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Pressure Shift of the U Band in KBr[†]

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The pressure derivative of the U-band peak position in KBr was determined to be $+27\times10^{-6}$ eV bar^{-1} and $+30\times10^{-6}$ eV bar^{-1} for H^- and D^- impurities, respectively. These are equal, within the uncertainty of $\pm3\times10^{-6}$ eV bar^{-1} for each coefficient. The shift of the peak of the U band with temperature is shown to arise almost entirely from thermal expansion.

THE U band arises from an electronic transition on a substitutional H^- impurity in an alkali halide.[1] It is a broad band near the fundamental absorption edge which, like the F band, shifts to higher energy and sharpens when the crystal is cooled. Baldini *et al.*[2] have studied the isotope effect in the U band of three alkali halides, measuring peak positions and half-widths as functions of temperature. They fitted these functions to expressions obtained by assuming linear coupling of the electron to odd lattice modes and quadratic coupling to all modes, because the isotope effect arises from even modes. In so doing, they had to fit the temperature dependence of the peak position to that calculated from the quadratic coupling to all lattice modes, ignoring, of necessity, that part of the temperature dependence of $E(T)$ caused by thermal expansion. This part can be estimated from the shift of the peak position with hydrostatic pressure.

We have measured the pressure shift of the U band in KBr at 78°K, using hydrostatic pressure in a system previously described.[3] We find $(\partial E/\partial P)_T=27\times10^{-6}$ eV bar^{-1} ($\pm10\%$). This value is about twice that for the F band in KBr.[3] With the compressibility of the bulk crystal, one can convert this coefficient to a volume coefficient $(\partial \ln E/\partial \ln a)_T=-2.2$, where a is the bulk interatomic distance. The Ivey rule[4] for the U band predicts $(\partial \ln E/\partial \ln a)_T=-1.10$. A similar discrepancy occurs for F centers, where it has been explained by introducing a local compressibility around the F center of about one-half that of the bulk crystal.[5–7] However, Benedek and Nardelli[8] have shown that for F centers in KBr, although the central force constant between the F center and a nearest-neighbor ion is only about 40% of the nearest-neighbor central force constant in the perfect lattice, the compressibility of the F center and its six nearest-neighbor ions is reduced only about 18%. This factor is not enough to account for the discrepancy between measured values of $(\partial \ln E/\partial \ln a)_T$ and the Ivey rule for F centers.[5–7] For U centers, the discrepancy is smaller, but the local compressibility should also depart less from the bulk value. A local compressibility model should have some validity if the ground and excited states are both reasonably confined to the vacancy (or impurity) and the nearest-neighbor ions. The first excited state of the U center seems to be no less compact than that of the F center.[9]

One can estimate the contribution of thermal expansion to $(\partial E/\partial T)_P$, the observed temperature shift of the peak position, by means of the equation

$$\left(\frac{\partial E}{\partial T}\right)_P=\left(\frac{\partial E}{\partial T}\right)_V-\left(\frac{3\alpha}{K}\right)\left(\frac{\partial E}{\partial P}\right)_T. \qquad (1)$$

The first term on the right is the electron-phonon (quadratic coupling) term and the second is the effect of thermal expansion. α is the linear thermal-expansion coefficient and K the compressibility. For defects, even though α and K may have local values, it seems reasonable that $3\alpha/K$ will be close to the bulk values. $E(T)$ at constant pressure is often fitted by the function $E_0-B\coth(\theta/T)$. However, in order to display the isotope effect in $E(T)$, Baldini *et al.*[2] used $E_0-B\times\coth(\theta/T)-D\coth(\theta'/T)$, the last term arising from just the infrared-active localized mode. D and θ' were evaluated from the isotope effect, infrared data, and reasonable estimates, while B and θ came from fitting data on $E(T)$. By taking the derivative of this function and evaluating it at 300°K, we get $(\partial E/\partial T)_P=-4.8\times10^{-4}$ eV $(K°)^{-1}$, while the thermal-expansion contribution to it is -4.8×10^{-4} eV $(K°)^{-1}$, leaving $(0.0\pm\sim0.5)\times10^{-4}$ eV $(K°)^{-1}$ for the true quadratic electron-lattice effect. Thus at 300°K, essentially all of $(\partial E/\partial T)_P$ arises from thermal expansion, and the values of B and θ of Ref. 2 are not correct, especially B. However, these are constants of only minor interest in that work; the half-widths and isotope effects constituted the most significant results of Ref. 2 and they are essentially unaltered by neglecting thermal expansion, i.e., the temperature dependence of E_0.

