

Optical, infrared and electron-microscopy studies of $(\text{Cd}_i)_n$ metallic clusters in layered CdI_2 crystals

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Abstract

An influence of $(\text{Cd}_i)_n$ metallic clusters on the optical absorption and phonon spectra of CdI_2 crystals was studied. Metallic clusters of spherical shape were formed during the growth of non-stoichiometric crystals. Radii of clusters are in range from 10 to 500 nm according to scanning electron microscopy (SEM) data. The density of clusters was estimated from fractal dimension calculations. The fractal dimension of $(\text{Cd}_i)_n$ clusters has been found to be varied from 1.488 to 1.793. In the framework of Mie theory the spectral and size dependencies of extinction coefficients were calculated. From the experimentally obtained spectra it is evident that the metallic clusters are responsible for the bands in the transparency region of CdI_2 crystals (360–430 nm) and for the peaks in the mid-infrared absorption spectra which are not present in the spectra of pure cadmium iodide. The nature of this additional optical and infrared absorption is concerned with the bulk and surface plasmons and the surface phonon modes of metallic clusters, respectively.

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1. Introduction

CdI_2 single crystals possesses a layered structure, typical for many halides. It is formed by identical I–Cd–I sandwiches; within the I–Cd–I layers atoms are held together with strong ionic–covalent bonds while interactions between the adjacent layers are due to the weak van der Waals forces. Highly anisotropic chemical bonds govern the experimentally proved specific character of electronic and ionic processes in the mentioned materials (Bolesta et al., 1995).

Having a direct energy gap of 3.8 eV cadmium iodide finds application as a scintillating material with the characteristic time of several nanoseconds. Due to the second-order

non-linear optical effects observed (Bolesta et al., 1994), CdI_2 is considered to be promising for industrial purposes, particularly for producing UV detectors. Significant increase of the second-order susceptibility in the CdI_2 –Cu nanocrystals (Hydaradjan and Voolless, 2003; Voolless et al., 2003; Olafsson and Stenberg, 2004) and specific properties of closed cage/nanotubular structures formed under electron beam irradiation in CdI_2 (Sallacan et al., 2003) determine the importance of the material in the field of nanotechnology.

The intercalated layered structures reveal fundamentally new properties which are not inherent to the host matrix or impurity.

The characteristic feature of CdI_2 consists in the formation of overstoichiometric cadmium atoms, Cd_i , during the crystal growth or further treatment. Preliminary studies indicated that the excess stoichiometric cadmium atoms in CdI_2 may occupy different crystallographic positions. They are predominantly localized between the neighbor iodine planes of I–Cd–I layers,

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i.e. in the tetrahedral or octahedral voids existing in the van der Waals gaps of the layered crystals. Therefore, the Cd_i atoms give rise to the change in the c lattice parameter and influence the optical and luminescence properties (Bolesta et al., 1995, 1997). Further increase in the Cd_i atoms concentration leads to formation of the metallic clusters (MCs) $(Cd_i)_n$ with nano- or submicron dimensions. It is well known (Milvidskii and Chaldyshev, 1998) that MCs can modify the properties of semiconductor and dielectric crystals. In particular, MCs effectively absorb light in the near UV and visible region (De Heer, 1993) and cause the luminescence in some dielectric media (Jian et al., 2004). The spectral characteristics of the absorption and luminescence bands strongly depend on the size and shape of MCs and medium properties. The existence of the boundary between the MC and host matrix induces the appearance of surface phonons, and, consequently, the changes in the phonon spectra of the material (Venger et al., 1999).

In this work, we investigate the influence of $(Cd_i)_n$ MCs on the optical and phonon spectra of CdI_2 single crystals.

2. Samples preparation and experimental techniques

The nominally pure and non-stoichiometric CdI_2 single crystals were grown from melt by Bridgman–Stockbarger method. To increase the probability of clusters formation, the excess stoichiometric cadmium (0.01–0.1 mol%) was introduced in the melt. Investigated crystals adopt 4H-polytype structure which is typical for the crystals, grown from melt (Lyskovych et al., 1982). For the optical measurements the crystalline plates with a thickness of 0.1–1.0 mm were cleaved from the crystals.

