

Phonon-Internal-Mode Hybridization in KCl:CN^-

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(Received 2 May 1977)

Recent work has shown that the resonant mixing of defect internal modes with lattice phonons can lead to striking modifications of the one-phonon coherent neutron-scattering cross section. Here, line shapes for phonons in KCl:CN^- are calculated from a two-level model and shown to agree reasonably well with experiment. Our results demonstrate that neutron scattering can be used to study the coupling of complex defects with the lattice even at very low defect concentrations.

In the first neutron-scattering experiments performed to observe the resonant mixing of impurity internal modes with lattice modes, Walton, Mook, and Nicklow¹ reported new structure in the one-phonon coherent cross section of KCl doped with CN^- ions. More recently, Nicklow *et al.*² have shown that $\langle 100 \rangle$ -split or dumbbell self-interstitials in copper, at a concentration of approximately 40 ppm, produce measurable shifts from the unperturbed phonon frequencies; these shifts had already been predicted theoretically.^{3,4} There is also some preliminary indication from neutron scattering experiments⁵ that thermally generated Ag^+ interstitials in AgBr behave as molecularlike impurities which strongly interact with the lattice phonons. These three sets of observations are important because they demonstrate that complex defects with their own internal degrees of freedom can have effects on the host-lattice phonons which are measurable by inelastic neutron scattering at very low concentrations (much lower than those required for simple substitutional impurities). Thus, the powerful tool of neutron scattering becomes available for a direct study of the lattice dynamics of these systems. From a theoretical standpoint, KCl:CN^- is a particularly attractive material in which to study phonon-internal-mode hybridization because a large body of experimental data from infrared, ultrasonic, and other measurements already exists on it. In this Letter, we show that adaptation of a simple two-level theory of internal-mode-phonon resonant mixing to the neutron-scattering case is capable of giving reasonably good agreement with experiment for KCl:CN^- .

Substitutional CN^- impurities in the alkali halides appear to behave as hindered rotators.⁶ Recent experiments by Lütty⁷ and Beyeler⁸ indicate that the rotational ground state is a tunnel-split multiplet involving the eight equivalent $\langle 111 \rangle$ orientations of the CN^- ions. An approximate de-

scription of the energy levels for CN^- ions in KCl has been given by Beyeler,^{8,9} who fitted a modified Devonshire potential to the observed level spacing in the ground-state multiplet and to the average splitting of the lowest excited states from the ground state. Ultrasonic measurements by Byer and Sack¹⁰ indicate particularly strong coupling of the interlevel transitions to E_g and T_{2g} lattice modes. Results taken from Beyeler's papers are shown in Fig. 1, which also shows the allowed transitions involving E_g and T_{2g} host-lattice phonons.

Since the work reported in Ref. 1, Nicklow⁵ has undertaken a more comprehensive study of the KCl:CN^- system, and some of his results are shown by the open circles and solid curves in Fig. 2. These results are for the transverse-acoustic modes of E_g character propagating along the $[1\bar{1}0]$ direction. A two-peaked structure is

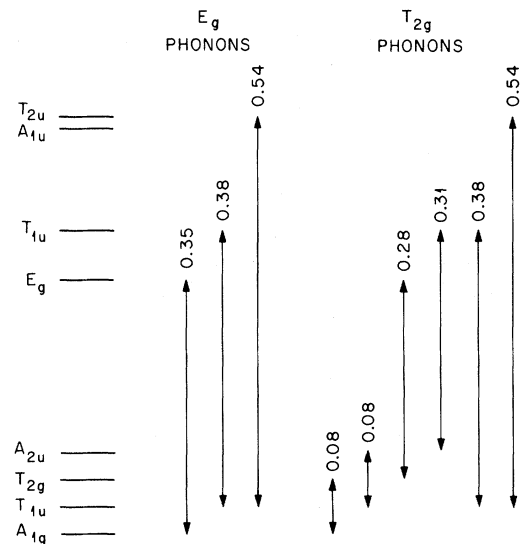


FIG. 1. Approximate level spacings and allowed E_g , T_{2g} transitions (in units of terahertz) for CN^- in KCl, from Beyeler (Refs. 8 and 9).

