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Photoluminescence properties of polycrystalline AgGaTe₂

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Abstract

Due to its high absorption coefficient and close to optimal bandgap energy, AgGaTe₂ is a promising material for solar energy conversion. In order to avoid recombination losses, the study of the defect structure of solar cell materials is very important. This paper reports the results of photoluminescence experiments on polycrystalline AgGaTe₂. Two emission regions centred at 1.32 and 0.8 eV were found. The first region appears near the bandgap energy and comprises three bands that are identified by the theory of heavily doped semiconductors as the band-to-band (1.337 eV), the band-to-tail (1.317 eV) and the band-to-impurity (1.287 eV) recombination. The second deep PL region consists of two bands with the peak energies of 0.835 and 0.75 eV. Both these deep bands have rather low thermal activation energy; 18.5 and 20.8 meV, respectively. The possible origins of these bands are discussed.

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1. Introduction

The seek for new nonlinear optical and solar cell materials has recently raised considerable interest in ternary chalcopyrite semiconductors. In the solar cell industry, the thickness of the absorber layer is one of the characteristics that determine the price of the device. Due to the high absorption coefficient, the chalcopyrite absorber layer can be made thinner than widely used crystalline silicon-based absorber layer. Accordingly, less material is needed and thinner cells can be produced. On the other hand, if we compare the

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highest efficiencies achieved, crystalline silicon solar cells still exceed the $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) based cells that are the most popular in the chalcopyrite class. The limitations of the chalcopyrite based solar cells are mainly caused by the bulk defects and interface recombination. Thus, defect investigation and control over the material growth parameters are very important. In the studies of the chalcopyrite solar cells, most of the effort has been put into the CIGS systems. Nevertheless, other chalcopyrite materials are worth studying because the members of the chalcopyrite class exhibit very similar electrical and optical properties. Among these materials AgGaTe_2 (AGT) has received less attention. Nevertheless, some efforts were already made to prepare AGT/Si heterojunction solar cells [1]. It is known that the growth of high quality AGT single crystals is quite difficult due to peritectic melting and negative thermal expansion coefficient. At the same time in thin film solar cells usually a polycrystalline material is used. Therefore, the properties of polycrystalline material and its defect structure are very important and must also be studied. The most convenient and sensitive method of defect structure studies is photoluminescence (PL). PL measurements on AGT are reported in Refs. [2–4]. In Refs. [2,3], two emission regions were described in single crystals grown by the Bridgman technique. The narrow edge emission peak at 1.34–1.35 eV is attributed to the excitonic emission whilst the deep broad emission band at 0.85–0.87 eV is attributed to the donor–acceptor pair (DAP) recombination. A similar deep band is also reported in Ref. [4] where the origin of the emission is assigned to native defect states.

In this paper, we present new PL spectra of polycrystalline AGT samples and provide an interpretation to the bands observed.

2. Experimental

The polycrystalline AGT material was synthesised from 5N-purity components. The phase equilibrium data from Ref. [5] was taken into account and Ag, Ga, Te were weighted according to the molar ratios of 1:1:2. The materials were inserted into the quartz ampoule, which was then put into high vacuum and sealed. The synthesis was carried out in the muffle furnace. In order to obtain a homogenous material, the ampoule was first held at 750 °C for 24 h. Then slow cooling (0.5 °C/h) was carried out in the region of the crystallisation point (730–710 °C). The final cooling followed at the rate of 5 °C/h until the room temperature was achieved. The XRD measurements of the samples showed pure chalcopyrite AGT phase, see Fig. 1.

For PL measurements, the samples were mounted into the closed cycle He-cryostat equipped with a temperature controller that facilitates the temperature tuning from 8 to 300 K. Samples were optically excited with 441.6 nm He–Cd laser line with the maximum output power of 40 mW and the laser spot diameter of 100 μm . The spectra were recorded via a 40 cm grating/prism computerised monochromator system and detected with the InGaAs or R632 photomultiplier detector according to the emission band energy. The emission spectra were corrected for grating efficiency variations and for the spectral response of the detectors.

