Crystal structure evolution in the van der Waals vanadium trihalides

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Abstract

Most transition-metal trihalides are dimorphic. The representative chromium-based triad, CrCl3, CrBr3, CrI3, is characterized by the low-temperature (LT) phase adopting the trigonal BiI3-type while the structure of the high-temperature (HT) phase is monoclinic of AlCl3 type ($C2/m$). The structural transition between the two crystallographic phases is of the first-order type with large thermal hysteresis in CrCl3 and CrI3. We studied crystal structures and structural phase transitions of vanadium-based counterparts VCl3, VBBr3, and VI3 by measuring specific heat, magnetization, and x-ray diffraction as functions of temperature and observed an inverse situation. In these cases, the HT phase has a higher symmetry while the LT structure reveals a lower symmetry. The structural phase transition between them shows no measurable hysteresis in contrast to CrX3. Possible relations of the evolution of the ratio $c/a$ of the unit cell parameters, types of crystal structures, and nature of the structural transitions in V and Cr trihalides are discussed.

Keywords: transition-metal trihalide, low-temperature x-ray diffraction, van der Waals material, structural transition, first-order transition, second-order transition

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Van der Waals (vdW) magnetic materials, including the transition-metal (TM) trihalides TMX3 (X = Cl, Br, I), have gained immense popularity in recent years after being studied for decades primarily as magnetic model structures in layered compounds. The crystal structure of TM trihalides given by a graphene-like honeycomb network of TM ions and their magnetic ordering at finite temperatures provide promising opportunities for spintronic device applications [1–5].

CrI3 has been the most extensively studied due to its ferromagnetism [6] with the highest Curie temperature ($T_C = 61$ K [7]) within the trihalide family. Also CrBr3 exhibits ferromagnetism below $T_C (=34$ K) [8] whereas CrCl3 becomes antiferromagnetic (AFM) at low temperatures ($T_N = 16.8$ K [9]). CrI3 and CrBr3 are the only trihalide ferromagnets listed in table 2 of the review paper of McGuire [10]. Recent research activities were successful in exploring one more TMX3 ferromagnet, namely VI3 [11–14], which has originally been reported much earlier [6]. Curie temperature of VI3 ($T_C = 50$ K [11, 12]) is somewhat lower than $T_C$ of CrI3. However, the physics of VI3 seems to differ from CrI3 in numerous important aspects.

The CrX3 compounds and probably most of the other TM trihalides are dimorphic [10]. The CrX3 $\alpha$-phases adopt the trigonal structure of the BiI3 type (space group $R-3$) and
the β-phase is monoclinic of the AlCl₃ type (C2/m), i.e. the lower symmetry crystallographic phase that is preferred at higher temperatures. When cooled from high temperatures the chromium trihalides undergo a first-order structural phase transition from the β to the α phase. The transition takes place near 210, 420, and 240 K in CrI₃, CrBr₃, and CrCl₃, respectively, and exhibits large thermal hysteresis (except CrBr₃, where the information is not known, yet) determining the temperature range over which both phases coexist [7, 15]. The transition is probably controlled by interlayer interactions, as the monoclinic structure of the β-phase develops from the trigonal α-phase by successive equal small shifts of the basal plane layers. Twinning and stacking faults were reported developing during the transition upon cooling as the layers rearrange themselves into the BiI₃ stacking [7].

Contrary to this behavior the high-temperature (HT) phase of VI₃ adopts the BiI₃-type trigonal structure [11, 12, 16] and when cooling below room temperature a structural phase transition to the lower-symmetry monoclinic structure has been observed [12, 16] at 79 K. Results of recent synchrotron and neutron experiments offered structural models for VI₃ [17] and exhibited a relative easiness of preparation of the recently reported LiVI₃ phase. Such material belongs to the insertion compounds which show promising properties in the field of applications including Li-ion batteries and beyond [18]. Similarly, the room-temperature BiI₃-type trigonal structure is reported for VBr₃ and VCl₃ [19–21] which both become AFM at low temperatures [6, 22]. In contrast to VI₃, the vanadium atoms are found in two sites in the structure of VBr₃; the majority of the vanadium atoms form a honeycomb lattice and a nonnegligible fraction occupies the central (normally) vacant site. This partial occupancy is attributed to the presence of stacking faults, which is significantly higher in VBr₃ compared to VI₃ [21]. A structural transition of VBr₃ at 90.4 K has been recently revealed by measurements of specific heat [21].

