Temperature Dependence of the Fano Resonance in Nanodiamonds Synthesized at High Static Pressures

A. A. Shiryaev\textsuperscript{a, b}, E. A. Ekimov\textsuperscript{c}, V. Yu. Prokof'ev\textsuperscript{b}, and M. V. Kondrin\textsuperscript{c}, *

\textsuperscript{a} Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119071 Russia
\textsuperscript{b} Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, 119017 Russia
\textsuperscript{c} Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, Moscow, 108840 Russia

* e-mail: mkondrin@hppi.troitsk.ru

Received March 24, 2022; revised April 18, 2022; accepted April 24, 2022

The temperature dependence of the Fano resonance recently discovered in infrared spectra of nanodiamonds synthesized from chloroadamantane at high static pressures is investigated. For the first time, marked variations of the resonance parameters are observed. On heating, the shape of the Fano resonance changes considerably; the effect completely disappears above 350\degree C, but is recovered after cooling to ambient conditions. Such behavior implies that assignment of the Fano effect to the surface transfer doping mechanism is not very plausible for the studied samples. The resonance shape varies due to a strong temperature dependence of the difference between the frequencies of infrared-active “bright” and Raman-active “dark” modes of nanodiamond. The frequency of the Raman dark mode is only weakly temperature-dependent.

DOI: 10.1134/S0021364022600720

1. INTRODUCTION

The Fano effect predicted by Ugo Fano in the 1930s [1, 2] attracts considerable attention in recent years [3–5]. Rapid switching from absorption to transmission induced by the Fano effect is of significant fundamental and applied interest. Fano resonances are observed in metamaterials, metasurfaces, nanoshells, and many other types of nanodisperse materials [3–9]. Recently, two groups reported observation of the Fano effect in the infrared (IR) absorption spectra of nanodiamonds larger than 2 nm, which synthesized from adamantane and its derivatives at high static pressures [10, 11]. Note that synthesis from halogenated hydrocarbons is a rapidly developing technology [12–16], allowing growth of nanodiamond grains with well-controlled sizes from 1 nm and larger. Such nanodiamonds are promising for applications in biomedicine, quantum optics, and cryptography [17]. The Fano resonance in nanodiamonds is manifested as a “transparency” window at about 1330 cm\(^{-1}\), i.e., near the Raman frequency of diamond. Recall that the Raman mode in pure diamond is IR-inactive. The origin of the Fano resonance in nanodiamond remains debatable. Infrared absorption at the Raman frequency is assumingly due to conductive states on surfaces of nanodiamond grains. The appearance of these states is not yet fully understood: they might be related to adsorbed water/oxygen/etc. (so-called surface transfer doping mechanism [18–20]) on hydrogenated nanodiamonds [10] or arise from surface reconstruction [11]. In the latter case, the reconstruction leads to the formation of trans-polyacetylene-like fragments on the surfaces. Correlation between the electrical conductivity of nanodiamonds and the appearance of the Fano effect in IR absorption was established earlier: 8-nm grains exhibit the Fano effect and significant conductivity (\(10^5–10^6\ \Omega \text{cm}\)), whereas both these features are absent for grains smaller than 2 nm [11]. To elucidate the origin of conductive states in nanodiamonds demonstrating the Fano effect at room temperature, we performed in situ measurements of IR reflection spectra in a wide temperature range both in inert atmosphere (dry N\(_2\) flow) and in air. These results are presented below.

The Fano effect is caused by the coherent interaction of an optically-active (“bright”) broadband mode with an optically inactive (“dark”) narrow mode. Due to this interaction, the dark mode is manifested in optical spectra as a peak with a peculiar asymmetric lineshape. Despite a quantum origin of the Fano resonance, the resulting effects can be modelled with two classical coupled oscillators, which can be described using the matrix equation [5, 9, 21, 22]

\[
\begin{pmatrix}
\omega - \omega_1 - i\gamma & g \\
g & \omega - \omega_2
\end{pmatrix}
\begin{pmatrix}
x_1 \\
x_2
\end{pmatrix}
= i
\begin{pmatrix}
f_1 \\
f_2
\end{pmatrix}
\]

Here, \(\omega_1\) and \(\omega_2\) are the characteristic frequencies of the bright and dark modes, respectively; \(\gamma\) is the
width of the bright mode; and \( g \) is the coupling constant between the bright and dark modes. These constants, driving force amplitude \( f_1 \), and frequency \( \omega \) are given in energy units. The system response \( x_1 \) is dimensionless. Note that the driving force consists of a single component \( f_1 \), implying that only one of the oscillators directly interacts with the external field.