3. Discussion

Fig. 2 shows the typical low-temperature PL spectrum of AGT. Two emission regions are indicated. The first region comprises a relatively narrow edge emission band, slightly

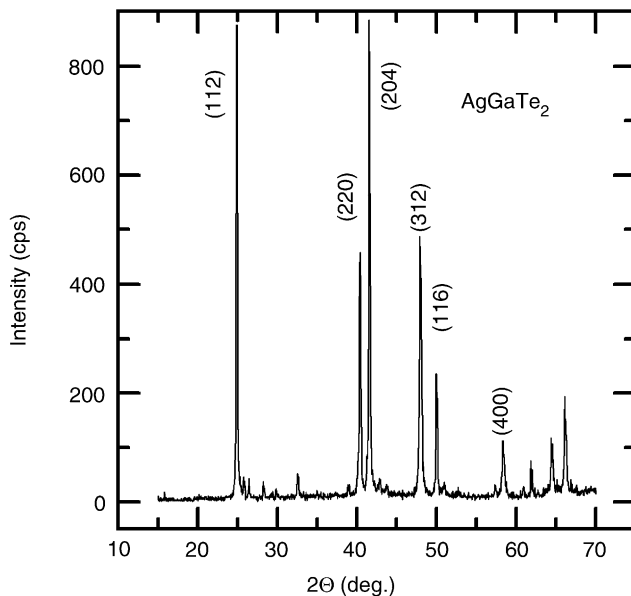


Fig. 1. X-ray diffraction pattern of polycrystalline AgGaTe_2 sample. Only major peaks are labelled.

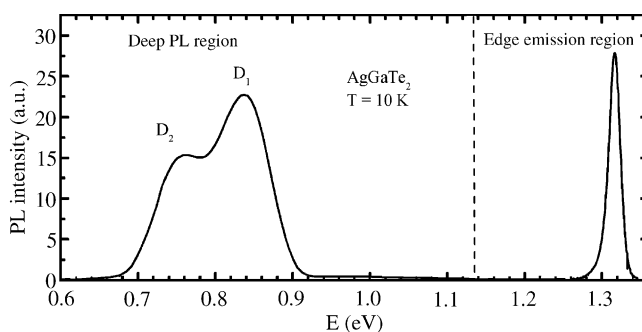


Fig. 2. Low temperature photoluminescence spectrum of polycrystalline AgGaTe_2 . Typical pattern of the chalcopyrite photoluminescence emission which consists of narrow edge emission bands and relatively wide deep photoluminescence bands is revealed.

above 1.3 eV and the second region contains deep broad emission bands D_1 (0.835 eV) and D_2 (0.755 eV). Because different dispersive media and detectors were used, Fig. 2 provides the qualitative rather than quantitative comparison of the two emission regions. Because of the stronger electron–phonon coupling of deep defect states, the spectrum confirms the rule that edge emission bands are narrower than deep bands.

The laser power dependence of the edge emission is shown in Fig. 3. In the logarithmic scale, three emission bands can be clearly distinguished. They are located at 1.337 eV (BB), 1.317 eV (BT), and 1.287 eV (BI). The band with the largest intensity (BT band) is visually asymmetric and has a steeper incline on the high energy side. That phenomenon is not common to ordinary band-to-band transition in perfect crystals, where the tilt of the peak

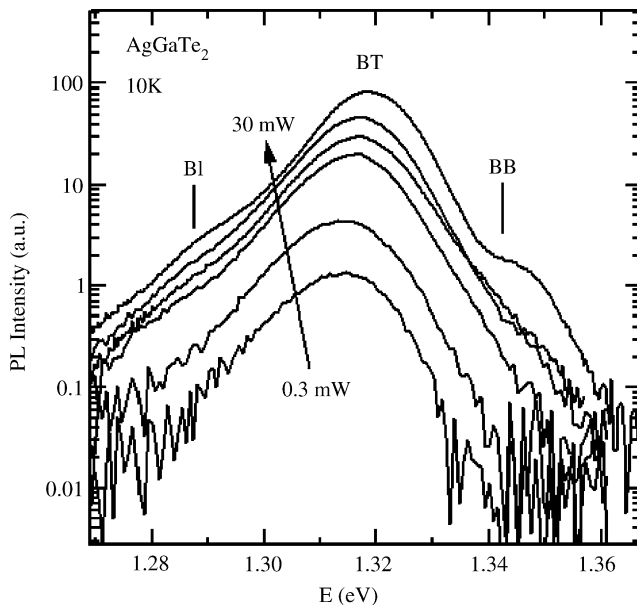


Fig. 3. Laser power dependence of the edge photoluminescence emission of AgGaTe₂ sample. Three bands are positioned as follows: band-to-impurity (BI) (1.287 eV), band-to-tail (BT) (1.317 eV), and band-to-band (BB) (1.337 eV). The asymmetric shape and the j-shift of the BT band are easily seen.