The apparent controversy between the structural evolution in CrX₃ and VX₃ motivated us to extend our x-ray diffraction, specific-heat, and magnetization investigation on VBr₃ and VCl₃ to investigate the HT and low-temperature (LT) crystal structures and the character of structural phase transition between them. After these experiments, we can confirm that the HT crystal symmetry of VCl₃, VBr₃, and VI₃ is reduced below certain own characteristic temperature Tₛ. The phase transition between the two structure phases is most probably of the first-order type. Contrary to ferromagnetism in VI₃, VCl₃ and VBr₃ order AFM as demonstrated by specific heat in magnetic fields. No symmetry lowering is observed in VBr₃ in connection with the transition to the AFM state. The change in the thermal evolution of the crystal symmetry of the crystal structure in the TMX₃ halides between the V and Cr-based compounds will be discussed concerning the variations of structure parameters c, a, and the ε/a ratio.

2. Methods

Single crystals of VBr₃ were synthesized by chemical vapor transport technique by recrystallization of the powder precursor VBr₃ (Thermo Fisher Scientific) sealed in a silica tube under vacuum. The tube was placed in a gradient horizontal tube furnace with the hot end at 480 °C and the cold end at 350 °C for approximately two weeks. We obtained shiny plate-like single crystals with dimensions of several square millimeters fast degrading in air similarly to VI₃ [23]. Their composition and purity were checked by microprobe analysis which confirmed the 1:3 molar ratio of V and Br, respectively.

The VCl₃ powder (97% purity) was obtained commercially from Sigma-Aldrich. The powder was pressed into pellets for specific heat and magnetization measurements. For the LT x-ray powder diffraction, we attached the powder to the sample holder with a thin layer of Apiezon grease and aligned the flat surface of the sample without pressing it. Initial attempts to grow single crystals of VCl₃ chemical vapor transport were not successful so far, showing that their preparation might be not that straightforward compared to the other VX₃ compounds.

Concerning the moisture sensibility, we minimized the sample’s exposure to the necessary mounting time only in the case of all performed experiments. The magnetization data were obtained utilizing MPMS 7 T and the specific heat was measured using PPMS 9 T (both Quantum Design Inc.) at temperatures down to 2 K. The x-ray diffraction measurement from 300 K down to 5 K was performed using a refurbished Siemens D500 θ–θ diffractometer (D500-HR-4K) equipped with a Mythen 1 K position-sensitive detector in Bragg–Brentano geometry using the non-monochromatic CuKα₁,₂ radiation. The single-crystalline sample was placed on the piezo-rotator (Attocube ANR 31) which allows aligning the sample in φ direction, connected to the ‘cold finger’ of the cryostat (101J Cryocooler from ColdEdge). The reciprocal space map was measured by single sample rocking scan using the linear detector. To reach good thermal stabilization, the inner cap was filled with He gas. As a cooling source a Gifford–McMahon refrigerator was used. The stabilization of temperature was better than 0.1 K with an absolute uncertainty of 0.5 K.

