Contribution from the Department of Chemistry,
Rutgers University, New Brunswick, New Jersey 08903

Lattice Dynamics and Hyperfine Interactions in M_2FeO_4 ($M = K^+, Rb^+, Cs^+$) and $M'FeO_4$ ($M' = Sr^{2+}, Ba^{2+}$)

ROLFE H. HERBER* and DAVID JOHNSON†

Received March 27, 1979

A number of alkali and alkaline earth ferrates [Fe(VI)] have been prepared and characterized by powder X-ray diffraction and temperature-dependent ^{57}Fe Mössbauer effect studies. The isomer shift parameter (78 K) is only weakly dependent on the nature of the cation and reflects the large covalency in the Fe–O bond. The temperature dependence of the isomer shift yields, via the second-order Doppler shift formalism, a value for the effective vibrating mass, M_{eff}, of ~105 g mol^{-1}, nearly independent of the nature of the cation and intermediate between the bare ion atom mass (57 g mol^{-1}) and the formula weight of the FeO_4^{2-} moiety (121 g mol^{-1}). The temperature dependence of the recoil-free fraction, when combined with the effective vibrating mass calculation, yields the "Mössbauer lattice temperature" θ_M, which is ~197 ± 5 K and is insensitive to the nature of the cation or the stoichiometry of the ferrate salt. Magnetic ordering has been observed for the K^+, Rb^+, Cs^+, and Ba^{2+} ferrates and has been examined in detail for the potassium salt in the temperature range $0.015 \le T \le 4.2$ K. For the potassium salt, the magnetic ordering temperature is 4.2 ± 0.1 K and the internal hyperfine field in the low-temperature limit is ~147 ± 1 kOe. These data are in reasonable agreement with the spontaneous magnetization temperature behavior expected for an $S = 1$ (3d^2) spin system.

The combination of high oxidation state (6+), high metal ion symmetry ($\sim T_d$), and paramagnetic electron configuration (3d^2) has made the alkali ferrates the subject of a large number of spectroscopic studies. In these studies the effects of these properties on the physical and chemical behavior of such compounds have been investigated in detail.[1-3] Among the spectroscopic techniques which have been utilized is ^{57}Fe Mössbauer effect spectroscopy,[4] since these compounds provide an interesting reference point for the correlation of observed isomer shifts with electron configuration.[5] Early studies of this correlation, using the anhydrous potassium salt as an absorber in a typical transmission–geometry experiment,[4] showed that the isomer shift of the 14.4-keV ^{57}Fe γ radiation was considerably smaller (with respect to the metallic iron reference point) than was predicted on the basis of formal 3d-electron population calculations. The apparent discrepancy between the observed isomer shift for K_2FeO_4 (−0.79 mm/s at 78 K) and that predicted on the basis of an electron configuration corresponding to [Ar]3d^2 was rationalized on the basis of the large covalency contribution to the Fe–O bond. This covalency, which is manifest in the tetrahedral metal–ligand bonding in terms of sp^3 hybridization, is presumed to reduce the s electron density at the Fe nucleus and thus make the isomer shift more positive than that expected for a "bare" Fe(VI) ion.

More recently,[6] detailed self-consistent Xα scattered-wave calculations on the ferrate ion have been performed in spin-restricted and spin-unrestricted schemes, and valence ionization energies have been obtained and compared to experimental values. In particular, charge and spin densities at the Fe nucleus derived from these calculations have been related to isomer shift and hyperfine field values, and a detailed correlation between electron densities [$\Psi(0)^2$] and electron configuration has been effected, using the ferrate ion values as an extremum reference point.

There are two additional noteworthy characteristics of the alkali and alkaline earth ferrates which can be advantageously examined by using ^{57}Fe Mössbauer effect spectroscopy, and the nature of the cation may play a significant role in each: the lattice dynamics of the iron atom and the magnetic ordering temperature.

