Fermi Resonance in the Phonon Spectra of Copper Halides

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Several theoretical concepts such as two-phonon bound states, off-center ions, and Fermi resonances have been suggested to explain the strong anomalies in the phonon spectra of copper halides, with no conclusive results. We take into account the anharmonic coupling of the TO(Γ) phonons with the two-phonon states and calculate the line shapes in the framework of an anharmonic valence-shell model. We show that the anomalies are Fermi resonances; other mechanisms need not be invoked.

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The phonon spectra of copper halides exhibit unusual features, in particular, the double-peak structure of the long-wavelength transverse-optic mode, TO(Γ), in CuCl.[1-7] Various explanations of these anomalies have been given in recent years, e.g., a mixture of one- and two-phonon spectra[1-4] (superposition model), a near degeneracy of the TO mode and two-phonon states (Fermi-resonance model) involving a two-phonon bound state,[5,6] and an off-center position of the Cu^+ ion (defect model).[7] While the superposition model was ruled out experimentally[6] the other models are still under discussion. Despite these efforts, no conclusive calculation exists up to now for any of these models that quantitatively reproduces the experimental data and rules out the other models.

In this Letter we give evidence for a strong Fermi resonance in CuCl, a weak one in CuBr, and an even weaker one in CuI. A Fermi resonance occurs if the frequency of a quasiharmonic phonon nearly coincides with the frequency of two-phonon combination bands at a high density of states and if the two-phonon states are coupled to the one-phonon state by a cubic anharmonicity. This phenomenon, though rather well known in molecules and for defect modes,[8] seems to be rare in perfect solids. We were stimulated by a recent study of the pressure dependence of the Raman spectra of the copper halides by Blacha, Kourouklis, and Cardona.[9] These data show new anomalous features and seem to obscure the situation even more.

We started out by reinvestigating the lattice dynamics of these compounds in terms of a valence-shell model used by Kunc and Bilz.[10] This model describes very well both the phonon dispersion curves and the Raman spectra of III-V and II-VI compounds with zinc-blende structure. In addition, it seems to be one of the few models which give satisfactory results for the phonon eigenvectors in GaAs.[11] The model represents a successful combination of the shell model with the valence–force-field model and also allows us to take into account the effect of overlap polarization. The values of the model parameters as obtained by least-squares fitting to the neutron data[12-14] are given in Table I. The dispersion curves of CuCl are shown in Fig. 1. The calculations reproduce the measured data within experimental error. A detailed discussion of the lattice dynamics will be given elsewhere.[15]

In Fig. 2 the two-phonon densities of states are shown for all three compounds. For CuCl, one observes a position of the TO(Γ) mode near 5 THz in the middle of a $TA(X)+LA(X)$ summation band and of a $TO(X)-TA(X)$ difference band between 4 and 6 THz. Therefore, in this case, a strong temperature-dependent Fermi resonance is expected. In CuBr, the TO(Γ) mode has moved from the middle part to the upper tail of the $LO(X)-TA(X)$ difference band. This corresponds to a more off-resonant situation. In CuI the situation is similar to that in CuBr but even less resonant.

These statements find a quantitative description in a complete numerical calculation of the TO(Γ) phonon line shape given by

$$I(\omega)=\frac{\Gamma(\omega)}{[\omega_{TO}+\Delta(\omega)-\omega]^2+\Gamma^2(\omega)}, \quad (1)$$

where $\Delta(\omega)$ and $\Gamma(\omega)$ are the real and the imaginary

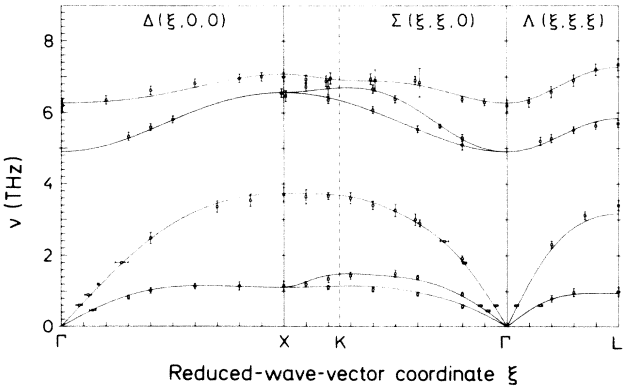

FIG. 1. Phonon dispersion curves of CuCl at 4.2 K. The solid curves are calculated with a ten-parameter valence-overlap shell model. The symbols represent the experimental data of Prevot *et al.* (Ref. 12).