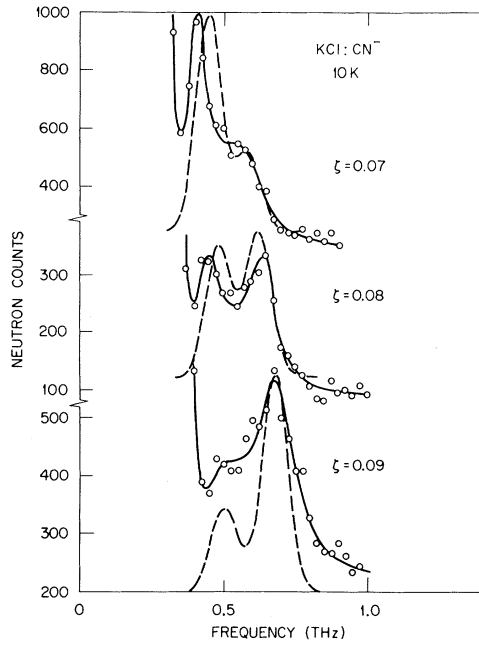


FIG. 2. Neutron scattering from KCl containing 3700-ppm CN^- -ion impurities. The results shown are for phonons with wave vectors $\vec{q} = (2\pi/a)(\xi, \xi, 0)$, polarized in the $[1\bar{1}0]$ direction. The sharp increase in intensity at low frequencies is due to the tail of the Bragg peak.

observed for this branch, and the intensity shifts from the lower-frequency peak to that at higher frequency as the wave vector is varied through resonance. The resonance frequency of approximately 0.5 THz is consistent with one of the E_g transitions shown in Fig. 1.

Along major symmetry directions in reciprocal space for cubic crystals, the coherent one-phonon cross section is branch diagonal,

$$S_{\text{coh}}(\vec{q}, j; \omega) \propto \text{Im}G(\vec{q}, j; \omega). \quad (1)$$

Here \vec{q} is the scattering wave vector, j the branch index, and $\hbar\omega$ is the energy transfer. $G(\vec{q}, j; \omega)$ is the phonon Green's function, defined in the usual way as the Fourier transform of the retarded displacement-displacement correlation functions. For a low concentration c of impurities, the Green's function is given by¹¹

$$G(\vec{q}, j; \omega) = [\omega^2 - \omega^2(\vec{q}, j) - ct(\vec{q}, j; \omega)]^{-1}, \quad (2)$$

where $\omega(\vec{q}, j)$ is a host-crystal phonon frequency, and $t(\vec{q}, j; \omega)$ is the scattering matrix for a single impurity.

Klein¹² has treated the resonant scattering of lattice modes by a substitutional impurity which has two energy levels at $\pm \frac{1}{2}\hbar\omega_0$ in the static lat-

tice. The t matrix for a two-level impurity can be written in the form

$$t(\vec{q}, j; \omega) = \frac{\lambda^2 f_e(\omega_0/\omega_r)}{\omega^2 - \Omega_0^2(\omega, T)} \langle \eta \rangle F(\vec{q}, j). \quad (3)$$

Here λ is a coupling parameter which scales as the square of a frequency, f_e is an oscillator strength, and $F(\vec{q}, j)$ is a dimensionless geometrical factor. $\Omega_0(\omega, T)$ is a complex, renormalized internal-mode frequency given by

$$\begin{aligned} \Omega_0^2(\omega, T) &= \text{Re}\Omega_0^2(\omega, T) + i \text{Im}\Omega_0^2(\omega, T) \\ &= \omega_0^2 - \lambda^2 f_e(\omega/\omega_r) g_T(\omega + i\epsilon); \end{aligned} \quad (4)$$

ω_r is the frequency at which resonance occurs, determined from Eq. (4) by $\omega_r^2 = \text{Re}\Omega_0^2(\omega_r, T)$. The imaginary and real parts of the temperature-dependent Green's function g_T in Eq. (4) are, respectively,

$$\begin{aligned} \text{Im}g_T(\omega) &= (\pi/2\omega) \coth(\hbar\omega/2KT) \\ &\times \sum_{\vec{q}, j} X^2(\vec{q}, j) \delta(\omega - \omega(\vec{q}, j)), \end{aligned} \quad (5)$$

$$\text{Re}g_T(\omega) = 2\pi\omega P \int_0^\infty d\omega' \frac{\text{Im}g_T(\omega')}{\omega'^2 - \omega^2}, \quad (6)$$

in which $X^2(\vec{q}, j)$ gives the projection of the host-crystal mode specified by (\vec{q}, j) onto a suitably chosen local symmetrized coordinate, X , involving the displacements of the neighbors of the impurity. Finally, $\langle \eta \rangle \approx \tanh(\hbar\omega_r/2KT)$ represents the thermal population difference between the ground and excited states of the impurity.