SEM investigations were performed on freshly cleaved (0001) basal surfaces. Fractal dimension (FD) of clusters structure has been determined by means of the box counting method (Mandelbrot, 2002).

Optical absorption measurements in the 360–430 nm range were performed using a MDR-23 grating monochromator.

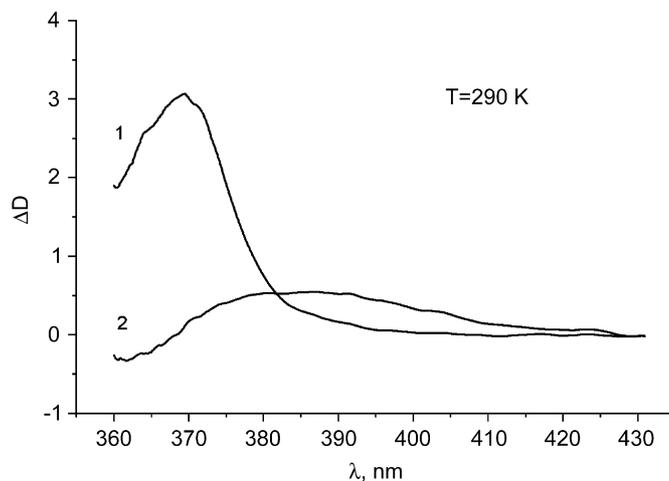


Fig. 2. Difference absorption spectra of CdI_2 -0.1 mol% Cd (1) and CdI_2 -0.01 mol% Cd (2).

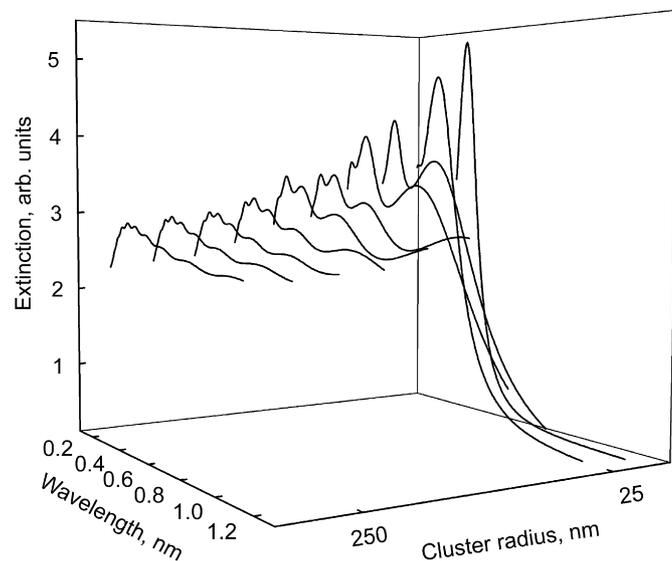


Fig. 3. Calculated spectral dependencies of extinction coefficients for $(Cd_i)_n$ metallic clusters.

Transmittance in the far-infrared (from 50 to 600 cm^{-1}) and the mid-infrared (from 600 to 1300 cm^{-1}) domains was measured using BRUKER Equinox 55 interferometer at the infrared station of the Synchrotron Radiation facility DAPHNE (Laboratori Nazionali di Frascati, Italy). IR characterization was done in a wide temperature range, starting from 10 K.

3. Results and discussion

Fig. 1 shows a typical SEM micrograph of the $(Cd_i)_n$ MCs on the basal surface of CdI_2 crystals. As estimated from the SEM data, radii R of MCs are distributed within the range of 10–500 nm. Since $R = r_s N^{1/3}$, where $r_s = 2.59a_B$ (Ashcroft and Mermin, 1976) denotes the average distance between free electrons in cadmium clusters (a_B is the Bohr radius), the number of Cd atoms in a single MC varies from 3.9×10^5 up to

