cationic Short-Range Order in the Hollandite $K_{1.54}Mg_{0.77}T_{7.23}O_{16}$: Evidence for the Importance of Ion-Ion Interactions in Superionic Conductors

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Analysis of the diffuse x-ray scattering in the one-dimensional ionic conductor $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$ (hollandite) yields a detailed microscopic picture of the cationic short-range order. This order is characterized by large shifts of some ions off their crystallographic sites, evidencing that in a superionic conductor the ion-ion interaction may be stronger than the periodic potential of the host crystal.

The rapidly growing interest in electrochemical devices based on solid electrolytes has stimulated an intensive search for new materials with high ionic conductivities, the so-called superionic conductors.[1,2]

The mobile ions in a superionic conductor typically reside on a fractionally occupied sublattice with open pathways between adjacent sites. The number of sites available to the mobile ions is often not much larger than the number of occupied sites, and diffusion in such systems is no longer a single-particle process as described by the traditional random-walk theory. The path probability method by Sato and Kikuchi[3] is a major and significant step towards a correct description of diffusion in concentrated systems. More recently, Monte Carlo calculations have been performed on simple model systems[4] which go beyond the nearest-neighbor interaction of the path probability method.

Experimental and theoretical studies of the dynamics of ionic motion in superionic conductors[5] have shown that interaction among the mobile ions leads to structure in $\sigma(\omega)$ in the frequency range of a typical jump rate and affects the parameters describing the high-frequency behavior. The structure of the static short-range order among the mobile species gives in principle the most direct information about ion-ion interactions; but, unfortunately, the complex diffuse x-ray scattering observed in solid electrolytes[6-8] inhibits in general an unambiguous determination of the local atomic arrangement.

By considering a one-dimensional model system with the hollandite structure, I have now for the first time been able to obtain a precise microscopic picture of the state of order in a solid electrolyte. My results give direct evidence that the effective ion-ion interaction in a solid electrolyte is potentially of the same strength as the periodic potential of the host crystal. As a consequence, all models which treat ion-ion interactions in terms of occupational short-range order are incomplete, and it is necessary to include strong deviations of the equilibrium positions from crystallographic sites.

In the composition $K_{2x}Mg_xTi_{8-x}O_{16}$ $(0.75 \leq x \leq 1)$, hollandite[9,10] consists of a framework of edge- and corner-sharing TiO_6 and MgO_6 octahedra forming parallel, nonintercommunicating channels of nearly square cross sections along the *c* axis of the tetragonal unit cell. The distance between the potassium sites within the channels is 2.9 Å (equal to c, the length of the unit cell); in the investigated samples 77% of the channel sites were occupied (i.e., $x = 0.77$). Various authors have reported evidence of ionic motion in polycrystalline[11-13] and in pseudo-single-crystal hollandites.[14] I have grown optically pure single crystals of hollandites by a flux method.[15]

An example of diffuse scattering in hollandite is shown in Fig. 1. Extensive sampling of the diffuse intensity in reciprocal space showed that the diffuse scattering is localized in planes perpendicular to the c^* axis (i.e., the reciprocal channel axis). The order is thus predominantly one-dimensional (1D). The intensity variations within the planes indicates some 3D correlations which I shall neglect in the following, since they in no way affect my conclusions. A comparison with the hollandite $K_{1.54}Ti^{+3}_{1.54}Ti^{+4}_{6.46}O_{16}$ showed that diffuse scattering does not depend on the composition of the framework; thus, it originates exclusively from the potassium ions.

The diffuse intensity $I_{\text{exp}}(\vec{s})$ produced by the cationic short-range order is then

$$I_{\text{exp}}(\vec{s}) = NI_e f_k^2 I,$$

where $\vec{s}$ is the vector in reciprocal space, N the number of scattering K$^+$ ions, I_e the scattering of a single electron, f_k the scattering factor of the K$^+$ ion, and I the interference function which alone contains the structural information relevant here. The experimentally determined average value of I as a function of the distance from the central Bragg plane is shown in Fig. 2.

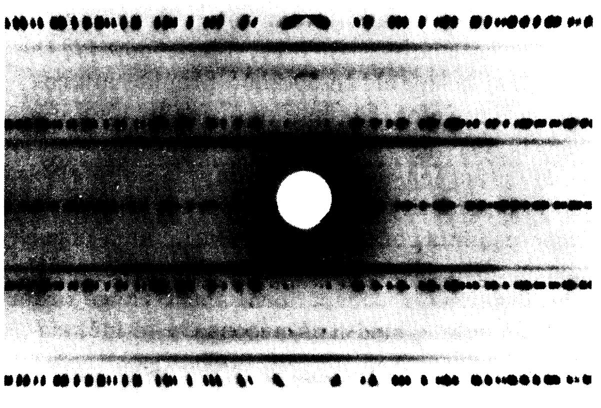

FIG. 1. Rotation photograph of x-ray scattering in the hollandite $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$. The rotation axis is parallel to the channels, the incident Mo $K\alpha$ radiation in a plane perpendicular to them. The rows of Bragg spots correspond to the (hkl) reflections with $l = 0$, ± 1, and ± 2. Weak spots in intermediate planes are due to $\lambda/2$ harmonic radiation.