should be to the opposite side. Because of strong asymmetry, it is neither common to excitonic nor shallow impurity emission. It should be noted that peak positions found in our samples have lower energy than these measured in single crystals [2,3]. In single crystals the free exciton (FE) peak at 10 K had a maximum at 1.352 eV and the bound exciton peak was found at 1.338 eV [3]. These facts and the shift of the BT band toward higher energy with increasing laser power (see Fig. 3) suggest that the model of heavily doped semiconductors should be applied for our polycrystalline samples.

The theory of the PL of heavily doped semiconductors is described by Levanyuk and Osipov [6] and has been successfully applied to PL spectra of other chalcopyrite compounds [7–9]. According to Levanyuk and Osipov, the asymmetric shape of PL bands is caused by the potential fluctuations in the material. These fluctuations are probably caused by high concentrations of charged defects. It should be mentioned that in ternaries compositional fluctuations can also give rise to disorder and cause very similar fluctuations of the bandgap energy. In the case of heavy doping, the defects do not constitute a discrete distribution of defect levels inside the bandgap. Instead, the energy levels form a continuous distribution function. Consequently, the distribution function of shallow states overlaps the distribution function of conduction and valence band states. As a result, the so-called band tails are developed. It is shown that in this case no exciton emission can be observed [6]. The graphical illustration and theoretical discussion of this kind of configuration can be found in Ref. [6]. A short overview of this theory can also be found in Ref. [9]. The large concentration of impurities does not necessarily refer to the heavy doping by non-native atoms. On the contrary, chalcopyrite compounds tend to have the high concentration of charged native defects such as interstitials and vacancies.

Due to the band tails, new recombination mechanisms emerge. The first type of recombination is possible between free electrons in the conduction band and free holes in the valence band. By free charge carriers we mean electrons and holes that are not localised in the band tails and can move freely. The recombination between free carriers results in the band-to-band recombination (BB-band). Usually this BB recombination can be observed at higher temperatures. The second type of recombination is possible between free electrons in the conduction band and localised holes in the valence band tails (BT-band). In our spectra, the BB- and the BT-band appear at 1.337 and 1.317 eV, respectively.

The temperature dependence of the edge emission spectrum in Fig. 4 justifies the assumption of heavy doping. At low temperatures, the BT-band prevails and at higher temperatures, the BB-band starts to dominate. As the temperature rises, more and more holes that are localised in the valence band tail are thermally liberated. Therefore, the emission transforms from the BT- to the BB-band. The same behaviour was observed in CuInGaSe₂ [7] and CuGaSe₂ [8].

The blue shift of the BT-band with the increasing excitation power (j-shift)(see Fig. 3) can be explained by the filling probability of the hole states in the valence band tail. As the excitation power increases, the filling probability of the “shallow states” in the valence band tail also increases and the filling probability of the “deeper states” decreases. Accordingly, the states closer to the unperturbed band edge will be preferentially occupied by holes. Thus, the peak position of the BT-band shifts towards higher energies.

We observed another asymmetric band at 1.287 eV. This band can be attributed to the band-to-impurity recombination (BI-band). The BI recombination occurs between free electrons, and the holes that are localised at the defect states with the distribution function that does not overlap with the zones. In the case of heavy doping, the distribution of defect states is “smeared out” in the energy scale. Therefore, we can observe the characteristic asymmetric shape of the PL band. The intensity of the BI-band was not sufficient to obtain the activation energy directly from thermal quenching. However, assuming that the bandgap of AGT at 8 K is 1.358 eV [3] and because AGT tends to have p-type conductivity, we suggest that the BI-band originates from the conduction band to the shallow acceptor recombination and thus the acceptor’s activation energy can be found by subtracting the BI-band peak position energy from the AGT bandgap energy. By doing this we get a value of about 70 meV.

