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ANALYSIS OF THE SHAPES OF KUBELKA–MUNK SPECTRAL FUNCTIONS OF SUPERIONIC CONDUCTORS CuI, AgI, Cu_2HgI_4 AND Ag_2HgI_4 IN A WIDE TEMPERATURE RANGE

MLADEN PAIĆ

Institute of Physics of the University Zagreb, Bijenička 46, 10000 Zagreb, Croatia

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The changing shapes of the Kubelka–Munk spectral function of different solid phases of CuI, AgI, Cu_2HgI_4 and Ag_2HgI_4 were studied in a wide temperature range. The spectra consist generally of a single, light absorption like, band. The parameters of the spectra were compared. Their distribution as functions of frequency or temperature in the case of the phases of CuI and AgI are similar. Distributions of parameters related to the phases of Cu_2HgI_4 and Ag_2HgI_4 are alike only in the case of the full width at half maximum. The existence of already reported phases of the investigated compounds is confirmed.

1. *Introduction*

The interesting problems of light absorption spectra of solids and their change with temperature are rarely investigated, probably because of inherent experimental difficulties. The indirect way to obtain relevant information is the use of the Kubelka–Munk (KM) spectral function. Spectrometry gives the necessary data concerning the diffusely reflected light from the powdered substances, as well as from a white standard powder. The substance studied, of about 0.1 g, sealed in a quartz ampoule, can be treated thermally up to the melting point of quartz. The same procedure is applied to the standard.

2. *The Kubelka–Munk spectral function*

One point of the KM function [1-3] of a powder is given by the relation

$$F(\rho_{\infty}^{'})_{\sigma,T} = \left[\frac{(1-\rho_{\infty}^{'})^2}{2\rho_{\infty}^{'}}\right]_{\sigma,T},$$

where T is temperature of the sample, σ the wave number of the radiation and $\rho_{\infty}^{'}$ the monochromatic diffuse reflectance of the powder divided by the corresponding reflectance of a white standard. Measurements in a appropriate σ interval give the KM spectrum

$$F(\rho_{\infty}^{'})_T = f(\sigma)_T$$

of a crystal phase. This spectrum resembles the linear absorption coefficient spectrum of the same phase.

In the optical region, the spectra given by the superionic conductors CuI, AgI, Cu_2HgI_4 and Ag_2HgI_4 are known [4-7] in a wide temperature range. No particular attention was given to their shapes. This problem is treated in the present study.

3. *Measurements and discussion*

Two KM spectra of a solid phase of one of the mentioned substances are considered: one corresponding to the beginning of the temperature range, in which the phase exists, the other to the end of this range. These spectra are shown in Figs. 1 and 2. In each spectrum, obtained in ≈ 400 s, the phase and the temperature are indicated. One set of spectra corresponds to the heating, the other to the cooling run, both begining at ≈ 293 K. In order to specify the differences between the spectra of the phases, $F(\rho_{\infty}^{'})_{max}$ (not including the background) and the full width at half maximum, $\omega_{1/2}$, of each spectrum were determined. For a given phase, the measured values are a function of σ and T. Relevant values of two KM spectra of a phase, joined by a straight line, form a couple characterising the phase.

Figure 3 shows the distributions of such couples due to CuI and AgI, respectively, formed by pairs of values of the function $F(\rho_{\infty}^{'})_{max} = f(\sigma, T)$. The two distributions are generally similar: $F(\rho_{\infty}^{'})_{max}$ diminishes as σ rises. The various positions, orientations and lengths of the couples support the existence of the reported γ, δ and ε CuI [4] and γ, $\beta^{'}$ and $\alpha^{'}$ AgI [5] phases.