The solution of the above equation has the form

\[
\|x_1^2\| = \frac{|f_1|^2}{(\omega - \omega_0 + \Gamma F)^2 + \Gamma^2},
\]

(1)

where \( F, \Gamma, \omega_0 \), and \( A \) are functions of the frequency \( \omega \) given by the expressions

\[
F = \frac{\omega - \omega_0}{\gamma},
\]

(2)

\[
\Gamma = \frac{g^2}{\gamma(1 + F^2)},
\]

(3)

\[
\omega_0 = \omega_0 + \Gamma F,
\]

(4)

\[
A = \frac{1}{\gamma(1 + F^2)}.
\]

(5)

At the same time, near the frequency of the dark mode (infinitely narrow in the coupled oscillators model), these functions can be approximated by constants with the substitution \( \omega \to \omega_0 \) in Eq. (2). In this case, Eq. (1) becomes asymmetric, thus giving the characteristic Fano lineshape. Accordingly, the parameter \( A \) is the absorption amplitude; \( \Gamma \) and \( \omega_0 \) are the width and characteristic frequency of the absorption line, respectively; and the Fano parameter \( F \) is the line asymmetry coefficient. A typical example of such lineshape is shown in Fig. 1, where the experimental IR absorption spectrum of 8-nm nanodiamonds synthesized from chloroadamantane at high pressures is fitted. Note that the lineshape asymmetry leads to the appearance of the transmission window at frequencies above the Fano resonance.

An important note about the fitting shown in Fig. 1 should be made. We employed Eq. (1) together an additional incoherent background approximated by a straight line. Equation (1) implies a positive parameter \( A \) for the absorption line. In the course of arbitrary fit of experimental data, this coefficient of proportionality can become negative. In such cases, an additional spectral density can be added according to the formula

\[
\frac{(F + \Omega)^2}{(1 + F^2)} + (1 + F^2) = F^2 \frac{(1/F - \Omega)^2}{(1 + \Omega^2)}.
\]

(6)

where \( \Omega = (\omega - \omega_0)/\Gamma \). Consequently, the amplitude of the Fano resonance (equal to \(-1\)) can be converted into a positive number \((F^2)\) with simultaneous substitution \( F \to -1/F \). We note that in our previous work [11], this procedure was not applied (the resonance amplitude was negative), leading to a wrong value of the Fano parameter. Figure 1 shows corrected values of the \( F \) parameter.

2. EXPERIMENT

Spectroscopic studies of nanodiamonds with 8-nm grains (see also [11]) were performed at the Geochemistry Laboratory, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences. Nanodiamond powder was measured on an Al mirror placed into a Linkam THMSG600 heating stage [23] controlled by a T95 temperature controller [24]. The mirror with the sample was covered by an IR-transparent BaF\(_2\) plate having a direct contact with the heater, thus assuring uniform equilibrium heating. The temperature was calibrated using a reference phase transition at 289°C; the measured temperature was 288°C. Therefore, the accuracy of the temperature readings was 1°C, which is comparable with earlier studies of mineralogical thin sections [25]. Infrared spectra were recorded in reflection geometry using a Lumos II FTIR microscope at a spectral resolution of 2 cm\(^{-1}\) with 600–1000 scans (5–10 min). The measurements were performed in air between 22 and 400°C, and in inert atmosphere of continuous flow of dry N\(_2\) between –80 and 380°C with temperature steps of 20–50°C. The spectra were also recorded at room temperature after

![Image](image-url)
Comparison of several independent runs showed that the results were insensitive to the heating regime.

The absence of the Fano effect for nanodiamonds smaller than 2 nm was shown in [11]. In these samples, several IR absorption peaks are observed near the Raman frequency. In the intermediate size range, the Fano resonance is heavily modulated by IR absorption bands [11]. Nanodiamonds with a grain size of 8 nm demonstrate a pronounced Fano effect; this sample was used in our work for the step heating spectroscopic experiments.

3. RESULTS

Experimental IR reflection spectra recorded at temperatures between –80 and 400°C are shown in Figs. 2 and 3. At high temperatures, the Fano resonance disappears. Only the Fano band at ~1330 cm⁻¹ and valence vibrations of C–H bonds at ~3000 cm⁻¹ are observed in spectra, no other bands are present. The C–H groups are common for nanodiamonds. Irreversible surface reconstruction and disappearance of the surface charge contribution to the conductivity are observed for hydrogenated diamond films after heating in air to 230°C [18]. This effect is obviously due to the removal of physically adsorbed water/oxygen molecules, since such low temperatures do not affect H-containing functional groups [26]. In our experiments, cooling from 380–400°C to room temperature leads to recovery of the Fano effect both in air and in inert atmosphere. Persistence of the Fano effect in nanodiamonds after prolonged (24 h) heating at 250°C in air was demonstrated earlier [11].