Fig. 5 shows the shift of the BT-band’s peak position according to the sample temperature. At low temperatures, the peak shifts towards higher energies with the increasing temperature. This tendency continues to some characteristic temperature where the peak position has its maximum value (1.323 eV at 45 K). After that, the peak starts to shift towards lower energies. A similar behaviour was observed in Refs. [2,3]. Because the BT-band position is strongly influenced by the bandgap energy, the shift can be explained by the characteristic bandgap energy temperature dependence of AGT. Unfortunately this dependence in AGT is not known, but analogous behaviour of the bandgap has also been observed in other silver containing chalcopyrites like AgGaSe₂ and AgGaS₂ [10]. In AgInSe₂ for example the bandgap energy increases about 8 meV from $T = 4.2$ to 150 K [11].

Fig. 2 shows also the deep PL emission region of AGT. Two PL bands at 0.755 and 0.835 eV can be easily resolved. Usually, those deep bands are attributed to a recombination through deep defect levels. In amorphous semiconductors like arsenic chalcogenides these midgap levels are related with bonding defects. However, our samples

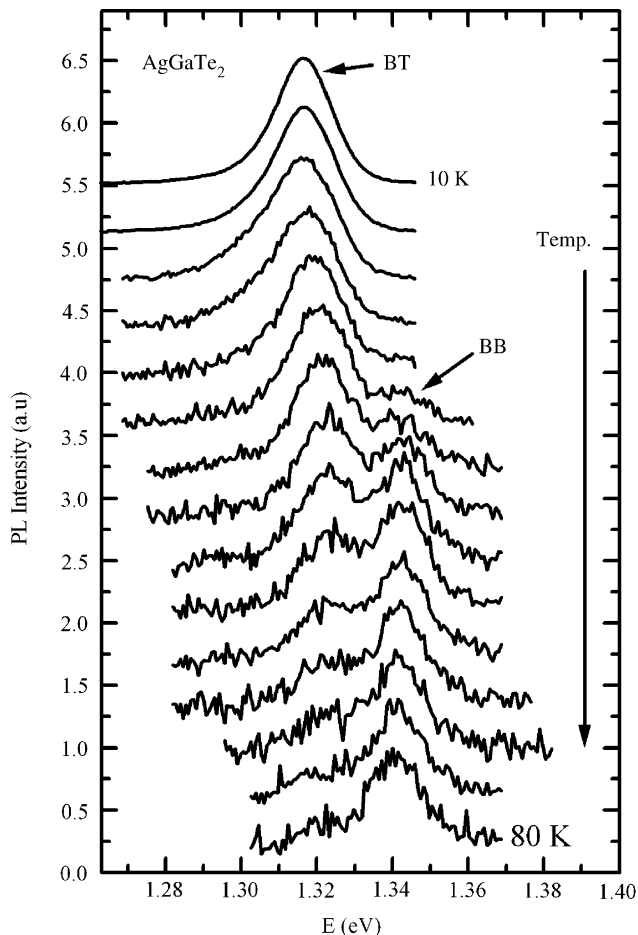


Fig. 4. Normalised photoluminescence spectra of the edge emission bands of AgGaTe_2 at various temperatures. At low temperatures the band-to-tail band prevails. As the temperature rises, the band-to-band recombination starts to dominate.

show quite good crystallinity (see Fig. 1), therefore, the presence of bonding defects is very improbable. The usual DAP recombination is also questionable, because no j-shift of D_1 and D_2 bands according to laser power variations was detected.

Furthermore, because of their deep position and rather low activation energy (see Figs. 6 and 8 and the explanation below) D_1 and D_2 bands cannot be the products of free-to-bound recombination. Nevertheless, one possible explanation for those bands can be the so-called deep donor–deep acceptor (DD–DA) pair model, where optical transition occurs between donor and acceptor that are positioned in the same unit cell of the crystal. In that case there is no distance distribution between DAP parts and j-shift cannot be observed. This DD–DA pair model has also been applied to other chalcopyrite materials like CuGaSe_2 , CuInS_2 , CuInGaSe_2 , and AgInS_2 [12–15].

