Possibility of Observing Self-Interstitials in Cu and Al by Neutron Scattering*

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The librational modes of the ⟨100⟩-split interstitial in fcc metals can undergo resonant hybridization with the phonons of the perfect crystal. As in the analogous case of KCl :CN^-, this hybridization leads to effects which can be observed by inelastic neutron scattering at concentrations orders of magnitude smaller than those required for the observation of effects introduced by simple substitutional impurities.

The configuration of the self-interstitial in fcc metals has long been a matter of controversy. Very recently, however, experimental and theoretical studies have almost conclusively established that the split-interstitial or ⟨100⟩-dumbbell configuration is the correct one for copper[1] and aluminum[2] at low temperatures. The interstitial joins a host-lattice atom to form the dumbbell which resembles a diatomic molecule centered at a normal lattice site and oriented along a cubic axis. Large lattice distortions occur and the point symmetry around the interstitial site is reduced from O_h to D_{4h}. Calculations by Dederichs, Lehmann, and Scholz[3] for copper indicated that A_{1u} and E_g modes of the interstitial occur at frequencies of about $\frac{1}{7}$ of the maximum of the perfect-crystal copper phonon spectrum. The E_g mode is the twofold degenerate libration of the dumbbell, which is strongly coupled to elastic shear stresses; this coupling leads to the large effects on the shear moduli which have been observed.[1,2]

An analogous situation occurs in ionic crystals, where the introduction of molecular impurities with internal degrees of freedom whose frequencies lie within the host-crystal spectrum produces resonant phonon scattering and large effects on the shear elastic constants. Recently Walton, Mook, and Nicklow[4] have shown that in KCl doped with $6\times10^{19}/\text{cm}^3$ CN^- ions this resonant mixing is so large that it is easily observable by coherent inelastic scattering. It is important to understand that at such small concentrations the effects due to simple substitutional impurities with no internal degrees of freedom are not presently measurable by neutron scattering. In this Letter we show that the same kind of direct observation of the internal modes by neutron scattering should be possible for interstitials in aluminum and copper, provided that the concentration can be made high enough (~0.01%) and that annealing of the interstitials can be avoided.

An interstitial produces significant lattice distortions out to relatively large distances, and there may be substantial changes in the force constants between atoms in the region of relaxation. However, direct coupling to the interstitial, and hence to its internal modes, will remain restricted primarily to its first shell of neighbors. Resonant perturbations of the host-crystal phonons, characterized by frequency denominators of the form $1/(\omega^2-\omega_0^2)$, are produced by the mixing of the phonons with the internal modes. The A_{1u} and E_u modes of the interstitial correspond to its three center-of-mass translational motions. While they appear to have relatively low frequencies,[3] they do not represent additional degrees of freedom, do not lead to resonant denominators in the perturbations, and do not contribute directly to the elastic constants. Of the three internal modes, the A_{1g} vibration is expected to have a frequency well above the perfect-crystal spectrum. The E_g modes are the only ones that produce a resonant perturbation of the phonons which may possibly be observed directly by coherent inelastic neutron scattering. Here we adopt a somewhat simplified approach in which only the direct coupling to these E_g modes is included as a perturbation and lattice relaxation is not treated explicitly. Relaxation effects, insofar as they are not already contained in our parametrized calculations, could be included in a more rigorous treatment but they would increase the complexity of the analysis without adding significant physical insight into the problem. Our treatment follows the work of Wagner[5] and Klein.[6]

The equations of motion for the coupled system consisting of the lattice and the internal modes are

$$(\omega^2-D)u+(\lambda/M)x=0\,, \tag{1a}$$

$$(\lambda/M)u+(\omega^2-\omega_0^2)x=0\,. \tag{1b}$$

Here u and x are the mass-reduced dynamical coordinates for the lattice and the internal modes, respectively, D is the dynamical matrix of the perfect crystal, and M is the mass of a host atom. ω_0 is the frequency of the decoupled internal modes (i.e., with the lattice ions fixed), and λ is the vector of coupling coefficients between the internal modes and the lattice. Elimination of the internal coordinates yields

$$[\omega^2 - D - M^{-2}(\omega^2 - \omega_0^2)^{-1}\lambda\lambda]u = 0 . \tag{2}$$

This equation has the form $(\omega^2 - D - \Delta)u = 0$ encountered in localized perturbation theory for substitutional impurities without internal degrees of freedom, but the important difference is that Δ has a resonant denominator which can greatly enhance the interaction.

