sotopic shift of exciton lines in the absorption spectrum of Cu_2O

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A shift of the exciton series was observed following isotope substitution of oxygen in cuprous oxide crystals. The phenomenon is interpreted on the basis of the polaron model.

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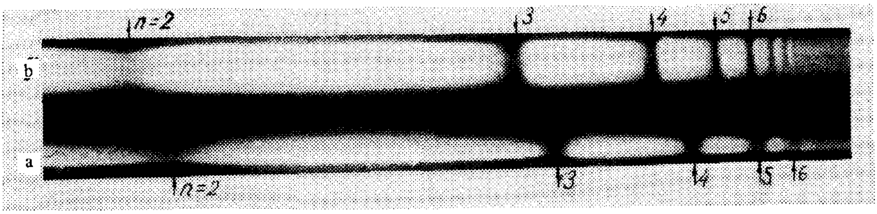
Isotopic substitution is widely used in the investigation of the vibrational pectra of crystals. Recently, isotope substitution has been successfully used n the study of the electronic exciton bands in molecular crystals.[1] In semi-



conductor crystals, isotope substitution has been used to determine the nature of the impurity centers.[2,3]

We present here the results of an investigation of the effect of isotope substitution on the exciton spectrum of cuprous-oxide crystals. We have observed that when all of the O^{16} is replaced by O^{18}, all the exciton-absorption lines are shifted. The absorption lines of the green and yellow exciton series are shifted equally. The shift is towards the short-wave side of the spectrum and its value is $\Delta E = 18$ cm^{-1}. The energy of the isotopic shift in the temperature interval 4.2–77 °K is independent of temperature for these series.

Simultaneously with the isotopic shift of the exciton lines, we measured the change in the energy of the longitudinal optical phonon ($\hbar\omega_{L0} = 660$ cm^{-1}). In the substituted crystal, the phonon energy decreased by $\Delta\hbar\omega_{L0} = 25$ cm^{-1}. In the case of about 50% substitution of the oxygen atoms (see the figure), the isotopic shift of the exciton lines was 12 cm^{-1}. Crystals with 50% substitution were grown by the hydrothermal synthesis method, and we succeeded in measuring for these crystals the shift of the exciton-series lines located near the allowed-transition bands (the azure and blue series). Within the limits of experimental accuracy, the magnitude of the shift at $T = 77$ °K was the same as for the yellow and green series, but oppositely directed, towards the long-wave side. At $T = 4.2$ °K, only an insignificant shift was observed.

The exciton-series shift observed by us is large and cannot be attributed to the isotopic shift of the atomic levels. This is all the more so because the excitons are made up of carriers from those bands which are "made up" in the main of copper levels. Attention is called to the fact that the Rydberg constants undergo no changes whatever in the isotopic shift (accurate to 0.5 cm^{-1} for the yellow series). One can therefore expect the main cause of the shift in the isotopic substitution to be the change of the electron-phonon interaction.

The magnitude of the electron-phonon interaction in the cuprous-oxide crysta can be estimated by using the "large-radius" polaron model. The polaron coupling constant α for Cu_2O at $\epsilon_0 = 7.5$, $\epsilon_\infty = 6.25$, $m_e = m_0$, and $\omega_{L0} = 1.54 \cdot 10^{13}$ sec is approximately equal to 0.3. The polaron binding energy is then $E = -\alpha\hbar\omega_{L0} = 220$ cm^{-1}, and the change in the binding energy is 12 cm^{-1}, which is very close to the shift observed by us for forbidden transitions. Within the framework of the polaron model, difficulties arise when it comes to explaining the reversed shift of the excitons of the allowed series. To agree with the experiment, we must assume the existence of other mechanisms that lead to the shift, for example, interaction with acoustic phonons. This assumption is favored by the appreciable sensitivity of the allowed bands to deformation of the crystal, and by the temperature dependence of the isotopic shift.

The isotopic shifts can be connected with the temperature dependence of the width of the forbidden band. We use for this purpose the results of[4], where a theory is developed for the isotopic shift of zero-phonon lines in the case of an optical transition in impurity centers. The isotopic shift should, according to[4], be proportional to the temperature shift of the band of the host lattice at high temperature

$$\left(\gamma = \frac{\partial E_G}{\partial kT}\Big|_{HT}\right)$$

and is due to the simultaneous change of the energy of the zero-point vibrations of the impurity atom and the force constants of the host lattice. It appears that in the case of isotopic substitution of the host atoms of the crystal the shifts should also be proportional to γ, to the relative change of the isotope mass $\Delta M/M$, and to the change in the energy of the zero-point vibrations. The corresponding estimates yield in our case reasonable values of the shift. For a more complete explanation of the mechanisms of the spectral shift of the exciton levels following isotopic substitution additional experiments are needed, involving isotopic substitution of the copper atoms.

It should be noted in conclusion that the isotopic shifts are large enough, they can be easily measured, and therefore the method of substituting the isotopes of the host lattice can be used successfully to investigate electron-phonon interactions.

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