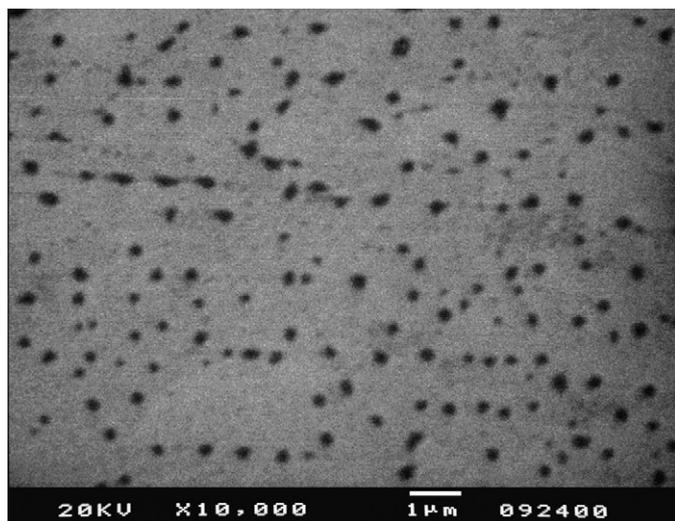


Fig. 1. SEM image of CdI_2 -0.1 mol% Cd surface, showing the subsistence of $(Cd_i)_n$ metallic clusters.

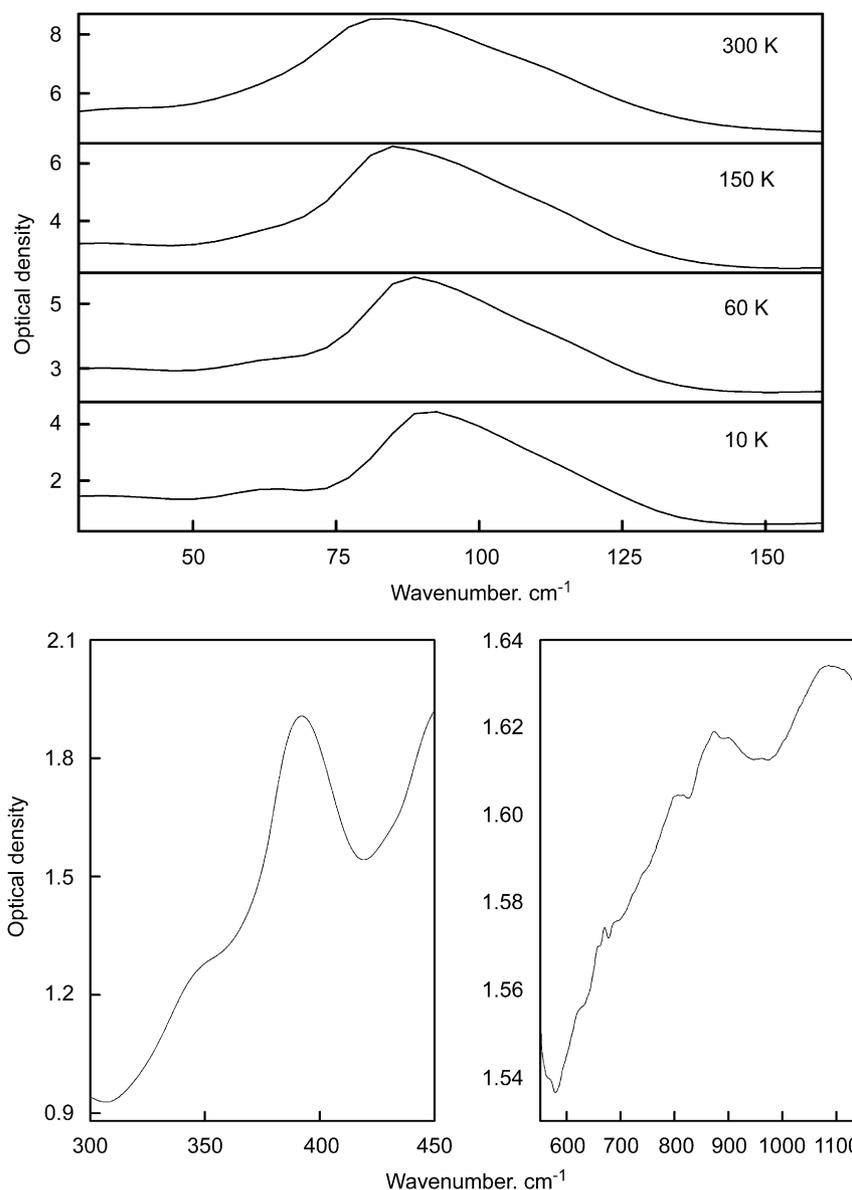


Fig. 4. Room temperature FTIR spectra of non-stoichiometric CdI₂ layered crystals in the mid-infrared (below) and far-infrared (above) domains. Mid-IR spectrum is shown as two appropriately scaled plots.

