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Coarsening behavior of γ' and γ'' phases in GH4169 superalloy by electric field treatment

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Abstract: The coarsening behaviors of γ' and γ'' phases in GH4169 alloy aged at 1023 and 1073 K with electric field treatment (EFT) were investigated by transmission electron microscopy (TEM) and positron annihilation lifetime spectroscopy (PALS). It is demonstrated that precipitation coarsening occurs, and the growth activation energies of γ' and γ'' phases can be decreased to 115.6 and 198.1 kJ·mol^{-1}, respectively, by applying the electric field. The formation of a large number of vacancies in the matrix is induced by EFT. Due to the occurrence of vacancy migration, the diffusion coefficients of Al and Nb atoms are increased to be 1.6-5.0 times larger than those without EFT at 1023 or 1073 K. Furthermore, the formation of vacancy clusters is promoted by EFT, and the increase in strain energy for the coarsening of γ' and γ'' phases can be counterbalanced by the formation of vacancy clusters.

Keywords: superalloys; nickel alloys; precipitation; electric fields; aging; vacancies

1. Introduction

Precipitation coarsening in precipitation-strengthening alloys is of great significance for controlling the mechanical properties of the alloys. For GH4169 alloy, the main contribution to strength is provided by γ'' phase (Ni_3Nb). Coarsening of γ'' phase has been investigated based on the theory by Lifshitz and Slyozov [1] and Wagner [2] (LSW theory), and it follows the $t^{1/3}$ law in the aging temperature range of 873-1073 K [3-6]. The other commonly observed strengthening phase in the alloy is γ' phase (Ni_3Al). In many Ni-based alloys, the coarsening of γ' phase also follows the $d \propto t^{1/3}$ law from 898 to 973 K [7-10]. The above-mentioned characteristics of the coarsening process of γ' or γ'' phase were just discussed under a conventional thermodynamic field.

Over the past several years, for the sake of further improving the relevant properties of materials, the electric field as an energy field has been occasionally applied to the materials during deformation, solidification, quenching, etc. It has been found that the movement of defects (e.g., vacancies, dislocations, or grain boundaries) in materials can be accelerated, resulting in the superplastic deformation of 7475 Al alloy [11-12], an increase in the grain size of polycrystalline NaCl [13], as well as an improvement in the hardness of carbon steel [14-15]. Compared with the traditional process, as a low-cost and environment friendly method for material manufacturing, electric field treatment (EFT) on materials could bring about many advantages for their properties. Recently, Wang *et al.* [10] reported the growth activation energy of precipitation in GH4199 alloy under the action of dual energy fields consisting of the electric and the thermodynamic fields, and Guo *et al.* [16] reported the active coefficient of Al in the liquid alloy of Cu-0.2wt%Al with the increase of electric current, but there are no reports yet on the diffusion rate of solute atoms in the investigated material matrix.

In the present study, a 6-kV/cm electric field was carried out on GH4169 alloy during aging processes to investigate the mechanism for the effect of EFT on the coarsening behavior of both γ' and γ'' phases.

2. Experimental procedures

A GH4169 alloy bar with a diameter of 31 mm was provided by Fushun Special Steel Co. Ltd., China, and

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its chemical composition is listed in Table 1. The bar was machined to plates of 120 mm×20 mm×1 mm by wire cutting. The plates were solution treated at 1473 K for 8 min, followed by air cooling (AC), and then, the specimen was connected to the anode of a direct current voltage. A 6-kV/cm electric field was provided between poles. For comparison, the specimen was aged with the same procedures without EFT.

Table 1. Chemical composition of GH4169 alloy used in the present study wt%

Fe	Cr	Nb	Mo	Ti	Al	Co	Si	C	Cu	B	Ni
19.25	18.78	4.96	3.09	1.00	0.65	<0.10	0.082	0.036	0.0056	0.0028	Bal.

The samples for transmission electron microscopy (TEM) were first sliced from the central region of the sheet type specimen by spark cutting parallel to the specimen surface, then mechanically thinned down to around 60 μm, and finally polished by a twin-jet method using a 9vol% solution of HNO_3 in ethanol at 243 K and 36 V. TEM examination was performed with a JEOL JEM-2100F transmission electron microscope, operated at 200 kV. About 100-200 individual γ' or γ'' phase particles were measured for each treatment condition to establish their size distributions.