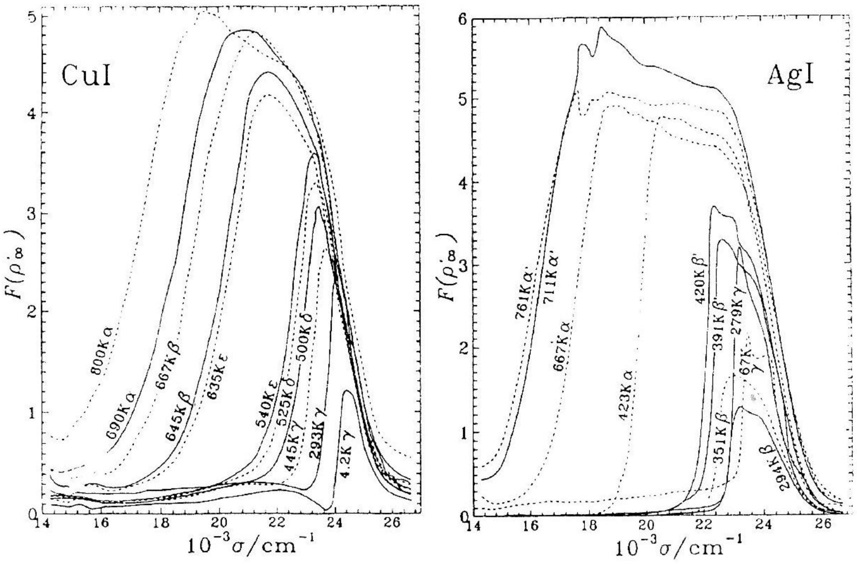

Fig. 1. Kubelka–Munk spectral functions $F(\rho'_\infty)_T = f(\sigma)_T$ of CuI *and* AgI *solid phases obtained during heating or cooling runs (the initial temperature was* 293 K*).*

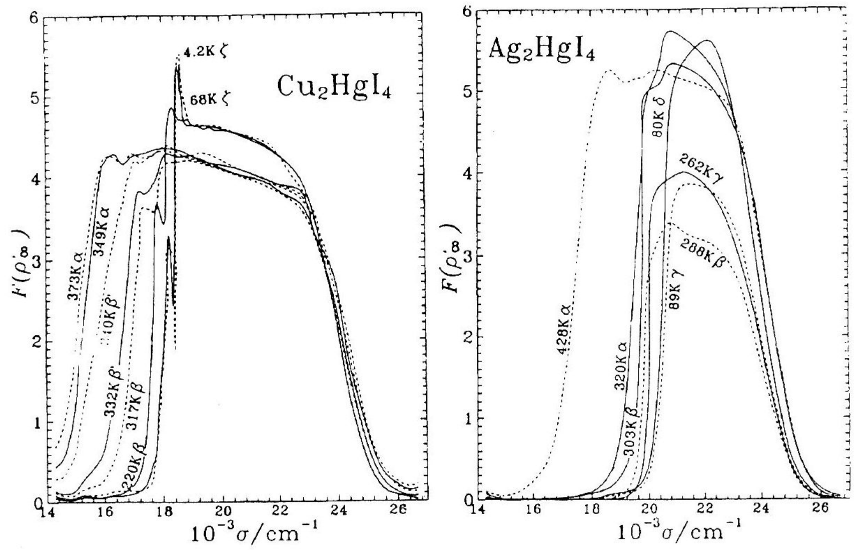

Fig. 2. Kubelka–Munk spectral functions $F(\rho'_\infty)_T = f(\sigma)_T$ of Cu_2HgI_4 *and* Ag_2HgI_4 *solid phases obtained during heating or cooling runs (the initial temperature was* 293 K*).*

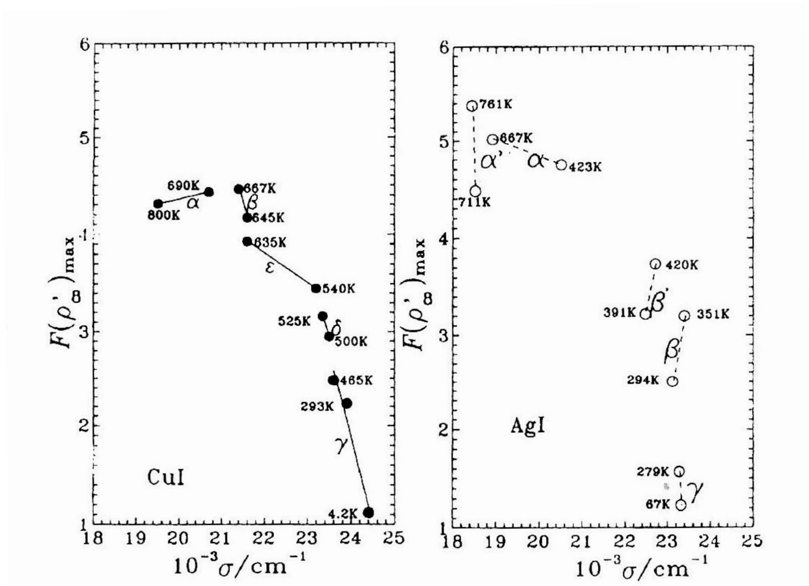

Fig. 3. Couples of maxima of $F(\rho_\infty^{'})_T = f(\sigma)_T$ *of* CuI *and* AgI *solid phases as function of* σ.