3. Results and discussion

Figure 1 summarizes the specific heat and magnetization of the VBr₃ single crystal and the VCl₃ polycrystal. The specific heat of VBr₃ confirms the previously reported emergence of a structural transition Tₛ = 90 K and AFM transition at Tₐ = 26.5 K as shown in figure 1(a). VCl₃ polycrystals reveals also a structural transition at Tₛ = 100 K reported for the first time to our knowledge, and an AFM transition at Tₐ = 21 K (see figure 1(b)). The powder character of the pellet sample is responsible for the somewhat smeared transitions. One can see in the inset of figure 1(a) that while the magnetic transition is shifted by ~2 K to lower temperatures in the 9 T magnetic field applied perpendicular to the vdW layers in VBr₃, the structural transition seems to be untouched by the magnetic field. The AFM transition shifts slightly to lower temperatures while the structural transition remains conserved in the magnetic field of 9 T in the case of VCl₃, too. This observation contrasts sharply with the behavior of the structural transition in the VI₃ compound which reveals a shift by ~2 K to lower temperatures in a comparable magnetic field applied perpendicularly to the
Figure 1. Temperature dependence of the specific heat $C_p$ of (a) VBr$_3$ and (b) VCl$_3$ measured at zero and 9 T magnetic field applied perpendicularly to the single-crystal layers (in case of the VBr$_3$ single crystal). The inset shows the detail of the specific heat in the vicinity of the magnetic transition. (c) Temperature dependence of $\partial M/\partial T$ of VBr$_3$ measured in 1 T magnetic field applied perpendicularly to the single-crystal layers is depicted in the vicinity of the structural transition measured upon cooling and warming. No measurable hysteresis was detected. (d) Temperature dependence of the magnetization $M/H$ of VCl$_3$ measured in 1 T and 7 T magnetic fields. For a complete information on the magnetization, the temperature dependence of $\partial M/\partial T$ of VCl$_3$ and the temperature dependence of $M/H$ of VBr$_3$ are shown in the supplementary materials as figures S3 and S4, respectively. The vertical dashed lines mark the positions of the structural and AFM phase transitions at $T_s$ and $T_N$ obtained from the specific heat, respectively.

Figure 2. (Left panel) Evolution of the (1 1 21) diffraction peak of a VBr$_3$ single crystal in the temperature interval from 89 to 90 K (top) and from 26 to 27 K (bottom). The vertical solid and dotted markers on the upper figure indicate the CuK$\alpha_1$ and CuK$\alpha_2$ positions of the CuK$\alpha_{1,2}$ doublet, respectively. Note, that the scales of the x-axis in both figures are slightly different. (Right panel) Temperature dependence of $2\theta$ of the (1 1 21) and ($-1$ 2 21) diffraction peaks (upper panel) and the diffraction-peak half-width FWHM of ($-1$ 2 21) (lower panel). The vertical dashed lines mark the positions of the structural and AFM phase transitions. The error bars are smaller than the markers.
Figure 3. Temperature dependence of lattice parameters and unit cell volume of VBr$_3$ compared to VI$_3$ [16]. The left $y$-axis is related to VBr$_3$ while the right $y$-axis is related to VI$_3$ data as depicted by the arrows. The full symbols mark the HT phase while the empty ones mark the LT phase of VBr$_3$ and VI$_3$ data as depicted by the arrow. The vertical dashed and dotted lines mark the magnetic and structural transitions of VBr$_3$ and VI$_3$, respectively.

layers [16]. The insets in figures 1(a) and (b) offer a comparison of the AFM transition in the zero and 9 T-magnetic fields.

Figure 1(c) presents the temperature dependence of $\partial M/\partial T$ in VBr$_3$ focusing on the vicinity of the structural transition. The data were measured upon cooling down and warming up to be able to recognize any possible thermal hysteresis. The difference between both curves does not provide any clear answer regarding the hysteresis and thus, the nature of the structural transition in VBr$_3$.

Due to the scattered polycrystalline VCl$_3$ data, no peak or bump revealing the structural transition was observed, unlike the Néel transition, as shown in figure 1(d). However, the change of slope in the $H/M(T)$ data is a clear sign of the $T_s$ presence (see figure S2 [https://stacks.iop.org/JPCM/34/294007/mmedia] in supplementary material). A linear Curie–Weiss fit to the VCl$_3$ data was performed above $T_s$ as the structural transition alters the slope of the susceptibility. We have extracted an effective moment of $\mu_{\text{eff}} = 2.96(15) \mu_B/V$ corresponding to the value of $2.85 \mu_B$ reported by Starr et al [22] within error and it is also close to the expected $S = 1$ value. The extrapolated Curie temperature $\theta_C$ from the fit is $-63(2)$ K, which differs from the reported one $-30.1$ K [22] but still clearly confirms the emergence of AFM order in VCl$_3$.

Turning our attention to the structural analysis, we emphasize that, analogically to the VI$_3$ single crystals, the VBr$_3$ sample shape is a thin (0 0 L) platelet. Together with the geometrical limitations of the LT diffraction setup, only measuring diffraction maxima with $L > 0$ is possible. Therefore, it is not possible to determine the exact structure of VBr$_3$ by mapping selected diffraction peaks, but the temperature dependence of the lattice parameters can be studied and some predictions about the LT structure can be made based on the splitting of the diffraction peaks.