The coherent neutron-scattering cross section is found by substituting the t matrix given by Eq. (3) into Eq. (2) for $G(\vec{q}, j)$ and taking the imaginary part. As discussed by the authors in connection with self-interstitials in fcc metals,³ the scattering cross section can exhibit a two-peaked structure or a resonance-frequency shift and line broadening, depending on the size of the damping represented by $\text{Im}\Omega_0^2(\omega, T)$. Furthermore, a long-wavelength expansion shows that the velocity of sound for sound waves of the appropriate polarization is reduced by the resonant lattice-impurity coupling; this reduction is proportional to the impurity concentration, and for the two-level impurity, unlike an impurity with vibrational internal modes, is strongly temperature dependent, in agreement with the ultrasonic measurements of Byer and Sack.¹⁰

As shown in the approximate energy-level diagram in Fig. 1, the CN^- ion in KCl is a multilevel impurity. A theory for the multilevel impurity can be developed¹³ along the lines used by Klein

for the two-level system. To determine the t matrix for a multilevel impurity, a superficially formidable set of matrix equations must be solved to determine the contributions from the various pairs of levels, and the results summed to find the total. Qualitatively, there are two principal new features of these more complicated equations: First, a lattice mode of a given local symmetry may have a resonant coupling to two or more interlevel transitions; second, there are temperature-independent as well as temperature-dependent self-energy terms. A multilevel impurity can therefore produce more complicated structure and temperature dependence in the neutron-scattering cross section than a two-level impurity.

We have used the two-level model corresponding to Eqs. (1)–(6) in extensive calculations; only a few of the more important details and results can be given here. $\text{Im}g_T(\omega)$ was calculated by integrating over the Brillouin zone, and $\text{Re}g_T(\omega)$ was then determined numerically from Eq. (4). Details of this type of calculation have been given elsewhere.¹⁴ The symmetrized coordinates X used for the calculation were the E_g modes of the six nearest neighbors of the CN^- ion. The parameters ω_0 and $\lambda^2 f_e$ were varied until a value of the resonance frequency, ω_r , was obtained that was in approximate agreement with the value of 0.54 THz shown in Fig. 1 for E_g phonons, and the splitting between the two peaks in the neutron-scattering cross section at $\zeta = 0.08$ was approximately that measured at 10 K. The results of this calculation are shown in Fig. 2 by the dashed curves; they closely resemble the corresponding experimental curves, although the peak splittings are somewhat too small. We found that $\nu_0 = \omega_0/2\pi = 1.65$ THz, and $\lambda^2 f_e$ corresponded to a frequency $\nu_1 = (K/M)^{1/2}$, where $K = 16\,400$ dyn/cm and M is the mass of a potassium atom. These values confirm that the coupling between the impurity and the lattice is relatively strong.

We have also performed calculations of $\delta C/NC$ as a function of temperature, where N is the number of defects per cubic centimeter³ and $\delta C/C$ is the relative change in the particular elastic constant of interest, $C = C_{11} - C_{12}$. The overall shape of the results was very close to that observed experimentally,¹⁰ but the values of the elastic-constant changes, like the peak splittings, were somewhat too small. The form of the equations suggests that we need to take somewhat larger values of ω_0 and $\lambda^2 f_e$ while keeping the value of ω_r fixed. This may be done by increasing the in-

teractions with the first-nearest-neighbor ions or by including interactions with second or further neighbors.

Corresponding to the temperature dependence of the elastic constants, the splitting of the neutron-scattering peaks decreases with increasing temperature such that by 120 K the effect of the resonant perturbation has very nearly vanished. The calculated and measured temperature dependences are in reasonably good overall agreement, but theoretically there is a shift in intensity, for phonons with \vec{q} values in the resonance region, from the lower peak to the higher peak as the temperature is raised. This shift, which apparently has not yet been observed experimentally, is produced mainly by the temperature dependence of $\Omega_0(\omega, T)$. There also seems to be some evidence from the experimental data that the two-level model used here may underestimate the magnitude of the residual shifts in the phonon dispersion curves which are still observed at 120 K.

We conclude that the simple two-level impurity model used here gives reasonably good agreement with the neutron-scattering data presently available for KCl:CN^- . A multilevel treatment could be applied to this system if the theoretical and computational complications introduced by such a treatment were warranted by more extensive experimental results. From a more general point of view, it now seems clear that neutron scattering can be used to investigate a whole class of defect problems in a very direct manner. This is of interest not only for insulators such as KCl:CN^- , but especially for metallic systems where optical measurements cannot be used.

The authors are grateful to R. M. Nicklow for many helpful discussions. This research was sponsored by the U. S. Energy Research and Development Administration under contract with the Union Carbide Corporation.

¹D. Walton, H. A. Mook, and R. M. Nicklow, *Phys. Rev. Lett.* **33**, 412 (1974).

²R. M. Nicklow, R. R. Coltman, F. W. Young, Jr., and R. F. Wood, *Phys. Rev. Lett.* **35**, 1444 (1975).

³R. F. Wood and Mark Mostoller, *Phys. Rev. Lett.* **35**, 45 (1975).