The one-phonon neutron coherent-scattering cross section at wave vector $\vec{q}$ and frequency ω is[7]

$$S_{\mathrm{coh}}(\vec{q}, \omega) \propto \lim_{\delta \to 0^+} \mathrm{Im} \sum_{j,j'} [\vec{q} \cdot \vec{\epsilon}(\vec{q}j)] G_{jj'}(\vec{q}, \omega + i\delta) [\vec{q} \cdot \vec{\epsilon}(\vec{q}j')] . \tag{3}$$

Here $\vec{\epsilon}(\vec{q}j)$ is the polarization vector for branch j and G is the Green's function for the crystal containing defects. Only the case in which $G_{jj'}$ is diagonal is considered here; this occurs along the major symmetry directions for defects of D_{4h} symmetry in cubic crystals. In the approximation of Elliott and Taylor,[8]

$$G_j(\vec{q}, \omega) = G_j^0(\vec{q}, \omega)[1 - cG_j^0(\vec{q}, \omega)\Sigma_j(\vec{q}, \omega)]^{-1}, \tag{4}$$

$$\Sigma_j(\vec{q}, \omega) = \vec{\epsilon}(\vec{q}j) \cdot \{\sum_{l,l'} \exp[i\vec{q} \cdot (\vec{R}_l - \vec{R}_{l'})\vec{t}(\vec{R}_l, \vec{R}_{l'})\} \cdot \vec{\epsilon}(\vec{q}j), \tag{5}$$

where G_j^0 is the unperturbed Green's function, Σ_j is the self-energy, c is the concentration of interstitials, and $\vec{R}_l$ is a lattice vector. The t matrix is $t = \Delta[1 - (1-c)G^0\Delta]^{-1}$, where from Eq. (2), $\Delta = M^{-2}(\omega^2 - \omega_0^2)^{-1}\lambda\lambda$.

The perturbation matrix Δ has nonzero elements between those neighbors of the dumbbell which are directly coupled to the E_g internal modes in Eqs. (1a) and (1b). We introduce symmetry coordinates which are linear combinations of the displacements of the neighboring ions transforming according to the irreducible representations of D_{4h}. The t matrix is then block diagonal and since Δ has E_g symmetry, only the E_g block is nonzero; for coupling to first neighbors this reduces to two identical 4×4 matrices if the E_g basis functions are chosen appropriately. For each of these 4×4 matrices, the matrix $\lambda\lambda$ is a simple diadic, i.e., $(\lambda\lambda)_{ij} = \lambda_i\lambda_j$. A principal-axes transformation can be carried out so that the diadic becomes diagonal with only one nonzero element of magnitude λ^2. The transformed t matrix then also has only one nonzero element. For the self-energy, the result of all these transformations is

$$\Sigma_j(\vec{q}, \omega) = (qa)^2 f_j(\vec{q})\omega_1^4/(\omega^2 - \Omega_0^2), \tag{6}$$

in which $\omega_1^2 = \lambda/M$ and a is the lattice constant. $f_j(\vec{q})$ is a dimensionless geometrical function which is a sum of terms of the form $\sin(\vec{q} \cdot \vec{R}_l)\sin(\vec{q} \cdot \vec{R}_{l'})/(qa)^2$; for $\vec{q} \to 0$, it approaches a constant value quadratically. The internal-mode frequency, renormalized by the defect-lattice interaction, is

$$\Omega_0^2 = \Omega_{0r}^2 + i\Omega_{0i}^2 = \omega_0^2 + (1-c)\omega_1^4[\mathrm{Re}\bar{G}^0(\omega) + i\,\mathrm{Im}\bar{G}^0(\omega)] , \tag{7}$$

where $\bar{G}^0$ is the appropriate element of the transformed G^0. Here $c \ll 1$, so Ω_{0r} and Ω_{0i} are essentially independent of concentration. From Eqs. (4), (6), and (7), and using $G_j^0 = [\omega^2 - \omega^2(\vec{q}j)]^{-1}$, where $\omega(\vec{q}j)$ is the perfect-crystal phonon frequency at $\vec{q}j$, we find

$$\mathrm{Im}G_j(\vec{q}, \omega) = \frac{c(qa)^2 f_j(\vec{q})\omega_1^4\Omega_{0i}^2}{\{[\omega^2 - \Omega_+^2(\vec{q}j)][\omega^2 - \Omega_-^2(\vec{q}j)]\}^2 + \{\Omega_{0i}^2[\omega^2 - \omega^2(\vec{q}j)]\}^2}, \tag{8}$$

$$\Omega_\pm^2(\vec{q}j) = \tfrac{1}{2}\{\omega^2(\vec{q}j) + \Omega_{0r}^2 \pm [(\omega^2(\vec{q}j) - \Omega_{0r}^2)^2 + 4c(qa)^2 f_j(\vec{q})\omega_1^4]^{1/2}\} . \tag{9}$$