The pair of specimens with the size of ϕ10 mm×1 mm were cut from the aged specimen and mechanically polished to obtain a smooth surface for positron annihilation tests. The radioactive ^{22}NaCl source was used for positron annihilation spectroscopy, and the positron annihilation lifetime (PAL) and the corresponding vacancy intensity in two identical specimens were measured for 4 h at room temperature.

3. Results

The dark-field micro-morphologies of γ' and γ'' phases in the specimen aged at 1023 K are shown in Fig. 1. It can be seen that the average sizes of γ' and γ'' phases increase as the aging time prolongs. Meanwhile, it is obvious that both γ' and γ'' phases have been coarsen under the EFT. However, based on TEM observation, it is found that the volume fractions of γ' and γ'' phases in the alloy are still 1.8vol%±0.07vol% and 13.0vol%±0.12vol%, respectively, at 1023 or 1073 K, whether the EFT is applied or not for different time ranging from 30 to 193 h.

It is known that if the coarsening is controlled by atom

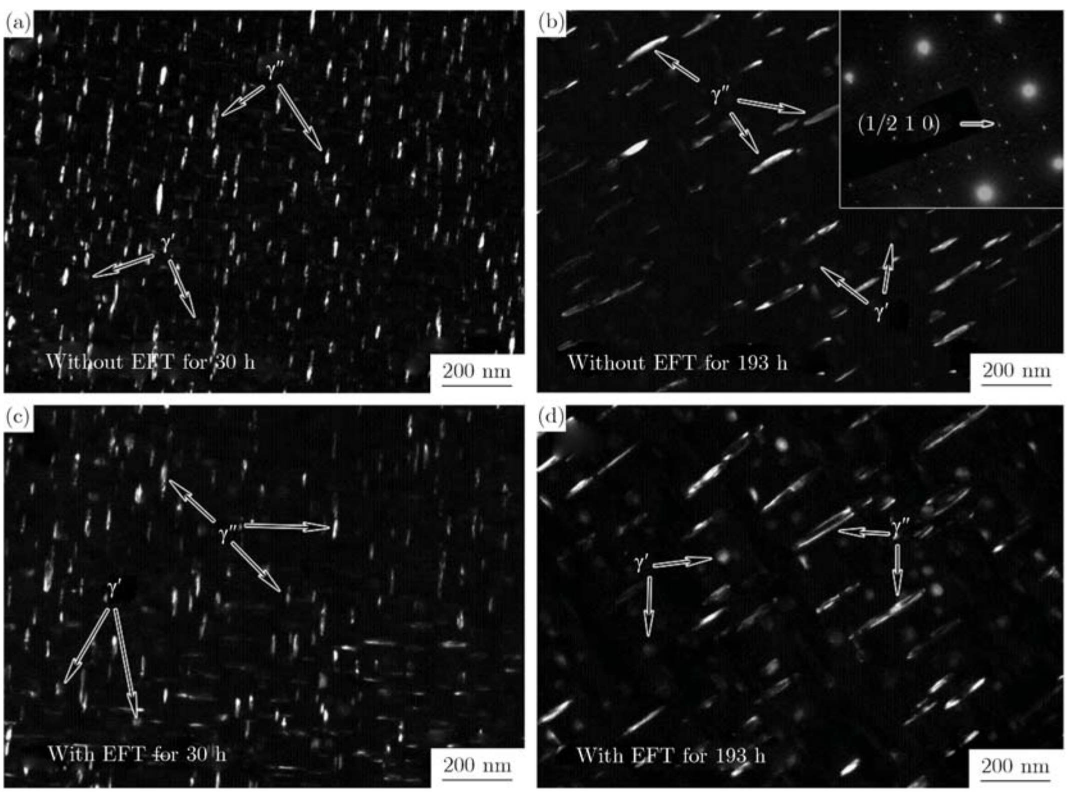

Fig. 1. Dark-field morphologies of γ' and γ'' phases on the (1/2 1 0)plane in the specimens aged at 1023 K: (a) without EFT for 30 h; (b) without EFT for 193 h; (c) with EFT for 30 h; (d) with EFT for 193 h.