The hexagonal unit cell for the trigonal crystal system and the corresponding H K L indices were considered according to previous studies [19–21]. The reciprocal space maps were measured around the symmetric (0 0 12), (0 0 15), (0 0 18), (0 0 21), and asymmetric (1 1 21), (−1 2 21), (−2 4 15), (3 3 12) diffraction peaks. The temperature dependence of the asymmetric diffraction peak is shown in figure 2, which confirms that the crystal symmetry lowers from a trigonal symmetry to a presumably monoclinic one by the structural transition at $T_s = 90$ K. Below 90 K, the (1 1 L) and (−1 −2 2 L) diffraction peaks are both split into two peaks; both split pairs have different $2\theta$ distances. The diffraction-peak splitting with two diffraction peaks moving to larger and the other to smaller $2\theta$ values, respectively, is ascribed to the reduction of the lattice
symmetry and it can be understood by opposite deformation of non-equivalent domains in analogy to the VI$_3$ compound [16]. Noticeably, we can see a coexistence of the diffraction peak belonging to the HT structure phase and of the pairs of diffraction peaks from the LT one at 89.5 K (upper panel in figure 2). Such effect can be either caused by the first-order character of the structural transition or by phase non-homogeneity of the sample. The nature of the transition will be discussed later in the text.

On the contrary, we do not observe any (H K 21) diffraction-peak splitting at temperatures below 27 K (see lower panel of figure 2), where the specific heat reveals the existence of an AFM transition. In other words, the LT crystal symmetry is not affected by the AFM transition in the same way as it was affected by the ferromagnetic (FM) transition in VI$_3$. The absence of further peak splitting down to the lowest temperatures suggests, that there is no lowering of lattice symmetry. Temperature dependence of lattice parameters and unit cell volume parameters of VBr$_3$ compared to VI$_3$ are summarized in figure 3. All lattice parameters and the volume V of both compounds are scaled to be able to compare the changes at the transitions directly. A small drop in the temperature dependence of the c-lattice parameter and the step-like change in the a, b, and β lattice parameters imply the transition at $T_s = 90$ K. The small step-like change of the unit cell volume in the vicinity of the structural transition is a sign of a typical first-order type phase transition. Although the step is small, the comparison of temperature trends above and below the transition suggests, that it is not an artifact of an experimental error or subsequent data processing. Noticeably, the change of volume is significantly larger compared to the equivalent data in VCl$_3$. The tiny changes in lattice parameters visible at temperatures below $T_N$ are most likely due to spontaneous magnetostriction in the AFM state.

To track the temperature evolution of diffraction peaks as performed by the single-crystal x-ray diffraction on VBr$_3$ and VI$_3$ [16], we have carried out the experiment and analysis on the VCl$_3$ powder sample. Since the diffraction pattern revealed a strong preferential orientation, i.e. texture, and broadened diffraction peaks, we did not employ the Rietveld analysis as usual in this type of experiment (for the diffraction pattern, see figure S1 in supplementary material). Nevertheless, we managed to index the low-angle part of the diffraction pattern using the structural model used in reference [20] and identify the 3 0 0 and 0 0 3 reflections that do not overlap with other peaks. Therefore, they were selected for further study of the diffraction peak splitting as shown in figures 4 and 5. Upon cooling, the FWHM of the studied diffraction peak increases, and below 100 K, it splits into two peaks; in line with the observation in VBr$_3$ and VI$_3$, both split pairs have different 2θ distances. The reduction of the lattice symmetry is demonstrated by the diffraction-peak splitting with two diffraction peaks moving to larger and the other to smaller 2θ values, respectively. Figure 4 depicts the coexistence of the diffraction peak belonging to the HT structure phase and of the pairs of diffraction peaks from the LT phase which takes place in the temperature region of $\sim$10 K, being a significantly larger interval compared to $\sim$1 K in VBr$_3$ and VI$_3$. Comparison of the 2θ temperature dependence of the 0 0 3 peak and the corresponding $d_{001}$ distance of the polycrystalline sample of VCl$_3$ is shown in figure 5. The scattered $d_{001}(T)$ evolution is caused by analyzing a diffraction peak with a low 2θ-angle.