Prior to discussion of the Fano effect on heated and annealed nanodiamond samples, we discuss the amplitudes of the bands in the reflection spectra. One might assume that the absorption coefficient is independent of the temperature with an accuracy to a multiplicative constant. However, in our experiments the
amplitude of the C–H modes increases with temperature (see also [27]). Such a behavior can be explained by changes in sample emissivity and/or by alterations of the specimen surface (e.g., redistribution of nanograins). For this reason, the experimental data shown in Figs. 2 and 3 are normalized to the amplitude of C–H modes. In any case, the variations in the multiplicative constant in the studied temperature range are moderate, do not exceed a factor of 2–3 and do not influence subsequent evaluation, accurate to an order of magnitude.

Solid black lines in the left part of Figs. 2 and 3 show results of fitting of the transmission window using Eq. (1). Despite marked changes in the line position and shape in the temperature range from –80 to 300°C, it is possible to obtain smooth variations of the fit parameters; some of the values obtained are presented in Table 1 and Fig. 4. The spectrum at 350°C can still be fitted, but the parameters become unphysical. At higher temperatures, the fit procedure fails. In our view, this behavior indicates the (reversible) destruction of the Fano resonance above 350°C.

The fit results show that the Fano parameter $F$ and $A$, $A_{\text{corr}}$ values change significantly by one and one-and-a-half to two orders of magnitude, respectively. Changes in the characteristic frequency $\omega_0$ and linewidth $\Gamma$ are relatively small. Let us consider correspondence of these variations of the experimental parameters with the properties of the model of coupled oscillators. To the best of our knowledge, despite intense discussions in literature, this model was not yet applied for qualitative evaluation of experimental data; misprints in published equations are partly responsible for this situation.

According to Eqs. (2)–(5), the nonlinear fit parameters $(\omega_0, F, \Gamma)$ expressed in absolute units allow one to calculate only the characteristic frequency of the dark mode $\omega_2$ (upper plot in Fig. 5). Figure 5 shows that this frequency in the temperature range from –80 to 200°C coincides with an accuracy of 10 cm$^{-1}$ with the Raman line of diamond, indicating that the Raman mode is involved in the Fano effect in nanodiamonds. Determination of other parameters of the model requires the evaluation of the temperature dependence of the width of the bright mode $\gamma$ from

---

**Fig. 4.** (Color online) Temperature dependence of the parameters from the experimentally observed Fano resonance (see Figs. 2, 3) using fit with Eq. (1). Red solid lines indicate general trends. Black and white symbols are experimental points obtained in air and N$_2$ atmosphere, respectively.

**Fig. 5.** (Color online) Temperature dependence of the parameters of the model of two coupled oscillators: (from top to bottom) the absolute value of the dark mode frequency $\omega_2$ (horizontal dashed line shows the position of the Raman line of diamond), the width of the bright mode $\gamma$, detuning between the dark and bright modes $\omega_0 - \omega_2$, and the coupling constant between the dark and bright modes $g$. Solid red lines indicate general trends. Black and white symbols are experimental points obtained in air and N$_2$ atmosphere, respectively.
the dependence of the Fano resonance amplitude $A$ (Eq. (5)). As noted above, the latter is known from experimental data (within a multiplication factor); in our work, we use the amplitude $A_{\text{corr}}$ normalized to the amplitude of C–H vibrations. This approach allows us to determine the strongest relative change in any parameter of the model. These values are shown in Fig. 5 in arbitrary units.

Figure 5 shows that the strongest temperature effect by a factor of almost 25 is observed for the difference $\omega_2 - \omega_1$ (detuning) between the frequencies of the bright and dark modes. A less pronounced change (a factor of ~8) occurs for the coupling constant $g$ between these modes. This implies that the main factor responsible for the temperature-induced change in the Fano resonance lineshape is the variation of the frequency of the bright mode. Since this mode is broad, it is impossible to determine its position in experimental spectra. At the same time, change in $\omega_3 - \omega_1$ affects the coupling constant $g$ of the bright and dark modes. Presumably, the position of the bright mode is close to that of the dark one, which is near the Raman mode of diamond, as shown above. This conclusion follows from a small value of the experimentally observed Fano parameter. We note also that the detuning factor $\omega_2 - \omega_1$ for larger nanodiamonds (~30 nm) nearly vanishes [10], giving the $F$ value close to zero and an almost symmetric transmission window.