diffusion, the growth of the precipitate will follow the LSW theory, and the kinetic equation for a spherical precipitate can be expressed as

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8\Gamma D C_\mathrm{e} V_\mathrm{m}^2}{9RT} t = K't \tag{1}$$

where $\bar{r}$ is the average radius of the precipitates at time t, $\bar{r}_0$ the radius in the initial coarsening process, Γ the particle/matrix interfacial energy, D the diffusion coefficient in the matrix, C_e the solute atom concentration in equilibrium with a particle of infinite radius, R the gas constant, T the aging temperature, V_m the molar volume, and K' the growth rate of the spherical precipitate. Usually, if the spherical shaped γ' particles grow up by volume diffusion, the relationship of $\bar{\gamma}^3$ against time t should be linear. The experimental data are plotted in Fig. 2 for the specimen aged at 1023 or 1073 K without EFT.

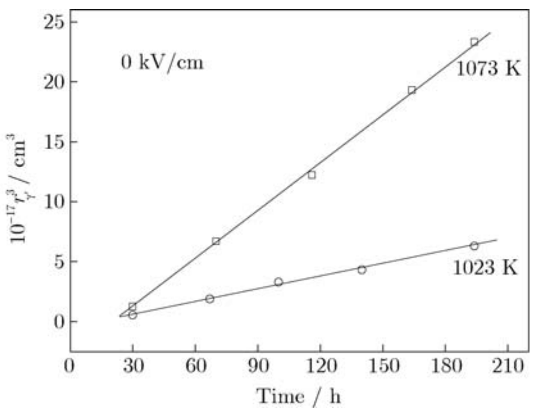

Fig. 2. Variation in $\bar{r}^3$ of γ' phase with aging time at different aging temperatures without EFT.

According to the LSW theory, the activation energy for the coarsening process should be equal to the diffusion activation energy of solute atoms. The diffusion coefficient D in Eq. (1) is defined as

$$D = D_0 \exp(-Q/RT) \tag{2}$$

where D_0 is the frequency factor and Q is the activation energy. Eq. (1) can be rewritten as

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8\Gamma C_\mathrm{e} V_\mathrm{m}^2 D_0}{9R} \frac{t}{T} \exp(-Q_{\gamma'}/RT) = K't \tag{3}$$

where the growth activation energy $Q_{\gamma'}$ is expressed by

$$Q_{\gamma'} = (A' - \ln K'T)RT \tag{4}$$

where A' is a constant. Thus, $Q_{\gamma'}$ of γ' phase without EFT can be calculated to be 241.7 kJ·mol^{-1}.

Similarly, γ'' phase coarsening without EFT is also controlled by volume diffusion, since the linear relationship exists between $\bar{d}^3$ and t at 1023 and 1073 K, as shown in Fig. 3. For the disc shaped γ'' phases, Eq. (1) has been modified by Boyd and Nicholson [17] to

$$\bar{d}^3 - \bar{d}_0^3 = \frac{128\Gamma q D C_\mathrm{e} V_\mathrm{m}^2}{9\pi RT} t = K''t \tag{5}$$

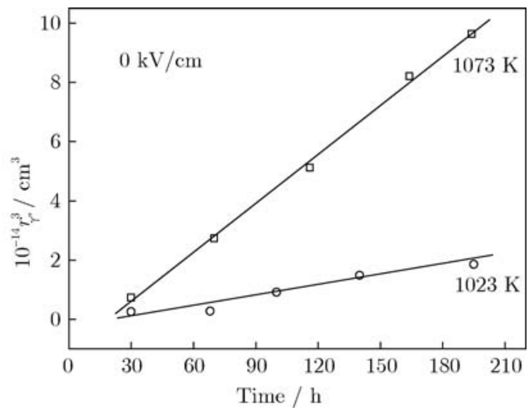

Fig. 3. Variation in $\bar{d}^3$ of γ'' phase with aging time at different aging temperatures without EFT.

where $\bar{d}$ is the mean diameter of the disc shaped precipitations, q the ratio of d to h (h is the thickness of precipitates), and K'' the growth rate of the disc shaped precipitate. Analogously, the growth activation energy $Q_{\gamma''}$ can be expressed by

$$Q_{\gamma''} = (A'' - \ln K''T)RT \tag{6}$$

where A'' is also a constant. Accordingly, $Q_{\gamma''}$ for γ'' phase without EFT can be measured to be 285.6 kJ·mol^{-1}. For the present alloy aged under the thermodynamic field, the calculated values of $Q_{\gamma'}$ and $Q_{\gamma''}$ are in good agreement with the measured values of (271±49) kJ·mol^{-1} for γ' phase and 198±41 kJ·mol^{-1} for γ'' phases reported by Han *et al.* [6] and 272 kJ·mol^{-1} for γ'' phases reported by Devaux *et al.* [18].