Detailed specific-heat measurements of all studied VX$_3$ (X = Cl, Br, I) compounds are summarized in figure 6. Despite the shallow peaks of VCl$_3$ caused by its polycrystalline origin, we can see a clear trend in the evolution of the structural and magnetic transitions across the halogen series Cl–Br–I. With increasing atomic number, the structural transition

![Figure 4](image-url) Evolution of the 3 0 0 diffraction peak of a VCl$_3$ powder pattern in the temperature interval from 80 to 106 K. The vertical solid and dotted markers indicate the CuK$_{\alpha1}$ and CuK$_{\alpha2}$ positions of the CuK$_{\alpha1,2}$ doublet.

![Figure 5](image-url)

(a) Temperature dependence of 2θ of the 3 0 0 diffraction peak in VCl$_3$, (b) temperature dependence of the 2θ angle of the 0 0 3 diffraction peak, and (c) the $d_{001}$ interlayer distance. The vertical dashed lines mark the positions of the structural and AFM phase transitions at $T_s$ and $T_N$, respectively.
respectively). For a complete information on the VX3 compounds, notation used in reference [24], and to supplementary materials as figure S5.

c/3 trigonal phases of these compounds are listed together with the temperature dependence of $M/H$ of VX3 is shown in the supplementary materials as figure S5.

The temperature dependence of the specific heat of the VX3 (X = Cl, Br, I) compounds in zero magnetic field showing the regions with the structural transition at $T_s$, and magnetic transition at $T_m$, where $T_m$ corresponds to $T_C$ in case of V13, according to the notation used in reference [24], and to $T_N$ in VBr3 and VCl3, respectively. For a complete information on the VX3 compounds, the temperature dependence of $M/H$ of VX3 is shown in the supplementary materials as figure S5.

The temperature decreases, and the magnetic (AFM in case of Cl and Br, FM in case of I) transition temperature increases. This behavior suggests that the structural and magnetic behavior in these materials is tightly intertwined. While the magnetic field applied perpendicular to the layers tends to suppress the structural transition in V13 by almost 3 K in the 14 T field [16], it is intact in the Cl and Br compounds (up to 9 T). From the XRD, magnetization, and specific heat data, one can notice four aspects, which differ the behavior of VBr3 and VCl3 from the V13 system. Primarily, in the first two systems, we observe only one transition related to the peak splitting and thus, symmetry breaking at $T_s$, and second, this structural transition is not magnetic-field dependent contrary to V13. Next, we observe different magnetic ground states, AFM in VBr3 and VCl3 vs FM in V13, together with different magnetic anisotropy in the single-crystalline materials. The question of how are these differences related to different inter- and intralayer exchange interactions reflected in stacking faults, dimerization, etc is a subject of further study.

If we look at table 2 and related text in McGuire’s review [7] and consider the results of Dolezal et al on V13[16], we find that only in the Cr trihalides the HT phase is monoclinic and the LT phase is trigonal whereas in the Ti, V, and Fe analogs possess the trigonal HT phase. Then the CrX3 compounds seem to be exceptional within the family of the 3D-transition metal trihalides concerning the symmetry evolution between these two structural phases. When we inspect corresponding available crystallographic data on them, we find sets for a reasonable analysis only for the Ti, V, Cr, and Fe chlorides and the V, Cr, and Fe bromides. Iodides have been reported only with V and Cr. In table 1, the values of lattice parameters $a$ and $c$ of trigonal phases of these compounds are listed together with the $c/a$ ratio values. The trigonal phase exists at room temperature except for CrI3 and CrCl3, These two compounds when cooled from high temperatures undergo the monoclinic to trigonal structure transition near 210 and 240 K, respectively. Therefore the parameters of trigonal structure for CrI3 and CrCl3 have been determined at lower temperatures, namely at 225 K for CrCl3 [15] and at 90 K for CrI3 [7] and VI3 [16]. For a better comparison of structure parameters of iodides also data for V13 determined at the same temperature have been included. When looking at table 1 shown below we can conclude that the CrX3 compounds exhibit the maximum $c/a$ values within chlorides, bromides, and iodides, respectively.