TABLE I. Parameters of the anharmonic valence-overlap shell model. (Units: λ and all k in e^2/v_a, Z and Y in proton charges e, λ_α in $e^2/r_1 v_a$, and Δ_0 in terahertz.) Primed symbols refer to anion sites, and r_1 and r_2 to first- and second-neighbor distances, respectively.

Model parameters	CuCl	CuBr	CuI
λ	19.270 72	21.475 80	25.5452
$k_{r_1\theta}$	3.536 792	4.075 645	5.588 843
$k'_{r_1\theta}$	−0.644 675	−0.554 375	−1.446 74
$k_{r_2\theta}$	−0.538 87	−0.395 285	−1.908 770
$k'_{r_2\theta}$	−0.241 294	−0.138 008	1.389 28
Z	1.318 914	1.212 635	1.278 71
Y	3.201 653	3.636 485	3.876 912
Y'	−1.266 84	−1.018 062	−0.732 235
k	47.508 28	80.436	105.51
k'	53.3112	59.5825	94.158
λ_α	16	16	28
Δ_0	0.2	0.1	0.6

parts of the TO(Γ) phonon self-energy, respectively.

We have calculated the phonon self-energy using a self-consistent procedure, which takes into account the finite width of all phonons,[16] considering only the diagram in Fig. 3(c). The parameter used in this calculation is the radial nearest-neighbor cubic anharmonic coupling constant λ_a (Table I). In addition, a small constant shift, Δ_0 (Table I), of the real part of the self-energy due to first-order quartic and second-order cubic renormalization [Figs. 3(a) and 3(b)] has been considered. This parameter influences slightly the peak positions as can be seen from Eq. (1).

The calculated line shapes are shown in Fig. 4. The pronounced double-peak structure of CuCl gradually disappears when going first to CuBr (still exhibiting a shoulder) and then to CuI (showing a small kink at the low-frequency side of the main peak). Note that the calculated line shapes do not contain the Raman-scattering matrix elements. They may, therefore, also be compared with the neutron-scattering data.[6] The good agreement between the Raman and neutron-scattering data and the theoretical line shapes demonstrates the intrinsic nature of the phonon Fermi resonance independently of the details of the scattering processes. We find that the fitted values of λ_a are of the order of magnitude expected from the third derivative of a Born-Mayer potential for nearest-neighbor interaction.