The principal features of the diffuse scattering are these: (1) A diffuse plane situated at ±0.22 r.l.u. (reciprocal lattice units, 1 r.l.u. = 1/2.90 Å^{-1}) from the Bragg planes; and (2) the width of these planes is 0.08 r.l.u., which corresponds to a correlation length of 35 Å (i.e., twelve channel sites with respect to the Bragg planes), indicating both substitutional and displacive short-range order. Since the diffuse scattering originates only from the K$^+$ ions, one may abstract from the framework structure and base one's analysis on "channel unit cells," each containing just one channel site. In a first approximation, one may consider the diffuse scattering to occur in a superstructure with a fourfold unit cell along the channel axis. This "super" unit cell then contains four channel sites; by stoichiometry, there is on the average about one vacancy per supercell, and one is thus led to the supercell structure shown in Fig. 3, with the displacement parameter x. A regular sequence of such supercells within each channel, but with random displacements (by multiples of 2.90 Å, the channel site distance) between different channels, produces thin diffuse planes at $\frac{1}{4}$, $\frac{2}{4}$, and $\frac{3}{4}$ r.l.u. between the Bragg planes. In terms of the interference function, their intensity I is given by

$$I = f_{\text{sc}}^2 = \{1 + 2\cos[2\pi s(x+1)]\}^2,$$

where f_{sc} is the structure factor of the supercell,

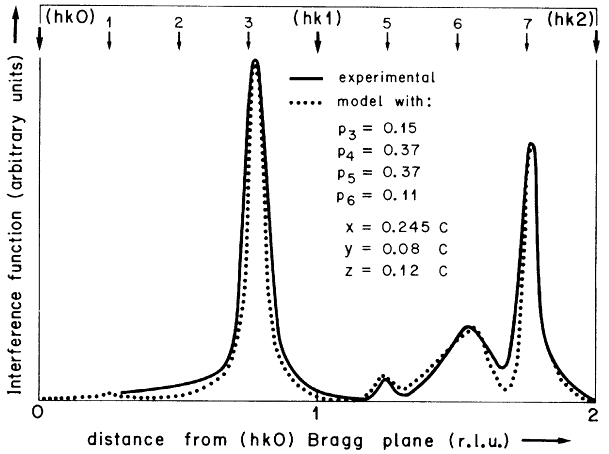

FIG. 2. Average value of the interference function as a function of the distance from the central Bragg plane derived from counter measurements. Heavy arrows indicate the positions of the Bragg planes; light arrows, the positions of diffuse planes according to the model shown in Fig. 3. The dotted line is a fit with the model based on a random sequence of the cells shown in Fig. 4.

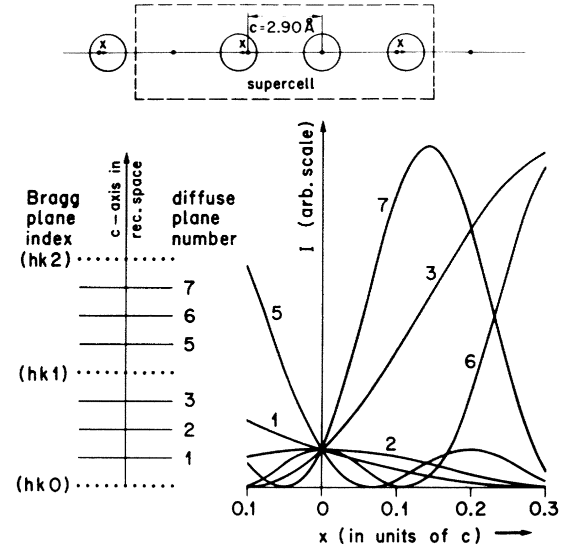

FIG. 3. Relevant features of the four-site model. Top, cell arrangement; left, corresponding diffuse planes in reciprocal space; right, interference function for the displacement x.

s the coordinate along the c^* axis (in r.l.u.), and x the displacement as defined in Fig. 3 in units of the site-to-site distance. As shown in the lower right of Fig. 3, the intensity of diffuse planes depends sensitively on x. Diffuse scattering in the hollandite is characterized by the dominance of the planes denoted 3 and 7 in Fig. 3 and a noticeable but weaker intensity on plane 6. This simple model thus indicates that x is of the order of 22%.

A more elaborate microscopic model has to account for the deviation of the stoichiometry from 75% occupation and for a certain randomness in the distribution of the vacancies which destroys the long-range correlation within the channels. As a natural extension of the foregoing model one may assume the channel order to consist of a random succession of supercells of variable lengths as those shown in Fig. 4, so that the average occupancy is 77%. We limit ourselves to cells containing three to six sites (with occurrence probabilities $p_3 \cdots p_6$); lengths differing too much from the average value of 4.3 are highly improbable because the electrostatic interaction tends to keep the vacancies at more or less regular intervals. Within each type of cell we introduce the displacements as defined in Fig. 4.