⁴H. R. Schober, V. K. Tewary, and P. H. Dederichs, *Z. Phys. B* **21**, 255 (1975).

⁵R. M. Nicklow, in *Proceedings of the Conference on Neutron Scattering, Gatlinburg, Tennessee, 1976*, edited by R. M. Moon, CONF-760601 (National Tech-

nical Information Service, Springfield, Va., 1976), Vol. 1, p. 117. See also R. F. Wood and Mark Mostoller, *ibid.*, p. 160.

⁶V. Narayanamurti and R. O. Pohl, *Rev. Mod. Phys.* **42**, 201 (1970).

⁷F. Lüty, *Phys. Rev. B* **10**, 3677 (1974).

⁸H. U. Beyeler, *Phys. Rev. B* **11**, 3078 (1975).

⁹H. U. Beyeler, *Phys. Status Solidi* **52**, 419 (1972).

¹⁰N. E. Byer and H. E. Sack, *Phys. Status Solidi* **30**,

569 (1968).

¹¹R. J. Elliott and D. W. Taylor, *Proc. Roy. Soc. London, Ser. A* **296**, 161 (1967); K. Lakatos and J. A. Krumhansl, *Phys. Rev.* **180**, 729 (1969).

¹²M. V. Klein, *Phys. Rev.* **186**, 839 (1969).

¹³Mark Mostoller, unpublished.

¹⁴R. F. Wood, *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1976), Vol. 15, p. 119.

Three Surface Resonances on the (100) Face of W and Mo: An Angle-Resolved Synchrotron Photoemission Study

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(Received 18 July 1977)

We have studied the surface resonances on Mo(100) and W(100) with angle-resolved, $\hbar\omega$ -dependent photoemission using synchrotron radiation. For normal emission, two resonances are seen. They are located 0.3 and 3.3 (0.4 and 4.2) eV below E_F for Mo (W). The high-lying resonance remains symmetric and narrow for all photon energies used. Its intensity peaks at $\hbar\omega = 15$ and 30 (14 and 29) eV for Mo (W). For $\theta \geq 2^\circ$, a second high-lying resonance appears a few tenths of an eV below the first one. Many-body phenomena are not required to explain the data.

To explain the surface resonances observed in our field-emission measurements¹ of Mo(100), we have recently presented a parametrized linear-combination-of-atomic-orbitals calculation^{1,2} of the \vec{k}_{\parallel} - and orbital-resolved surface local density of states. We noted that this calculation could also serve as a theoretical basis for most of the previous angle-resolved photoemission studies of this resonance feature on W(100).³ However, recent photoemission studies of this resonance on both W(100)^{4,5} and Mo(100)⁶ seem to have generated considerable confusion and debate regarding the origin and characteristics of these surface resonances as well as the applicability⁶ of our tight-binding Green's-function calculation.¹

In this Letter, we report on angle-resolved photon-energy-dependent photoemission studies of W(100) and Mo(100) using synchrotron radiation. Our results on both metals are in sharp contrast to the previous reports by Egelhoff, Linnett, and Perry,⁴ by Feuerbacher and Willis,⁵ and by Noguera *et al.*⁶; and, considering the simplicity of the model, in amazingly good agreement with our calculation.¹ First, we find that for normal emission, the well-known high-lying resonance^{7,8} remains symmetric and sharp for $\hbar\omega$ between 10 and 40 eV. The peak width of this resonance is nearly identical with the width ob-

served in a field-emission energy distribution.^{1,7,8} Second, we find that, for emission angles θ greater than 2° , a second high-lying surface resonance appears just a few tenths of an eV below the first one, as predicted in our previous paper.¹ Third, our measurements confirm the existence of a low-lying surface resonance on both metal surfaces.^{1,9,10} Fourth, the overall dispersion of these resonances within the surface Brillouin zone (SBZ) is compatible with our \vec{k}_{\parallel} -resolved calculation.^{1,2} Fifth, we find that it is not necessary to invoke many-body phenomena to explain the photoemission from these resonances.

Angle-resolved photoemission spectra were obtained at the 240-MeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin using the same analyzer as recently used by Allyn, Gustafsson, and Plummer.^{11,12} The analyzer has an acceptance of $\pm 2^\circ$ and is independently rotatable around two orthogonal axes.¹² Its resolution is ≥ 0.12 eV.

In order for us to identify a peak in a photoemission energy distribution as a surface state/resonance, we feel that four criteria have to be fulfilled: (1) It should be sensitive to contamination. (2) Its energy position should be independent of the photon energy. (3) It should be consistent with (our) angle-integrated photoemission results.⁹ (4) It should be consistent with (our)