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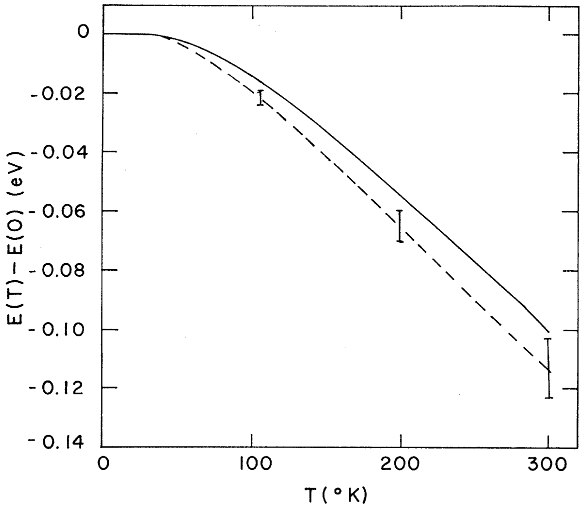

FIG. 1. Solid: observed temperature dependence of the U-band absorption peak (see Ref. 2). Dashed: that part of the temperature dependence that arises from thermal expansion,

$$E(T)-E(0)=\int_0^T \frac{3\alpha(T)}{K(T)}\left(\frac{\partial E}{\partial P}\right)_T dT.$$

We have integrated Eq. (1), using a temperature-dependent[10] α and calculating the temperature-dependent K with a constant C_{12} and temperature-dependent[11] C_{11} (elastic stiffness constants). The result is shown in Fig. 1. According to this, thermal expansion can account for all of $E(T)$ within the experimental limits of 10% (our data) and 0.005 eV [$E(T)$ data[2]]. Hence, trying to extract B and θ is not meaningful. We have also evaluated just $-D\coth(\theta'/T)$, and it is very small, being only -0.0078 eV at 300°K, largely a result of the large value of θ'.

$(\partial E/\partial P)_T$ was found to be $+30\times10^{-6}$ eV bar^{-1} for the U band in KBr:D$^-$. This is essentially equal to that for KBr:H^-, considering the sample-to-sample differences of $(2\text{–}3)\times10^{-6}$ eV bar^{-1} for such coefficients. One can also estimate the magnitude of the expected isotope effect in $(\partial E/\partial P)_T$. Such an effect will originate primarily in the pressure derivative of $-D\coth(\theta'/T)$. From uniaxial stress shifts[12] we can estimate the pressure shift of the energy of the infrared-active mode of the H$^-$ ion to be $(\partial\hbar\omega_g/\partial P)_T=+1.45\times10^{-6}$ eV bar^{-1}. The Θ' is $\hbar\omega_g/2k$ and ω_g also appears in D. We assume that the energy of the infrared-active mode when the electron is in the excited state, $\hbar\omega_u$, has negligible pressure shift, and no isotope effect.[2] For KBr:H$^-$ at 300°K, we get $\{(\partial/\partial P)[-D\coth(\theta'/T)]\}_T=-2.40\times10^{-6}$ eV bar^{-1}, a contribution of about -10% of the observed $(\partial E/\partial P)_T$, and one which will exhibit some temperature dependence (too small to detect) at higher temperatures. By replacing $\hbar\omega_g$ by $\sqrt{2}\hbar\omega_g$ in both D and θ' and assuming the infrared-active D$^-$ localized-mode frequency has the same pressure shift as that for H$^-$, we find that the term $\{(\partial/\partial P)[-D\coth(\theta'/T)]\}_T$ differs by only 0.14×10^{-6} eV bar^{-1} for the two isotopes. This difference is too small to be determined by subtracting directly measured values of $(\partial E/\partial P)_T$ for each isotope.

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