In the limit $\Omega_{0i} \to 0$, $\mathrm{Im}G_j(\vec{q}, \omega)$ has δ-function peaks at $\Omega_\pm(\vec{q}j)$. Then, precisely at resonance between the lattice mode and the renormalized internal modes, i.e., for $\omega^2(\vec{q}j) = \Omega_{0r}^2$, the peak frequencies are given to lowest order in c by

$$\Omega_\pm(\vec{q}j) = \Omega_{0r} \pm \tfrac{1}{2}\sqrt{c}\; qa[f_j(\vec{q})]^{1/2}(\omega_1^2/\Omega_{0r}); \tag{10}$$

an expression for the splitting, $\Delta\Omega(\vec{q}j)=\Omega_+(\vec{q}j)-\Omega_-(\vec{q}j)$, follows immediately. At resonance, and for $\Omega_{0i}{}^2\rightarrow 0$, the δ-function peaks at $\Omega_\pm$ in $\operatorname{Im}G_j(\vec{q},\omega)$ have the same strength to zeroth order in c. For finite values of Ω_{0i}, the situation becomes more complicated. If $\Omega_{0i}{}^2<\sqrt{2}\,\Omega_{0r}\Delta\Omega(\vec{q}j)$ at resonance, $\operatorname{Im}G_j(\vec{q},\omega)$ still has two peaks, but they are separated by less than $\Delta\Omega(\vec{q}j)$; for $\Omega_{0i}{}^2>\sqrt{2}\,\Omega_{0r}\Delta\Omega(\vec{q}j)$, $\operatorname{Im}G_j(\vec{q},\omega)$ has a single broadened peak at $\omega=\omega(\vec{q}j)=\Omega_{0r}$.

The effects of the internal modes on the elastic constants can be obtained by considering the $\vec{q}\rightarrow 0$ behavior of $\Omega_-(\vec{q}j)$. In this limit, $\omega^2(\vec{q}j)=v_j{}^2q^2=(C_j/\rho)q^2$, and

$$\Omega_-{}^2(\vec{q}j)=v_j{}'^2q^2=(C_j{}'/\rho)q^2=[v_j{}^2-ca^2f_j(0)(\omega_1{}^2/\Omega_{0r})^2]q^2\,, \tag{11}$$

where ρ is the density, and v_j, C_j and $v_j{}', C_j{}'$ are the sound velocities and elastic constants in the perfect and perturbed crystals. The fractional change in elastic constant per unit concentration is

$$\eta_j\equiv(C_j{}'-C_j)/cC_j$$
$$=-[\rho a^2f_j(0)/C_j](\omega_1{}^2/\Omega_{0r})^2\,. \tag{12}$$

A relationship between the splitting at resonance and η_j can be obtained by making two assumptions: (1) q is small enough to replace $f_j(\vec{q})$ by $f_j(0)$ in Eq. (10) and (2) $\overline{G}^0$ in Eq. (7) is approximately the same at resonance as at $\omega=0$. The first of these should be quite valid for the systems considered here because the resonances occur at small values of $\vec{q}$. The second assumption is less easily justified because $\omega_1{}^4$ in Eq. (7) is a large number and even small changes in $\overline{G}^0(\omega)$ can have large effects on Ω_0. Our calculations indicate that this assumption is quite valid for KCl:CN$^-$ but somewhat less so for Cu and Al. With these two assumptions, we find from Eqs. (10) and (12) that

$$\Delta\Omega(\vec{q}j)=\sqrt{c}\,v_jq(-\eta_j)^{1/2}\,, \tag{13}$$

a simple and useful result that contains no theoretical parameters.

We have carried out extensive calculations of S_{coh} for interstitials in Cu and Al and for KCl:CN$^-$. The matrix elements of G^0 in real space were constructed by Brillouin-zone integration and Kramers-Kronig dispersion relations. For copper, the frequency ω_0 and the vector λ were restricted to be roughly consistent with the force-constant estimates of Dederichs, Lehmann, and Scholz[3] and adjusted to give $\Omega_{0r}\simeq\frac{1}{7}\omega_{\max}$. The Cu values were subsequently used as a guide for the Al calculations. For KCl:CN$^-$, Ω_0 is known quite accurately from infrared measurements. In all three cases, the η's calculated directly from the dispersion curves were forced to be close to the measured values.