4.8×10^{10} . MCs are irregularly distributed on the size and surface density of clusters is non-uniform in different areas of the samples. Clusters concentration in the non-stoichiometric samples is higher than that in the nominally pure crystals. Thus, the CdI₂ with clusters can be treated as a nanostructured material (Karpov and Slabko, 2003).

In order to estimate the density of clusters we calculated the FD of such nanostructures. The estimated FD of cadmium MCs varies from 1.488 to 1.793 depending on the content of overstoichiometric cadmium.

The difference absorption spectra (i.e. obtained by subtraction the spectrum of nominally pure CdI₂ from spectra of crystals with MCs) are presented in Fig. 2. It is evident that MCs cause the additional absorption in the 360–390 nm region

for CdI₂0.1 mol% Cd (curve 1) and at 370–430 nm for CdI₂-0.01 mol% Cd (curve 2).

In the framework of Mie theory (Bohren and Huffman, 1983) we calculated the spectral dependencies of the extinction coefficients for (Cd_i)_n MCs with different size (see Fig. 3). From these calculations it follows that (Cd_i)_n clusters are the reason of the new bands in the 360–440 nm region. The number of additional peaks strongly depends on the MCs size. For small clusters ($R < 25$ nm) one may observe a single maximum only, while six peaks are apparent in the case of larger clusters. These bands may be due to the surface plasmon resonance of free electrons in clusters.

The analysis of experimental absorption spectra for the pure and doped CdI₂ single crystals reveals additional features in

the transparent region (365, 378 and 384 nm) (Lyskovych et al., 1982). Absorption spectra of the CdI₂ thin films reported by Tuagi and co-workers (Tuagi et al., 2001; Tuagi and Vedeshwar, 2002) also exhibit absorption bands in the 360–390 eV region, which are not connected with the band-to-band transitions. Summarizing our SEM, optical and FD studies and considering literature data we ascribe the above discussed additional bands to the (Cd_i)_n MCs embedded in CdI₂ matrix.

The FTIR spectra of pure cadmium iodide crystals containing the cadmium clusters are shown in Fig. 4. The phonon modes related to the intralayer vibrations are observed below 160 cm⁻¹. The phonon spectrum profile in the far-infrared region is temperature dependent. At temperatures below 60 K several bands can be resolved. In more detail the nature of these vibrational modes will be discussed in a particular report. In the mid-infrared domain (the lower part of Fig. 4) one may notice the peculiarities which cannot be attributed to the IR active modes of pure CdI₂.

Peaks at nearly 1100, 900 cm⁻¹, within the regions of 600–700 cm⁻¹ and 350–400 cm⁻¹ do not depend on temperature, being at the same time strongly dependent on the concentration of excess stoichiometric cadmium and, consequently, on the density of embedded clusters. Therefore, we suggest the mid-IR absorption features to be a manifestation of the surface phonon modes of MCs.

4. Conclusion

SEM studies confirmed the formation of (Cd_i)_n MCs during the growth of non-stoichiometric CdI₂ crystals. Clusters radii were found to be in range from 10 to 500 nm. Clusters concentrations in different areas were evaluated employing the FD approach. Spectral dependencies of the extinction coefficients of (Cd_i)_n MCs of different size were calculated. It was established that the MCs cause the additional absorption band within 360–430 nm and the evolution of the FTIR spectra mainly in the mid-infrared domain. While further studies are in progress we tentatively assign absorption bands in the visible range to the bulk and/or surface plasmons and the additional IR absorption peaks to the surface phonon modes of cadmium clusters.

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