The deep PL region was fitted with 3 Gaussian bands (see Fig. 7). In order to obtain information about the defect levels responsible for a particular PL band, the temperature

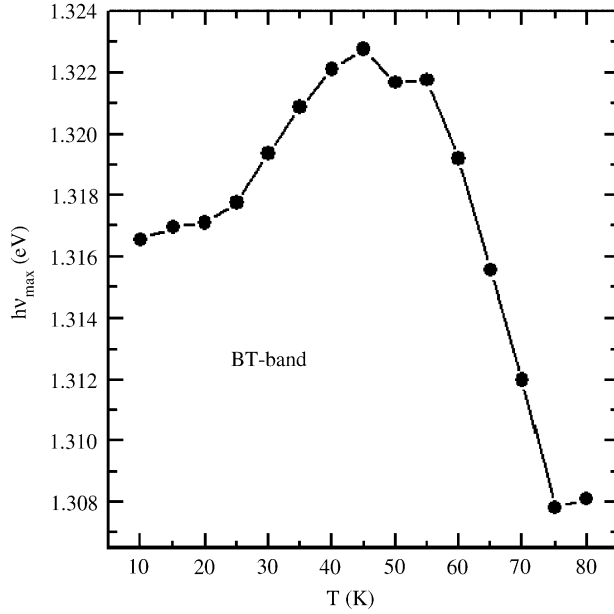


Fig. 5. Temperature dependence of the band-to-tail photoluminescence band of AgGaTe_2 . The shift of edge emission bands is mainly caused by the temperature dependence of the bandgap energy.

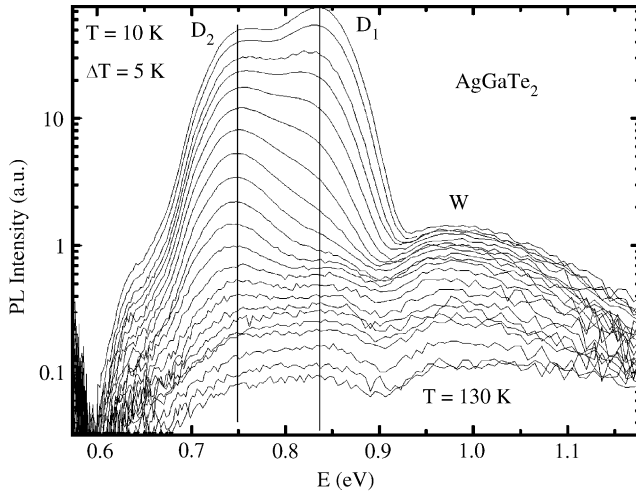


Fig. 6. Photoluminescence spectra of the deep emission bands of AgGaTe_2 at various temperatures.

dependence of the integrated intensity $I(T)$ is often used. Usually there are no problems with high temperature measurements, but sometimes low temperature quenching is erroneously characterised as a thermally activated process with well-defined activation energy. In Ref. [16], however, it was shown that the low-temperature quenching may not really be a thermal activation process, instead, it is caused by a temperature dependence of