Figure 1 shows the hybridization between the internal modes and the TA phonons along the [100] direction in copper; the curves were plotted directly from the peaks in S_{coh}. The concentration is the same as that used by Walton, Mook, and Nicklow for KCl:CN$^-$ and the calculations indicate that the hybridization effect should be even greater for the interstitials in Cu and Al if this concentration could be reached. At $q=0$ in Fig. 1, there is a modest but non-negligible difference between $\Omega_{0r}(\omega=0)$, shown as the dashed horizontal line, and $\Omega_{0r}(\omega=\Omega_{0r})$. This implies that the validity of the second assumption leading to Eq. (13) is beginning to break down, i.e., the change in Ω_{0r} and Ω_{0i} in going from $\omega=0$ to $\omega\approx\Omega_{0r}$ is not negligible. As indicated by Fig. 1, the calculated curves for S_{coh} in the region of resonance exhibit a two-peaked structure for $c=0.0037$. Calculations were also performed for two much lower concentrations ($c=0.0006, 0.000\,06$); for these cases, $\Omega_{0i}{}^2>\sqrt{2}\,\Omega_{0r}\Delta\Omega$ as discussed above, and single broadened peaks are produced. Table I lists results for Cu and Al interstitials and for KCl:CN$^-$. The final column gives values for the splitting at resonance calculated from Eq. (13) using the measured values of η.[1,2,9] As already

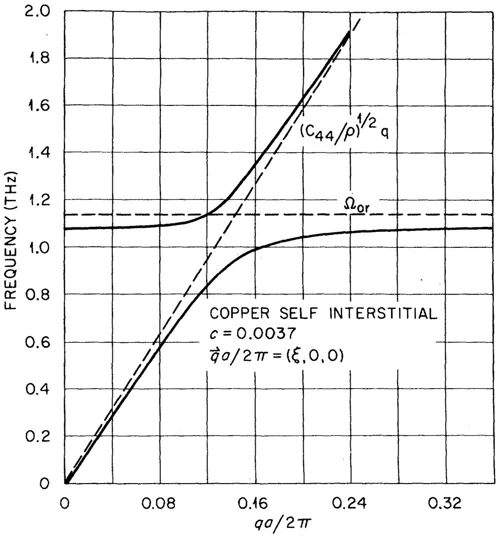

FIG. 1. Hybridization between internal and phonon modes in copper containing self-interstitials.

TABLE I. Results for Cu, Al, and KCl:CN$^-$. c is the concentration in parts per million, N the number of defects in units of $10^{18}/\text{cm}^3$, η is dimensionless, and $\Delta\nu = \Delta\Omega/2\pi$ is in THz.

	c	N	η	$\Delta\nu$
Cu	3700	310	-30[a]	0.40
	600	50		0.16
	60	5		0.05
Al	3700	230	-27[a]	0.37
	800	50		0.17
	80	5		0.05
KCl:CN$^-$	3700	6	-32[b]	0.16

[a] η related to C_{44}.

[b] η related to $C_{11}-C_{12}$.

mentioned, Eq. (13) appears to be a good approximation in KCl:CN$^-$, but in Cu and Al it appears to overestimate the splitting. However, since we are not certain of the experimental value of Ω_0 it is not yet possible to evaluate the accuracy in these cases.

The priciple question of interest here, of course, is whether or not the internal modes can be observed directly by neutron scattering via their coupling to the lattice modes. Table I clearly shows the problem. Whereas it is relatively easy to obtain a concentration of $c = 0.0037$ CN$^-$ ions in KCl it is not likely that this concentration of interstitials in fcc metals can be obtained. With present experimental techniques in neutron scattering, splittings, shifts, and broadenings of the order of 0.05 THz can be observed. Table I suggests that a concentration of 0.000 06 in Cu gives at best a marginal chance for observing the effects due to internal modes. At a concentration of 0.0006 on the other hand, both Table I and our calculations of S_{coh} indicate that the hybridization effects should be observable in a carefully controlled experiment. We believe that the direct observation of the internal modes of the split interstitial in fcc metals awaits only the attainment of the proper concentration in the near future.

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New Liquid-Crystal Phase Diagram

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The nematic–smectic-*A* transition temperature of mixtures of HBAB {*p*-[(*p*-hexyloxybenzylidene)-amino] benzonitrile} and CBOOA [N-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline] becomes multivalued with increasing concentration of HBAB. The nematic phase occurs at both a higher and a lower temperature than the smectic phase. Measurements of the bend elastic constant as a function of concentration are presented.

By mixing HBAB[1] {*p*-[(*p*-hexyloxbenzylidene)-amino] benzonitrile} in CBOOA[2] (N-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline) (Fig. 1), I have found that a smectic phase may be formed which reverts to the nematic phase at still *lower* temperatures. As far as I can ascertain, this is the first time such an effect has been observed. Measurements of the bend elastic constant, K_3/χ_a, on