The unique position of the CrX3 compounds within the TMX3 family based on the reverse structure sequence is further highlighted by the fact that we observe a large thermal hysteresis in CrX3 (X = Cl, I) pointing to the first-order nature of the structural transition. On the other hand, the nature of the structural transition in the VX3 compounds is not manifested so clearly although current data such as the step-like transition in the temperature evolution of V and the possible coexistence of different structure phases bring mild evidence for a first-order transition, as discussed further. No other reliable data regarding the nature of the structural transition in related TMX3 compounds are available so far, but some conclusions can be made already.

Generally, the first-order phase transitions are characterized by the release of the latent heat and a step-like change in the volume. In the case of the second-order phase transition, the volume is a continuous function of temperature and the latent heat is not released. Instead, the discontinuities in specific heat, isobaric thermal expansion, and isothermal compressibility are present. Experimentally, this theoretical classification might not be so obvious, if the volume change and latent heat are very small, which is the case of structural transitions. The $V(T)$ of V13 seems to be an almost continuous function in the vicinity of the transition while the $V(T)$ of VBr3 exhibits a very small, but visible step change of the volume. Concerning the presence of latent heat, the situation gets complicated. Its presence leads to the divergence of specific heat while its absence is reflected in a step change and a lambda-type anomaly. However, the measured shape of the anomaly in the specific heat of V13 and VBr3 does not support the first-order type scenario convincingly. Thus, the step-change in the volume of VBr3 is the only clear indication for the first-order

**Table 1.** Lattice parameters $a$, $c$, and the $c/a$ ratio of trigonal phases of several TMX3 compounds at room temperature (225 K for CrCl3; 90 K for V13, and CrI3).

| Compound | $a$ (Å) | $c$ (Å) | $c/a$ | Reference |
|----------|--------|--------|------|-----------|
| TiCl3    | 6.12   | 17.50  | 2.86 | [25]      |
| VCl3     | 6.01   | 17.34  | 2.89 | [25]      |
| CrCl3    | 5.94   | 17.33  | 2.92 | [15]      |
| FeCl3    | 6.07   | 17.42  | 2.87 | [26]      |
| VBr3     | 6.40   | 18.50  | 2.89 | [20]      |
| CrBr3    | 6.26   | 18.20  | 2.91 | [27]      |
| FeBr3    | 6.94   | 18.38  | 2.65 | [28]      |
| VI3      | 6.92   | 19.81  | 2.86 | [16]      |
| CrI3     | 6.87   | 19.81  | 2.88 | [7]       |
transition. Due to the similarity of transitions in VI\textsubscript{3} and VCl\textsubscript{3}, we can assume that these structural transitions are of the first order, too.

Another character that seems to be typical of these structural transitions is the athermal growth of LT- or HT new phases during the transition. The measurement of reciprocal space maps takes around 1.5 hours and during this time the temperature is kept constant. Also, the ratio of both phases seems to be constant and is only changed by the further change of the temperature. This behavior is similar to the one observed in martensitic transformations \cite{29}.

4. Conclusions

We have demonstrated by the results of measurements of x-ray diffraction, specific heat, and magnetization at various temperatures on VCl\textsubscript{3}, VBr\textsubscript{3}, VI\textsubscript{3} that these compounds are dimorphic similar to most of the other transition-metal trihalides. The structure of the LT phase is probably monoclinic whereas the structure of the HT phase has a higher symmetry (trigonal BiI\textsubscript{3}-type in case of VI\textsubscript{3}). The behavior of VBr\textsubscript{3} in the vicinity of the structural phase transition gives several hints that suggest the first-order nature of the transition; however, this scenario has to be confirmed by further experiments. These findings are in striking contrast with the structural behavior of compounds in the corresponding chromium-based triad, CrCl\textsubscript{3}, CrBr\textsubscript{3}, CrI\textsubscript{3}. In these materials, the LT phase has a higher-symmetry trigonal (BiI\textsubscript{3}-type) whereas the HT phase is monoclinic. The structural transition in CrCl\textsubscript{3} and CrI\textsubscript{3} is of the first-order type associated with a large thermal hysteresis with the coexistence of both phases. The CrX\textsubscript{3} compounds seem to be exceptional within the family of 3D-transition metal trihalides concerning the symmetry evolution between the HT- and LT phase. They also exhibit the largest $c/a$ values within the series of chlorides, bromides, and iodides, respectively.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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