4. CONCLUSIONS

The temperature dependence of the Fano effect in nanodiamonds synthesized from chloroadamantane at high static pressures has been studied. Significant temperature-induced changes in the Fano resonance in nanodiamonds (the Fano parameter varies by almost an order of magnitude) have been observed for the first time. Heating of nanodiamonds to 350°C both in air and in inert atmosphere (N2 flow) destroys the Fano effect; however, it is recovered upon cooling to room temperature. Such a behavior suggests that the surface transfer doping mechanism can hardly be responsible for the appearance of the Fano resonance in the studied samples. Experimental data have been used to investigate the temperature behavior of various parameters from the Fano effect equation. It is shown that the most important variations are observed for the detuning between the dark and bright IR-active modes, which changes by more than order of magnitude in the studied temperature range. The frequency of the dark mode at temperatures up to 200°C coincides with a high accuracy with the Raman mode of diamond.

ACKNOWLEDGMENTS

We are grateful to Dr. Stepan Stehlik for discussions.

FUNDING

This work was supported by the Russian Foundation for Basic Research, project no. 20-52-26017.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. U. Fano, Nuovo Cim. 12, 154 (1935).
2. U. Fano, Phys. Rev. 124, 1866 (1961).
3. B. Luk’yanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, P. Nordlander, H. Giessen, and C. T. Chong, Nat. Mater. 9, 707 (2010).
4. F. J. García de Abajo, Rev. Mod. Phys. 79, 1267 (2007).
5. M. F. Limonov, M. V. Rybin, A. N. Poddubny, and Y. S. Kivshar, Nat. Photon. 11, 543 (2017).
6. M. I. Tribelsky and A. E. Miroshnichenko, Phys. Usp. 65, 40 (2022).
7. F. Lapointe, E. Gaufres, I. Tremblay, N. Y.-W. Tang, R. Martel, and P. Desjardins, Phys. Rev. Lett. 109, 097402 (2012).
8. P. Gu, X. Cai, G. Wu, C. Xue, J. Chen, Z. Zhang, Z. Yan, F. Liu, C. Tang, W. Du, Z. Huang, and Z. Chen, Nanomaterials 11, 2039 (2021).
9. M. F. Limonov, Adv. Opt. Photon. 13, 703 (2021).
10. O. S. Kudryavtsev, R. H. Bagramov, A. M. Satanin, A. A. Shiryaev, O. I. Lebedev, A. M. Romshin,
11. E. Ekimov, A. A. Shiryaev, Y. Grigoriev, A. Averin, E. Shagieva, S. Stehlik, and M. Kondrin, Nanomaterials 12, 351 (2022).
12. V. A. Davydov, A. V. Rakhmanina, S. G. Lyapin, I. D. Ilichev, K. N. Boldyrev, A. A. Shiryaev, and V. N. Agafonov, JETP Lett. 99, 585 (2014).
13. E. Ekimov, S. Lyapin, Y. Grigoriev, I. Zibrov, and K. Kondrina, Carbon 150, 436 (2019).
14. E. Ekimov, M. Kondrin, S. Lyapin, Y. Grigoriev, A. Razgulov, V. Krivobok, S. Gierlotka, and S. Stelmakh, Diamond Relat. Mater. 103, 107718 (2020).
15. E. Ekimov, K. Kondrina, I. Zibrov, S. Lyapin, M. Lovgin, and P. Kazanskiy, Mater. Res. Bull. 137, 111189 (2021).
16. M. V. Kondrin, I. P. Zibrov, S. G. Lyapin, Y. V. Grigoriev, R. A. Khmelnitskiy, and E. A. Ekimov, ChemNanoMat 7, 17 (2021).
17. E. A. Ekimov and M. V. Kondrin, Phys. Usp. 60, 539 (2017).
18. F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley, Phys. Rev. Lett. 85, 3472 (2000).
19. W. Chen, D. Qi, X. Gao, and A. T. S. Wee, Prog. Surf. Sci. 84, 279 (2009).
20. K. G. Crawford, I. Maini, D. A. Macdonald, and D. A. Moran, Prog. Surf. Sci. 96, 100613 (2021).
21. Y. S. Joe, A. M. Satanin, and C. S. Kim, Phys. Scr. 74, 259 (2006).
22. B. Gallinet and O. J. F. Martin, Phys. Rev. B 83, 235427 (2011).
23. THMSG600 Temperature Controlled Geology Stage, User Guide, Linkam Scientific Instruments. https://linkamscientific.squarespace.com/archivemanuals.
24. PE95/T95 System Controller. UserGuide, Linkam Scientific Instruments. https://linkamscientific.squarespace.com/archivemanuals.
25. V. Y. Prokof’ev, I. A. Baksheev, F. Y. Korytov, and J. Touret, C. R. Geosci. 338, 617 (2006).
26. A. P. Koscheev, in Carbon Nanomaterials for Gas Adsorption (Pan Stanford, New York, 2012), p. 219.
27. A. Maturilli, A. A. Shiryaev, I. I. Kulakova, and J. Helbert, Spectrosc. Lett. 47, 446 (2014).