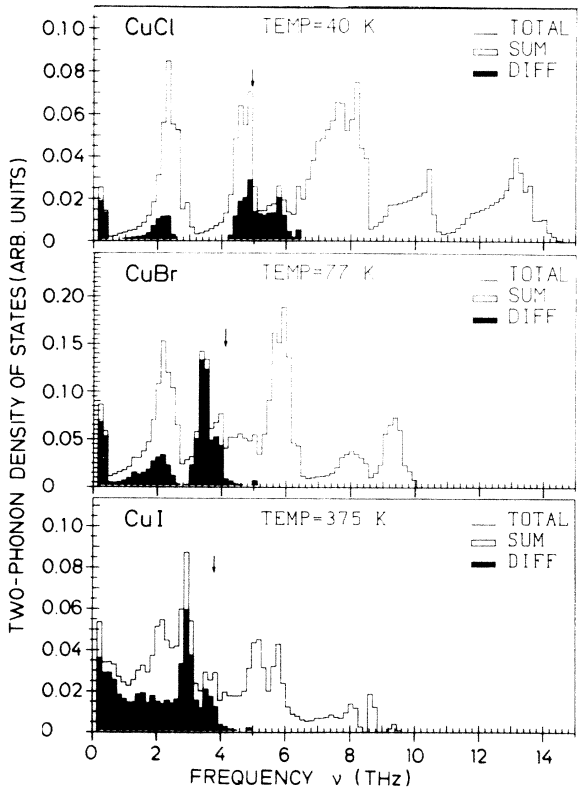

FIG. 2. Two-phonon densities of states of CuCl, CuBr, and CuI. The outline presents the total density which is the sum of the difference (darkened areas) and summation (blank areas) densities. The arrows indicate the quasiharmonic TO(Γ) frequencies.

teraction.

The difference between the present work and that of Hennion *et al.*[6] is that we carried through a consistent calculation of the self-energy starting from an appropriate lattice-dynamical model without any *ad hoc* approximation for the densities of states.

We have also studied the pressure dependence of the Raman spectra of Cu halides as measured recently.[9] It turns out that the experimental data can be reproduced quite satisfactorily by a straightforward anharmonic extension of the model.[15]

The close agreement between the experimental and theoretical line shapes shows that there is no need to consider a two-phonon bound state due to a fourth-order anharmonic interaction.[20] This interaction

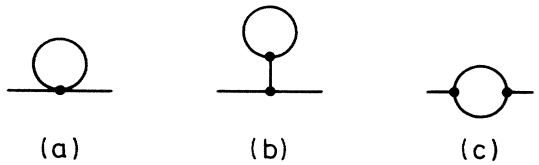

FIG. 3. Diagrams considered in the calculation of the self-energies.

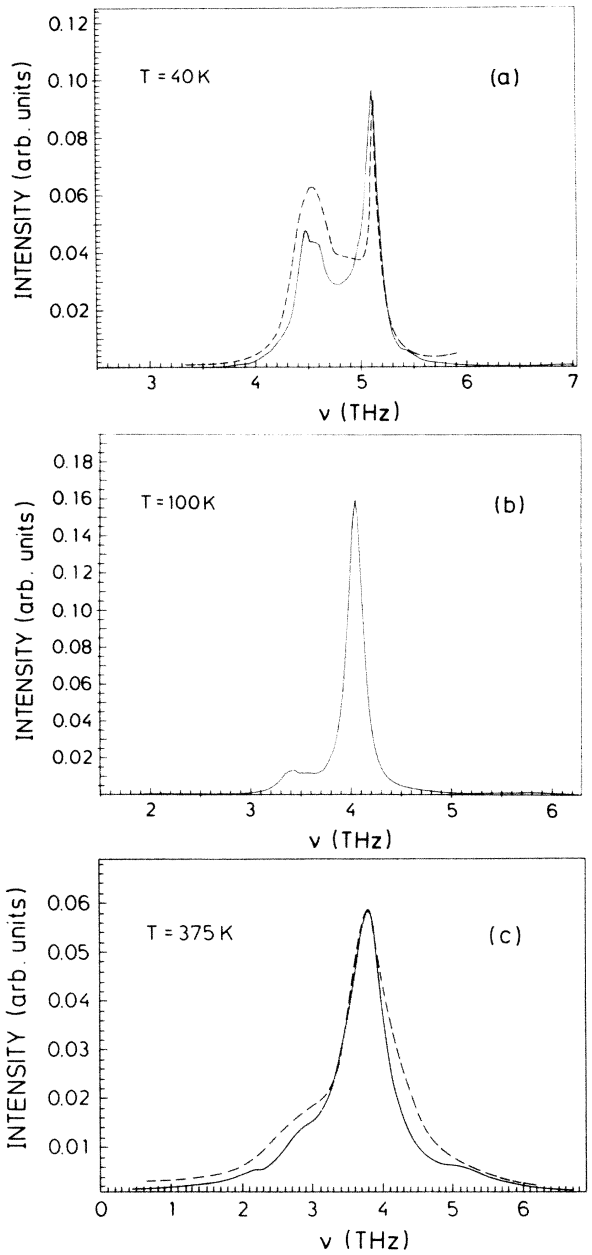

FIG. 4. Line shapes of the TO(Γ) phonons of (a) CuCl, (b) CuBr, and (c) CuI. Solid and dashed lines represent the calculated and measured spectra (CuCl, Ref. 5; CuI, Ref. 17), respectively. The spectra calculated for CuBr are in good agreement with the 1.5-kbar data of Hochheimer *et al.* (Ref. 18) and with recent low-pressure data of Blacha (Ref. 19).