In the present study, these properties of several alkali and alkaline earth ferrates(VI) have been examined in some detail in the temperature range $4.2 \le T \le 320$ K. Pumped liquid helium temperature experiments have been carried out to determine the approximate magnetic ordering temperature in K_2FeO_4, Cs_2FeO_4, and $BaFeO_4$ and the magnitude of the internal hyperfine field. A more detailed temperature dependence study on K_2FeO_4, using a ^{3}He–^{4}He dilution refrigerator, was undertaken to verify the temperature dependence of the hyperfine field. Finally, the temperature dependence of the isomer shift of the ^{57}Fe atom and its dependence on the nature of the cation were examined above the magnetic ordering temperature, and the room-temperature powder X-ray patterns were analyzed in terms of the *Pnma* space group to obtain unit cell dimensions.

Experimental Section

(a) Sample Preparation. K_2FeO_4, Rb_2FeO_4, and Cs_2FeO_4 were prepared by literature methods[7,8] in which a strongly basic metal hypochlorite solution is allowed to react with finely powdered $Fe(NO_3)_3 \cdot 9H_2O$ at a temperature below 20 °C. Isolation of the crude ferrate salt and its subsequent leaching with 3 M metal hydroxide and reprecipitation with saturated metal hydroxide were carried out as rapidly as possible to avoid reduction of Fe(VI) to Fe(III). Four to five leaching–reprecipitation cycles were needed to yield samples which showed no Fe(III) resonance peak in the Mössbauer spectra (less than ~0.2%). Attempts to use the method of Audette and Quail,[9] in which K_2FeO_4 is washed with dry methanol, consistently yielded samples contaminated with Fe(III), although these authors have claimed 99.86% purity for their samples. Similar results were also obtained in the attempted synthesis of Rb_2FeO_4 and Cs_2FeO_4, and in each case the methanol washing step was omitted in the procedures which ultimately yielded the purest samples as judged by their Mössbauer spectra.

$SrFeO_4$ and $BaFeO_4$ were prepared by using a method reported earlier by several authors,[10-13] in which a basic solution of the metal chloride is allowed to react with a solution of K_2FeO_4 at 0 °C. Again, rapid filtration of the strontium or barium ferrate which precipitates is required to obtain a pure product. All solutions used in this procedure were scrupulously freed of dissolved carbonates by purging conductivity water with nitrogen, and the whole procedure was carried out under an inert atmosphere to avoid contamination with atmospheric CO_2. The purity of the $SrFeO_4$ and $BaFeO_4$ with respect to possible contamination by K_2FeO_4 (which would not have been obvious from the Mössbauer spectra) was determined by using a Spectrometrics Inc. Spectraspan Echelle spectrometer calibrated at 100, 10, and 1 ppm with K^+ standards, using the 7699.8 Å potassium emission line. Both salts were found to have a potassium contamination of less than 0.2%.

All samples were dried on a vacuum line and stored in a vacuum desiccator over a drying agent prior to further use.

Attempts to prepare analytically pure samples of Na_2FeO_4, using the method of Becarud[14] and Gump et al.,[11] were unsuccessful, as Fe(III) was invariably found to be present. Also unsuccessful were

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[†] Henry Rutgers Undergraduate Research Scholar, 1977–1978.

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Table I. Summary of Crystal Structure Data

compd	space group	*a*, Å	*b*, Å	*c*, Å
K_2FeO_4	*Pnma*	7.7010 ± 0.0070	5.8520 ± 0.0064	10.3506 ± 0.0136
Rb_2FeO_4	*Pnma*	8.0151 ± 0.0104	6.0150 ± 0.0066	10.6194 ± 0.0156
Cs_2FeO_4	*Pnma*	8.3998 ± 0.0166	6.2737 ± 0.0105	11.0640 ± 0.0230
$SrFeO_4$	*Pnma*	9.1826 ± 0.0580	5.3980 ± 0.0263	7.2256 ± 0.0386
$BaFeO_4$	*Pnma*	9.1260 ± 0.0110	5.4563 ± 0.0067	7.3232 ± 0.0083

Table II. Summary of Mössbauer Data (Lattice Dynamics)

	K_2FeO_4	Rb_2FeO_4	Cs_2FeO_4	$SrFeO_4$	$BaFeO_4$
IS (78 K), mm/s	−0.845	−0.808	−0.793	−0.827	−0.805
$10^4 \times [d(IS)/dT]$, mm/(s K)	−4.05	−4.40	−4.27	−3.83	−4.05
$M_{eff} \pm 3$, g/mol	103	94	97	96	103
$10^3 \times [d(\ln A)/dT]$, K^{-1}	−2.00	−2.22	−2.21	−1.67	−1.97
$\theta_M \pm 5$, K	197	195	192	207	196

attempts to prepare ferrate(VI) salts of other large cations such as Ca^{2+}, Pb^{2+}, and Hg^{2+}. In each case, either precipitation could not be effected or only impure samples were recovered. Attempts to obtain analytically pure samples of $Co(py)_4FeO_4$ by the method of Negoiu and Schiopescu[15] yielded only an impure product.