The same kind of couples related to Cu_2HgI_4 (Fig. 4.), without considering the exciton maxima, are grouped around $\approx 18\ 500$ cm^{-1} in a rather small σ interval. For the α, β and γ Cu_2HgI_4 phases, $F(\rho_\infty^{'})_{max}$ rises as σ diminishes, yet it remains constant for the ζ phase.

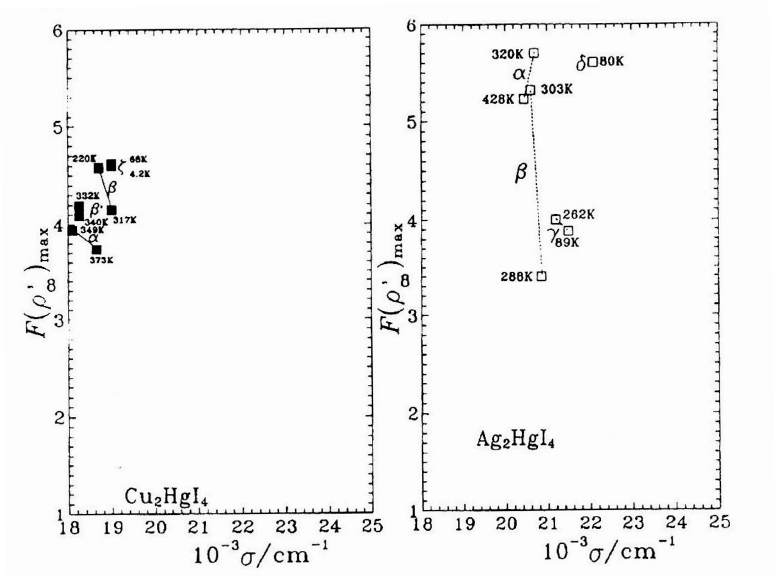

Fig. 4. Couples of maxima of $F(\rho_\infty^{'})_T = f(\sigma)_T$ *of* Cu_2HgI_4 *and* Ag_2HgI_4 *solid phases.*

The couples responding to Ag_2HgI_4 (Fig. 4) are grouped around 21 000 cm^{-1} in an even narrower σ interval than the couples in the case of Cu_2HgI_4.

The consideration of the two distributions, shown in Fig. 4, supports the existence of the reported β' and ζ Cu_2HgI_4 phases [6] as well as the existence of the γ and δ Ag_2HgI_4 phases [7], the δ phase being presented by one point only.

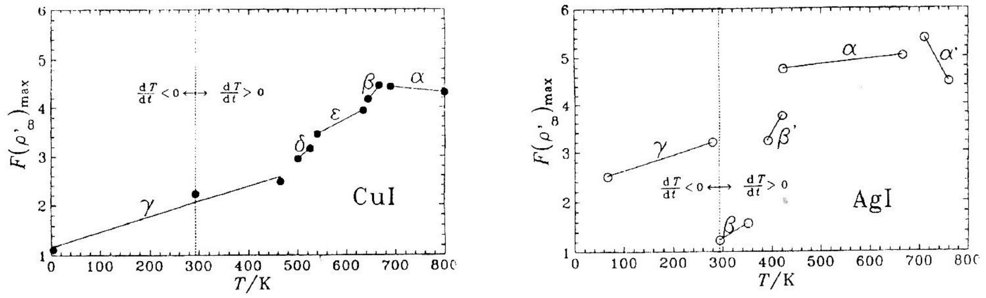

Fig. 5. Couples of maxima of $F(\rho'_\infty)_T = f(\sigma)_T$ of CuI *and* AgI *solid phases as functions of T.*

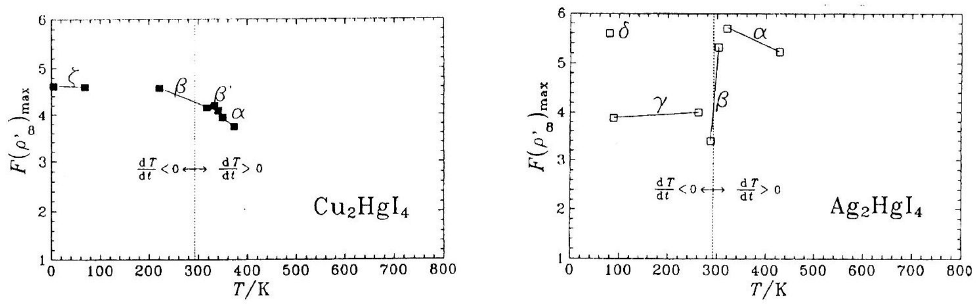

Fig. 6. Couples of maxima of $F(\rho'_\infty)_T = f(\sigma)_T$ of Cu_2HgI_4 *and* Ag_2HgI_4 *solid phases as functions of T.*