should be, indeed, very small if estimated from a Born-Mayer potential. Thus, any effect on the line shape or on the position of the double peak should be indistinguishable from the influence of other neglected contributions, e.g., scattering cross sections, etc.

The hypothesis of an off-center position of Cu^+ in CuCl is not consistent with our results for two reasons. Firstly, the increasing tendency of Cu^+ in the sequence CuCl → CuBr → CuI to a superionic phase transition should lead to a parallel increase of an "off-center" effect in the phonon spectra, contrary to experimental evidence. Secondly, the small but clearly visible peak near the middle of the double peak in CuCl is reproduced by our Fermi-resonance treatment and should, therefore, not be attributed to a second peak of the longitudinal LO(Γ) mode as is required in the off-center model.[7]

In summary, we have shown that the anomalous features in the phonon spectra of copper halides can be explained in a unique way in terms of Fermi resonances while all other suggested models can be ruled out.

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[1]I. P. Kaminow and E. H. Turner, Phys. Rev. B **5**, 1564 (1972).

[2]J. E. Potts, R. C. Hanson, C. T. Walker, and C. Schwab, Phys. Rev. B **9**, 2711 (1974), and Solid State Commun. **13**, 389 (1973).

[3]T. Fukumoto, K. Tabuchi, S. Nakashima, and A. Mitsuishi, Opt. Commun. **10**, 78 (1974), and Phys. Status Solidi (b) **73**, 341 (1976).

[4]M. L. Shand, L. Y. Ching, and E. Burstein, Solid State Commun. **15**, 1209 (1974).

[5]M. Krauzman, R. M. Pick, H. Poulet, G. Hamel, and B. Prevot, Phys. Rev. Lett. **33**, 528 (1974).

[6]B. Hennion, B. Prevot, M. Krauzman, R. M. Pick, and B. Dorner, J. Phys. C **12**, 1609 (1979).

[7]Z. Vardeny and O. Brafman, Phys. Rev. B **19**, 3276, 3290 (1979), and **21**, 2585 (1980).

[8]V. M. Agranovich, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems,* edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983), p. 83.

[9]A. Blacha, G. Kourouklis, and M. Cardona, to be published.

[10]K. Kunz and H. Bilz, Solid State Commun. **19**, 1027 (1976).

[11]D. Strauch and B. Dorner, to be published.

[12]B. Prevot, B. Hennion, and B. Dorner, J. Phys. C **10**, 3999 (1977).

[13]S. Hoshino, Y. Fujii, J. Harada, and J. D. Axe, J. Phys. Soc. Jpn. **41**, 965 (1976).

[14]B. Hennion, F. Moussa, B. Prevot, C. Carabatos, and C. Schwab, Phys. Rev. Lett. **28**, 964 (1972).

[15]G. Kanellis, W. Kress, and H. Bilz, to be published.

[16]K. Fischer, Phys. Status Solidi (b) **66**, 449 (1974).

[17]G. Burns, F. H. Decal, M. W. Schafer, and R. Alben, Solid State Commun. **24**, 753 (1977).

[18]H. D. Hochheimer, M. L. Shand, J. E. Potts, R. C. Hanson, and C. T. Walker, Phys. Rev. B **14**, 4630 (1976).

[19]A. Blacha, Ph.D. thesis, Stuttgart, 1985 (unpublished).

[20]J. Ruvalds and A. Zawadowski, Phys. Rev. B **2**, 1172 (1970).