(b) Powder Patterns. X-ray diffraction patterns were obtained by using filtered Cu Kα reaction with a Philips-Norelco 12045 B/2 recording diffractometer. Data were recorded over the range 5–85° (2θ) at a 1° min^{-1} recording speed. Intensities were calculated by using the POWD7 program[16] and lattice parameters were refined by using LATREF.[17]

(c) ^{57}Fe Mössbauer Spectra. The Mössbauer spectroscopic data were obtained with the constant-acceleration spectrometer described earlier[18] and the spectrometer calibration methods employed in previous studies.[19] Temperature monitoring and control was effected by using an Artronix proportional controller to actuate the 12-Ω heater in an Airco Helitran Dewar fitted with a platinum resistance thermometer and two (Cu–Au/Co and Fe–constantan) thermocouples. For the temperature range $78 \leq T \leq 320$ K, liquid nitrogen was used as a coolant, while liquid helium ($4.2 \leq T \leq 78$ K) and pumped liquid helium ($2.5 \leq T \leq 4.2$ K) were used as coolants in the same Dewar for the magnetic ordering studies. The low-temperature measurements (0.015–3.5 K) on K_2FeO_4 were carried out in the laboratory of Professor G. Hoy[20] and will be described in greater detail in a subsequent publication.

Data reduction was carried out as described previously.[18]

Results and Discussion

The crystal structure data are summarized in Table I. All of the alkali and alkaline earth ferrates examined in the present study were found to crystallize in space group *Pnma* (orthorhombic β-K_2SO_4 system) with four molecules per unit cell, consistent with results reported earlier.[21,22] Previous crystallographic data for K_2FeO_4 have been reported by several authors[22,23] who have pointed out the isomorphism with K_2SO_4 and K_2CrO_4. Audette and Quail[9] have inferred a similar isomorphism from their data for Rb_2FeO_4 and Cs_2FeO_4. Crystallographic data for $BaFeO_4$ have been reported by Grimm et al.[22] and by Krebs.[21] To the best of our knowledge, no lattice parameter data on $SrFeO_4$ have been published.

A typical Mössbauer spectrum of K_2FeO_4 at 78 K is shown in Figure 1 and is seen to consist of a sharp singlet resonance peak, as is expected for a structure in which the iron atom occupies the center of a tetrahedral environment of four oxygen atoms. The Mössbauer data are summarized in Table II, from which it is seen that the isomer shift (with respect to the centroid of a room-temperature metallic iron reference spectrum) is ca. −0.8 mm s^{-1} and is only weakly dependent on the nature of the cation. The data show a small decrease in the isomer shift as the size of the monovalent cation increases, and a similar size effect is observed for the strontium and barium salts, although such an effect is not evident in the data reported by Shinjo et al.[13,24] It should also be noted that the isomer shift data reported here are not identical with those reported by the Japanese group (it is assumed that their data refer to room temperature values, although this is not explicitly stated), even when allowance is made for the temperature dependence of the electronic hyperfine parameter (vide infra).

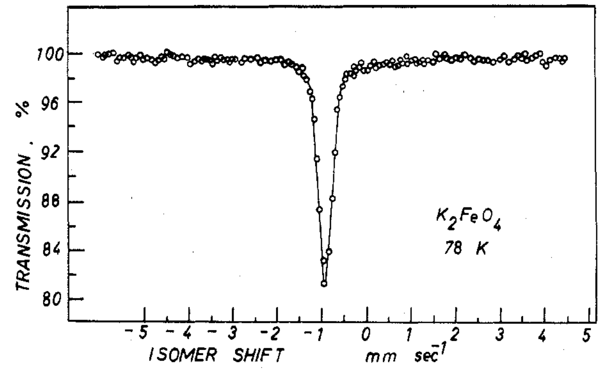

Figure 1. ^{57}Fe Mössbauer spectrum of K_2FeO_4 at 78 K. The isomer shift scale is relative to the centroid of a room-temperature 0.85-mil metallic iron spectrum obtained by using the same γ-ray source.