The sizes of γ' and γ'' phases EFTed at 1023 or 1073 K were also measured. It is evident that the coarsening of both γ' and γ'' phases is accelerated by EFT, e.g., the average size of γ'' phases in the specimen aged at 1073 K for 197 h with EFT is 653 nm, about 49.2% larger than that without EFT (the average size of γ'' phases is 457 nm). The cube of precipitate size against time t presents a linear relationship, as shown in Fig. 4. It implies that either γ' or γ'' particle grows up by volume diffusion even with the action of EFT. In this case, $Q'_{r'}$ and $Q'_{r''}$ are determined to be 115.6 and 198.1 kJ·mol^{-1}, respectively.

4. Discussion

4.1. Effect of EFT on the diffusion coefficient

Based on the above results, it is clear that the growth activation energy Q' for either γ' or γ'' phase with EFT is obviously lower than that without EFT. Since the growth of γ' or γ'' phase is mainly controlled by the diffusion of Al or Nb atom during aging, the diffusion coefficients of Al and Nb atoms in both electric and thermodynamic fields need to be determined. Based on the slope of straight lines of r^3 or d^3 versus t in Fig. 4, the growth rates K_exp of γ' and γ'' phases can thus be obtained, as listed in Table 2.

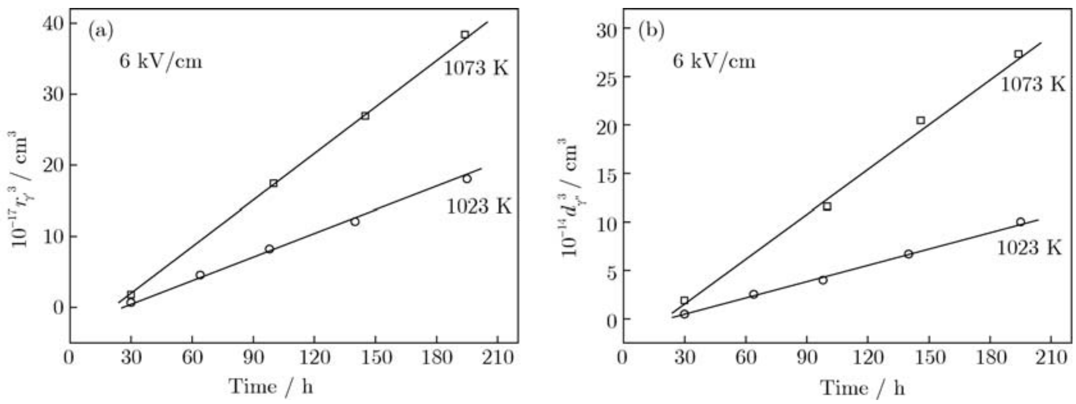

Fig. 4. Variation in the cube of precipitate size with aging time at different temperatures with EFT.

Table 2. Determination of the values of constant $K_{\rm cal}$ and $K_{\rm exp}$ without EFT

Phase	Γ / (mJ ·m^{-2})	q	D / (m^2·s^{-1})	$C_{\rm e}$ / (mol·m^{-3})	$V_{\rm m}$ / (m^3·mol^{-1})	$K_{\rm cal}$ / (m^3·s^{-1})	$K_{\rm exp}$ / (m^3·s^{-1})
γ'(1023 K)	25.3 [7]	—	0.53×10^{-17} [21]	1449.8	6.74×10^{-6}	9.20×10^{-29}	9.24×10^{-29}
γ'(1073 K)	90.9 [19]	—	2.20×10^{-17} [21]	1449.8	6.74×10^{-6}	0.31×10^{-27}	0.32×10^{-27}
γ'(1023 K)	95 [18]	4.9	0.71×10^{-17} [21]	2560.0	2.44×10^{-5}	2.70×10^{-27}	2.73×10^{-27}
γ'(1073 K)	296 [20]	10.3	2.81×10^{-17} [21]	2560.0	2.44×10^{-5}	1.32×10^{-25}	1.33×10^{-25}

Note: $K_{\rm cal}$ — the obtained growth rate of precipitates by the theoretical arithmetic; $K_{\rm exp}$ — the obtained growth rate of precipitates based on the slope of straight lines in Figs. 2, 3 or 4.