The diffuse scattering of such a state of order was computed following the treatment of lattice disorder by Guinier.[16] By averaging properly over all possible neighbor configurations, the correlations between the structure factors in different channel unit cells where computed; those are related to the Fourier coefficients of the interference function of the diffuse scattering. The best fit to the observed interference function and the values of the fitting parameters are shown in Fig. 2. The fit satisfactorily reproduces the peaks of finite width at incommensurate fractions between the regular Bragg planes. The widths of the diffuse planes are related to the broadness of the cell length spectrum (given by the quantities p_i). The slight discrepancy between experiment and model suggests that the assumed range of lengths is actually too narrow, i.e., there are also cells with less than three or more than six sites. The displacements of the ions adjacent to a vacancy, the principal parameter of our analysis, is independent of such details and turns out to be 24.5% of the site-to-site distance.

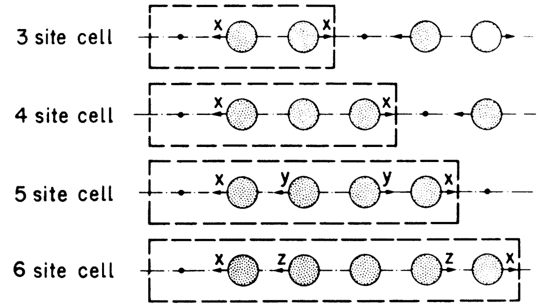

FIG. 4. Channel cells of variable lengths with the displacement parameter as used in the model computation.

While my interpretation of the diffuse scattering is an entirely static one, I do not imply, of course, that the state of order is not fluctuating locally on a time-scale slow compared to phonon frequencies. The large displacements indicate that ion-ion interactions are largely overriding the host crystal potential as a cationic ordering force. Since the regular sites are 2.90 Å apart, one can exclude the importance of short-range-order forces between the K^+ ions and may thus consider Coulomb repulsion to be the prime cause of the displacive short-range order.

A simple model may give a qualitative idea of the relative magnitude of the potentials involved. Assuming a sinusoidal host lattice potential of total amplitude $2V_0$ and an unscreened Coulomb interaction between the ions, one may compute the value of $2V_0$ that results in the observed 24% shift of the equilibrium positions of the ions neighboring a vacancy. It turns out that the barrier height would have to be of the order of 0.38 eV, i.e., 13 times less than the electrostatic interaction energy between neighboring ions. In reality the Coulomb interaction will be effectively screened by the very polarizable host lattice so that $2V_0$ must be correspondingly lower in order to remain consistent with the observed displacements.

It is beyond the scope of this Letter to elaborate on the consequences of this very peculiar situation. Barrier heights of tenths of electron volts are typical for superionic conductors; we therefore suggest that such a Coulomb-interaction-imposed order is characteristic of many solid electrolytes. It is evident that in a system with strong displacive short-range order, diffusion is by no means a single-particle process. For an understanding of the low-frequency and dc conductivity of superionic conductors, models have to be found which properly account for the constant trend to re-establish the short-range order during the diffusion of ions.

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Phonon Anomalies and Superconductivity in Transition-Metal Compounds

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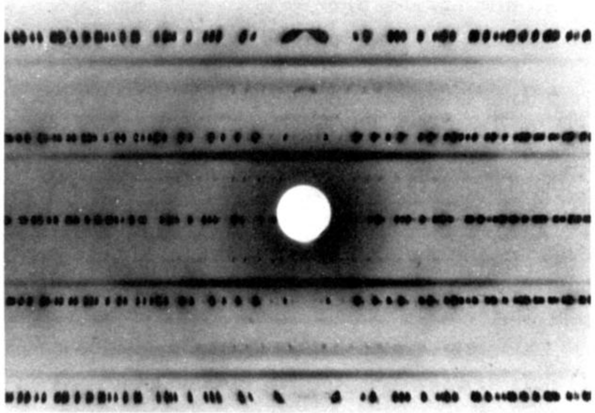
We present a physically simple but general argument that explains the phonon anomalies and their interrelation to high T_c's in transition-metal compounds. It is shown that covalent-bond formation due to hybridization of metal d (T_{2g}) states and nonmetal p states near E_F leads to a resonancelike increase of the nonlocal dielectric function. This anomalous increase of the screening produces the phonon softening and explains the interrelation with the high T_c's as resulting from a simultaneous increase of the electron-phonon matrix elements and a decrease in the phonon energies.

Neutron-scattering studies revealed the existence of phonon anomalies in superconducting transition-metal compounds (TMC) like carbides and nitrides,[1] thus establishing an empirical correlation between actual or incipient lattice instabilities and high transition temperatures, T_c. While several discussions of this correlation have been given,[2-8] it seems that there exists no microscopic theory which explains the interdependence of phonon softening and superconductivity.

We present a semiquantitative analysis based on a rigorous microscopic theory which, for the



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