The temperature dependence of the isomer shift is primarily due to the second-order Doppler shift and can be evaluated[25] in the high-temperature limit from the Thirring expansion

$$IS = \frac{-3E_\gamma kT}{2mc^2}\left[1 + \frac{1}{12}\left(\frac{\theta_M}{T}\right)^2 - \frac{1}{720}\left(\frac{\theta_M}{T}\right)^4 + \ldots\right] \qquad (1)$$

from which (ignoring all but the term linear in *T*)

$$d(IS)/dT = -\tfrac{3}{2}(E_\gamma k/mc^2) \qquad (2)$$

For ^{57}Fe, the free-ion value of $-d(IS)/dT$, obtained by setting *m* equal to the atomic mass, is -7.305×10^{-4} mm s^{-1} K^{-1}. For the purposes of the present discussion, the experimentally observed values of $d(IS)/dT$ have been used to calculate a value for the effective vibrational mass, M_{eff}, of the molecular moiety containing the iron atom. A typical data set is shown in Figure 2 for K_2FeO_4 in which the eight data points yield a slope of -4.05×10^{-4} mm s^{-1} K^{-1}, corresponding to a value of $M_{eff} = 103 \pm 2$ g mol^{-1}, with a correlation coefficient of 0.997. Similar data have been obtained for the other ferrates examined in this study and are summarized in Table II, from which it is seen that the effective vibrating mass of the iron containing moiety is ~100 g mol^{-1}, in contrast to the free-atom value of 58 g mol^{-1} and the formula weight value (for FeO_4^{2-}) of 120 g mol^{-1}. In view of the significant covalency of the Fe–O bond in these compounds these results are not unexpected, and the absence of a strong dependence of M_{eff} on the nature of the cation is again a reflection of the presence of independent FeO_4^{2-} moieties in the solid state as already suggested by the isomer shift data cited above.

More importantly, however, the experimentally determined M_{eff} values permit the calculation of a lattice temperature from the temperature dependence of the recoil-free fraction of the Mössbauer γ radiation. As has been noted previously,[18] in the thin-absorber approximation, the temperature dependence of the recoil-free fraction is given by the temperature de-

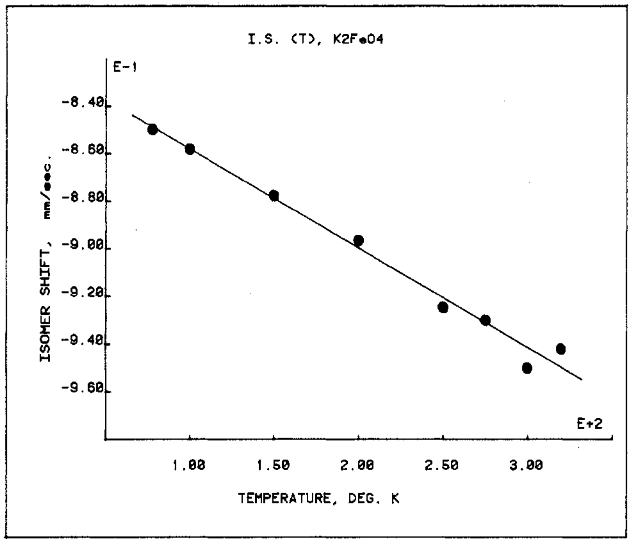

Figure 2. Temperature dependence of the isomer shift (relative to metallic iron at room temperature) for K_2FeO_4. The full line is the least-squares fit through the eight experimental data points and has a correlation coefficient of 0.997.