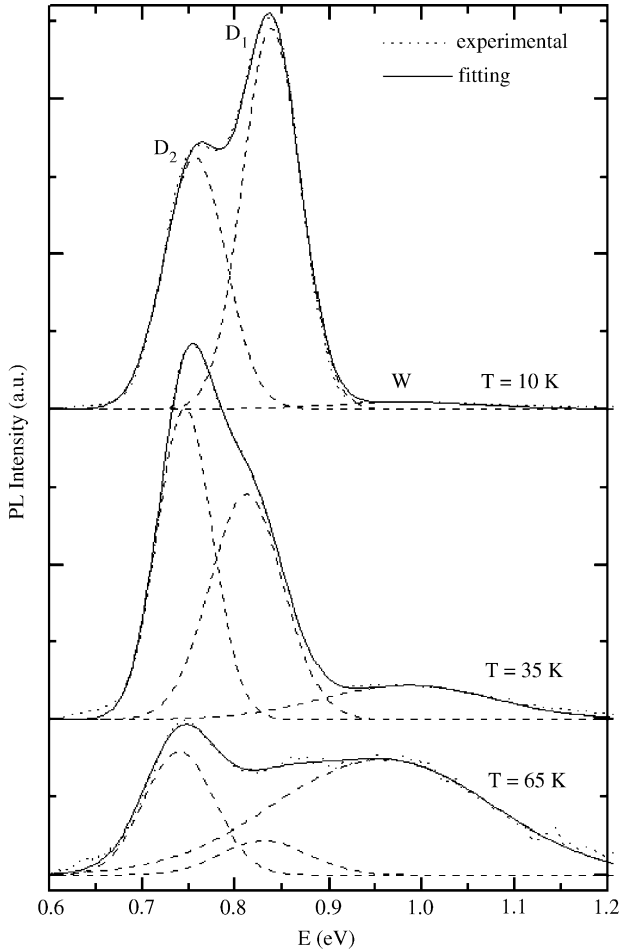


Fig. 7. Results of Gaussian fitting of the deep emission bands of AgGaTe₂ for 3 temperatures.

the capture cross sections of a particular recombination centre. According to this theory the temperature dependence of the integral intensity is

$$I(T) = \frac{I_0}{1 + c_1 T^{3/2} + c_2 T^{3/2} \exp(-E_T/kT)}, \tag{1}$$

where E_T is the activation energy. The results of the fittings with Eq. (1) showed very similar thermal activation energies about 20 meV for both D_1 and D_2 bands (see Fig. 8). The low activation energy for such deep bands can be explained by several models. The first involves DD–DA pair which energy levels inside the bandgap are shifted due to the Coulomb energy. In that case one pair component may find itself very close to band edge and thermal quenching comes from thermal ionisation of this state to the band. The second quenching mechanism can be the thermal activation of non-radiative recombination centre. The third quenching mechanism is explained by configuration coordinate model where electrons transfer directly from the excited state to the ground state (internal

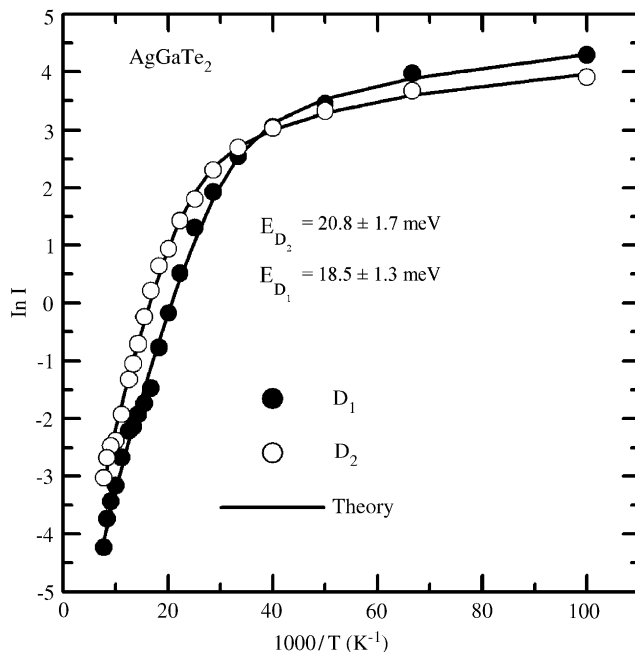


Fig. 8. Temperature dependence of integrated intensity of the D_1 and D_2 photoluminescence bands. Continuous curves show the result of fitting with Eq. (1).

quenching of luminescence). Which one of these models governs our quenching process is the subject of further studies.

At higher temperatures ($T \sim 40$ K) the new PL emission band (W-band) appears between 0.95 and 1.0 eV. The intensity of this band was not high enough for applying detailed studies on it.

4. Conclusion

The PL spectra of AGT prove that polycrystalline ternary chalcopyrite materials tend to have large concentration of native defects. This conclusion is based on the observation of the asymmetric shape of the edge emission bands and their temperature dependence. According to the model of heavily doped semiconductors, band-to-band (BB), band-to-tail (BT), and band-to-impurity (BI) bands are identified. From the latter band position an acceptor defect with energy $E_A = 70$ meV was estimated. The bands in the deep PL region show very rapid thermal quenching with the activation energies about 20 meV. We believe that these bands can be attributed to deep donor–deep acceptor pair recombination mechanism, but further studies are still needed.

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