According to the LSW theory, the growth rates of precipitates can be described from Eq. (3) and (5) as

$$K' = 8\ \Gamma D C_{\rm e} V_{\rm m}^2 / 9RT \quad (7)$$

$$K'' = 128\ \Gamma q D C_{\rm e} V_{\rm m}^2 / 9\pi RT \quad (8)$$

One of the critical parameters in Eqs. (7) and (8) is the interfacial energy Γ, which has been determined by the studies of precipitation coarsening kinetics. For example, most reported values are for Ni-Al binary alloys [7, 22-27], and there are few reports on the value of interfacial energy between γ' and γ (γ is the matrix) for multicomponent alloys, except that a value of 90.9 mJ·m^{-2} has been reported for a Ni-Fe-Cr system NIMONIC PE16 alloy aged at 1073 K [19], which is similar to the present alloy. In addition, Adrell and Nicholson [7] reported the interfacial energy between γ' and γ at 1023 K to be 25.3 mJ·m^{-2} for Ni-6.71Al alloy. The values of 296 and 95 mJ·m^{-2} for the interfacial energy between γ'' and γ of Inconel 718 alloy at 1063 and 1023 K were calculated by Oblak *et al.* [20] and Devaux *et al.* [18], respectively. In the present study, the diffusion coefficients of solute atoms in pure nickel can be adopted by the expressions D=1.0×10^{-4}exp($-260/RT$) (Al, 914-1212 K) and D= 0.44×10^{-4}exp($-250.5/RT$) (Nb, 973-1373 K) [21]. Moreover, an average molar concentration $C_{\rm e}$ for the Nb concentration of 1.8at% was reported to be 2560 mol·m^{-3} [18], and the Al molar concentration can therefore be evaluated to be 1449.8 mol·m^{-3} for the present alloy based on the alloy's chemical composition, as listed in Table 1. The molar volume $V_{\rm m}$ of precipitates can be obtained from $V_{\rm m} = 0.25 N_{\rm A} a_{\rm particle}^3$ where $N_{\rm A}$ is the Avogadro's number and $a_{\rm particle}$ is the lattice parameter of the precipitate [9].

Thus, the growth rates $K_{\rm cal}$ of precipitates at 1023 or 1073 K without EFT can be calculated, as shown in Table 2. Without EFT, it can be found that the $K_{\rm cal}$ values for γ' and γ'' phases are very close to the $K_{\rm exp}$ values at 1023 and 1073 K. Therefore, with EFT, the $K_{\rm exp}$ values for γ' and γ'' phases at 1023 or 1073 K are believed to be approximately equal to the $K_{\rm cal}$ values. According to Eqs. (7) and (8), the diffusion coefficients are calculated and listed in Table 3. Clearly, the diffusion coefficients of Nb and Al atoms in the matrix with EFT are about 1.6-5.0 times larger than those without EFT.

Table 3. Diffusion coefficients of Nb and Al atoms in GH4169 alloy during aging at different temperatures with a 6 kV/cm electric field

Atom	Temperature / K	$K_{\rm exp}$ / (m^3·s^{-1})	$D_{\rm cal}$ / (m^2·s^{-1})
Nb	1073	3.81×10^{-25}	8.12×10^{-17}
	1023	1.35×10^{-26}	3.57×10^{-17}
Al	1073	0.53×10^{-27}	3.54×10^{-17}
	1023	0.25×10^{-27}	1.46×10^{-17}

4.2. Effect of EFT on the vacancy variation

Fig. 5 shows the variation curves of vacancy with aging time. The relative concentration percentage of monovacancy with EFT is lower than that without EFT, as shown in Fig. 5(a). With EFT, the gradient force will be exerted to atoms [28]; more active atom vibration is encouraged, so that the atoms become easier to jump out from the normal lattice sites to form monovacancies. During EFT, the surfaces of specimens with a large number of positive charges form. A mass of monovacancies will migrate toward the charged surfaces by exchanging sites with solution atoms, leading to a rapid increase in diffusion coefficients of some atoms, e.g., Al and Nb. Therefore, the relative concentration percentage of monovacancy will be reduced due to the oriented migration of monovacancies.