pendence of the area under the resonance curve. Using a Debye model approximation in the high ($T \geq \theta_D/2$) temperature limit leads to

$$\frac{d(\ln f_a)}{dT} = \frac{d(\ln A)}{dT} = \frac{-3E_\gamma^2}{M_{eff}c^2k\theta_M^2} \tag{3}$$

in which f_a is the absorber recoil-free fraction, A is the area under the resonance curve, M_{eff} is as defined above, and θ_M is a lattice temperature calculated from the Mössbauer effect temperature dependence. Rearrangement of (3) and replacement of M_{eff} by the value calculated from (2) lead to

$$\theta_M = \frac{E_\gamma}{k}\left[\frac{2d(IS)/dT}{d(\ln A)/dT}\right]^{1/2} \tag{4}$$

which, in the case of ^{57}Fe, reduces to

$$\theta_M = 4.320 \times 10^2\left[\frac{d(IS)/dT}{d(\ln A)/dT}\right]^{1/2} \tag{4'}$$

The θ_M values calculated from the experimentally determined temperature dependence of the isomer shift and recoil-free fraction data for the alkali and alkaline earth ferrates are also summarized in Table II and are seen to be essentially insensitive to the nature of the cation or the stoichiometry (cation-to-iron ratio) of the complex. These results lend strong confirmation to the view expressed by Shinjo et al.[13] that the FeO_4^{2-} unit is acting as an independent moiety in these structures and that the ferrate ion must be considered as a single chemical unit.

The analysis of the ^{57}Fe Mössbauer data discussed in the preceding section has assumed that the resonance spectra could be fitted to a single Lorentzian, consistent with the absence of a quadrupole hyperfine interaction in the paramagnetic temperature range. While this assumption appears valid on the basis of the observed line widths for the K^+, Rb^+, Cs^+, and Sr^{2+} salts, it may not be applicable in the case of the barium salt. In a recent study of the calibration of ^{57}Fe isomer shifts, Ladriere et al.[26] have analyzed their 298 K data for $BaFeO_4$ in terms of a quadrupole hyperfine interaction of 0.16 mm s^{-1} (the apparent full width at half-maximum of their absorption profile is ~0.41 mm s^{-1}). In the present study it has not been possible to resolve the two components of a quadrupole hyperfine interaction from the data at any temperature, although the excess line width observed by Ladriere et al.[26] has been confirmed and is presumably due to a distortion of exact T_d symmetry around the iron atom by the presence of the relatively large cations in the structure. The relationship between this observation and the magnetic ordering temperature will be discussed further, below.

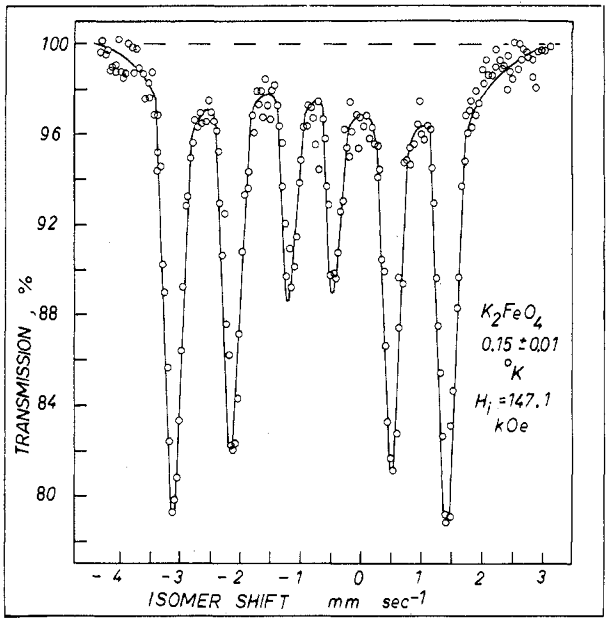

Figure 3. ^{57}Fe Mössbauer spectrum of K_2FeO_4 at 0.15 ± 0.01 K.

Table III. Summary of Mössbauer Data (Magnetic HFI)

	K_2FeO_4	Rb_2FeO_4	Cs_2FeO_4	$SrFeO_4$	$BaFeO_4$
H_{int} (2.8 K) ± 2, kOe	144	149	151	...	118
T_N, K	4.2	$2.8 < T_N < 4.2$	$4.2 < T_N < 6$	...	$7.0 < T_N < 8.0$

At sufficiently low temperatures, the single ^{57}Fe Mössbauer resonance line abruptly broadens and—on further cooling—a six-line magnetic hyperfine spectrum is observed in all cases except for $SrFeO_4$. The 0.15 ± 0.01 K data for K_2FeO_4 are summarized in Figure 3. The magnetic ordering temperature is readily obtained from the temperature dependence data and these are summarized in Table III and are in reasonably good agreement with the value reported by Shinjo et al.[13] for K_2FeO_4 and $BaFeO_4$.