Figure 5 illustrates the distributions of the couples of the function $F(\rho'_\infty)_{max} = f(T)$ due to CuI and AgI phases. In the case of CuI, $F(\rho'_\infty)_{max}$ rises generally with T. This is not the case for AgI. The existence of the γ, δ and ε phases of CuI and α', β' and γ phases of AgI appears even more clearly than if using the $F(\rho'_\infty)_{max} = f(\sigma)_T$ function (Fig. 3). The distributions of the couples, as a functions of temperature, for Cu_2HgI_4 and Ag_2HgI_4, differ considerably (Fig. 6). In the first case, $F(\rho'_\infty)$ falls rather regularly with rising temperature what is not observed in the second case. Both figures demonstrate the existence of the β' and ζ phases of Cu_2HgI_4 and γ and δ phases of Ag_2HgI_4.

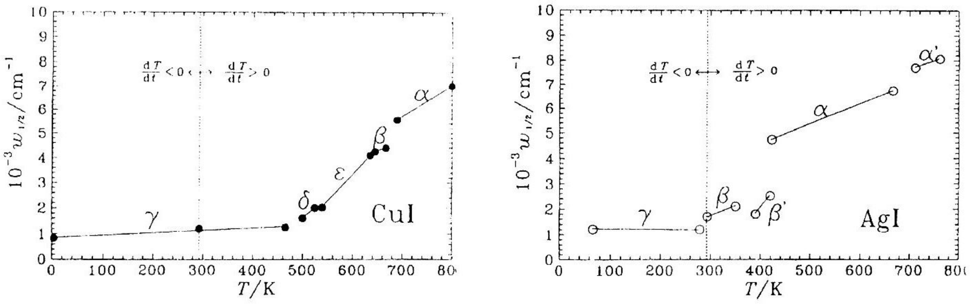

Fig. 7. Couples of full width at half maximum of $F(\rho'_{\infty})_T = f(\sigma)_T$ of CuI *and* AgI *solid phases as functions of T.*

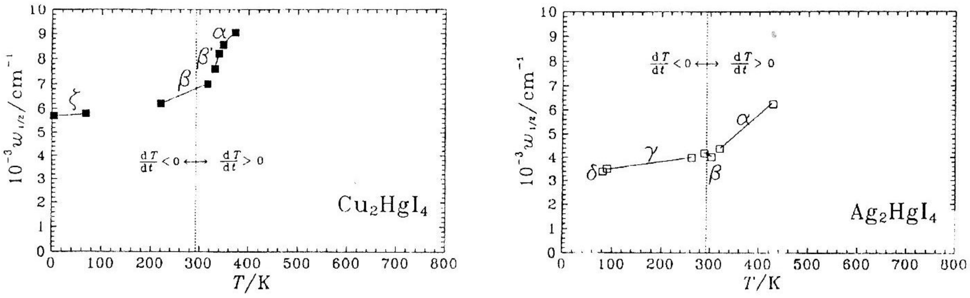

Fig. 8. Couples of full width at half maximum of $F(\rho'_{\infty})_T = f(\sigma)_T$ of Cu_2HgI_4 *and* Ag_2HgI_4 *solid phases as functions of T.*

The distribution of the couples of the function $\omega_{1/2} = f(T)$ for CuI and AgI (Fig. 7) are not very different. The $\omega_{1/2}$ values rise generally with T. The figures show the existence of the γ, δ and ε CuI phases as well as those of the α', β' and γ AgI phases. Very similar distributions of the couples exist in the cases of Cu_2HgI_4 and Ag_2HgI_4 (Fig. 8). Nevertheless, the existence of the β' and ζ Cu_2HgI_4 phases and of the γ and δ Ag_2HgI_4 phases is evident.

4. *Conclusions*

The analysis of the shapes of the Kubelka–Munk spectra, that are similar to the light absorption spectra, confirms the existence of the various CuI, AgI, Cu_2HgI_4 and Ag_2HgI_4 crystal phases reported in the literature.

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ANALIZA OBLIKA KUBELKA–MUNK SPEKTRALNIH FUNKCIJA SUPERIONSKIH VODIČA CuI, AgI, Cu_2HgI_4 I Ag_2HgI_4, U VELIKOM INTERVALU TEMPERATURA

Pokazano je da oblik Kubelka–Munk spektralne funkcije istraživanih spojeva ovisi o kristalnoj fazi u kojoj se nalaze. Potvrđeno je postojanje faza tih spojeva navedenih u literaturi.