Generally, the binding force between atoms around vacancy is a weak one, so that more vacancy clusters can form due to the high active atom vibration induced by EFT. However, compared with the monovacancy, the vacancy cluster is difficult to migrate because of its larger size. Thus, the relative concentration percentage of vacancy clusters with EFT is higher than that without EFT at either 1023 or 1073 K (Fig. 5(b)).

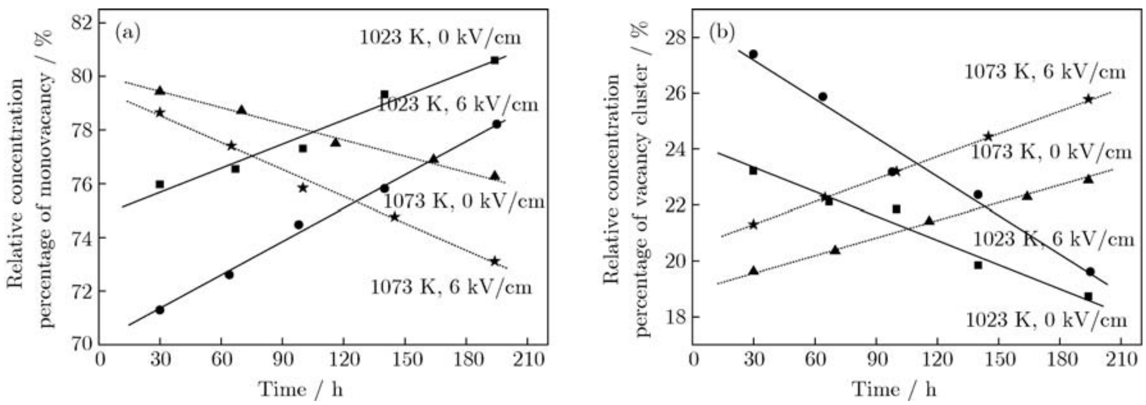

Fig. 5. Variation curves of the monovacancy (a) and vacancy cluster (b) with aging time.

With the decrease in growth activation energy for either γ' or γ'' phase by the action of EFT, it can be found that, on the one hand, the diffusion of Al and Nb atoms can be accelerated by monovacancy migration, which will enhance precipitation coarsening; on the other hand, the strain energy for precipitation coarsening can be counterbalanced by the increase of vacancy clusters, and it is also helpful for the coarsening of γ' and γ'' phases. Therefore, since the variation of vacancies in GH4169 alloy can be induced by the action of EFT, both the diffusion rate of atoms and vacancy clusters can be increased by the occurrence of vacancy flow, and it leads to decreased strain energy for precipitation coarsening. These are considered as the most important factors for precipitation coarsening in GH4169 alloy under a 6 kV/cm EFT.

5. Conclusions

(1) The migration of monovacancies toward the charged surfaces of specimens can be promoted by EFT, and the diffusion of Al and Nb atoms will be accelerated by exchanging their sites with monovacancies. With the application of EFT, the diffusion coefficients increase to 1.46×10^{-17} (Al, 1023 K), 3.54×10^{-17} (Al, 1073 K), 3.57×10^{-17} (Nb, 1023 K), and 8.12×10^{-17} $m^2\cdot s^{-1}$ (Nb, 1073 K), which are about 2.8, 1.6, 5.0, and 2.9 times larger than those without EFT, respectively.

(2) The coarsening of either γ' or γ'' phase is accelerated by the applying of EFT. The growth activation energies of γ' and γ'' phases with EFT are obtained to be 115.6 and 198.1 $kJ\cdot mol^{-1}$, respectively, which are much lower than the values of 241.7 and 285.6 $kJ\cdot mol^{-1}$ without EFT.

Acknowledgements

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