The SCF-Xα scattered-wave calculations of Guenzburger et al.[6] permit an evaluation of the individual contributions of each of the a_1 symmetry orbitals to the total internal field and give a value of 139 kOe, in excellent agreement with the experimental results for the case in which dipolar and orbital terms are zero.

The temperature dependence of the magnetic hyperfine field (H_{int}) is given by the Brillouin spontaneous magnetization functions which have been tabulated in reduced parameter form by Darby.[27] For FeO_4^{2-}, in which the d^2 iron atom is in a T_d symmetry environment, the e_g doublet lies below the t_{2g} triplet, and $S = 1$, consistent with the observed magnetic moment spin-only value of 2.98 (calculated value 2.83). When the usual ratio of ~110–120 kOe/μ_B is used, this value of μ_{eff} leads to an expected value of $H_{int} \approx 345$ kOe, which is ~2.3 times larger than the value actually observed. The Hartree–Fock calculations[6] show that, although the nominal electron configuration is $3d^2$, additional 3d density arises from covalency effects, which reduce the number of unpaired electrons in the e_g set significantly below 2. This covalency

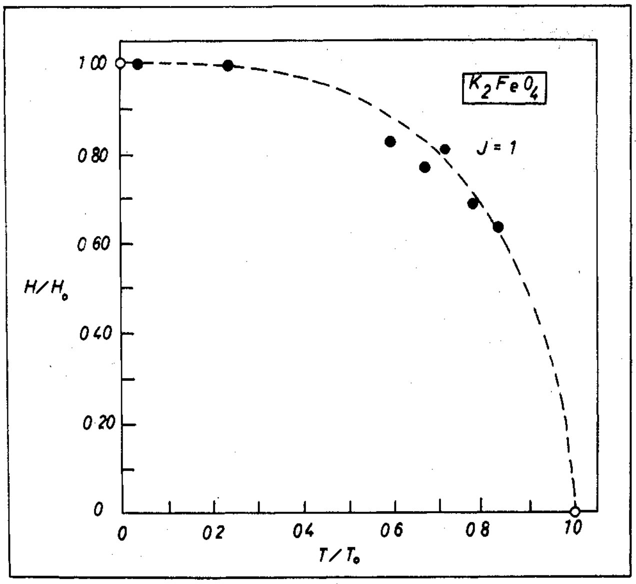

Figure 4. Temperature dependence of the magnetic hyperfine field at the iron atom in K_2FeO_4 in reduced-parameter space. The full line is the spontaneous magnetization curve (Brillouin function) for $S = 1$. The two open circles are for calibration only and do not represent experimental data.

is, of course, also reflected in the isomer shift value, referred to above. In order to extend the pumped ^{4}He low-temperature limit of ~2.5 K of the Helitran system, we carried out measurements of H_{int} at 0.15 ± 0.01, 1, 3, and 3.5 K, using a ^{3}He/^{4}He dilution refrigerator.[20] These data, as well as those obtained at 2.5, 2.8, and 3.25 K with ^{4}He(l) cooling, are summarized in Figure 4 in which $H_{\text{int}}(0)$, the extrapolated internal field at $T = 0$, is 148 kOe and $T_N = 4.2$ K.[29] The solid line is the spontaneous magnetization for $S = 1$ plotted in reduced-parameter space and is seen to be a reasonably good fit to the experimentally determined values.

The present data do not provide an unambiguous answer to the question concerning the detailed mechanism for spin–spin correlation which obtains in these alkali and alkaline earth ferrates. It is clear from the narrow resonance lines which are observed for K_2FeO_4 that the quadrupole hyperfine interaction—if any—is too small to be resolved from the data and, hence, that the departure from ideal T_d symmetry of the FeO_4^{2-} moiety must be very small. Indeed, these results, as well as the X-ray diffraction data, rule out a strong superexchange mechanism through one of the four oxygen atoms of the ferrate ion to the next iron atom, and thus the spin correlation which gives rise to the antiferromagnetic coupling of the iron spins presumably arises from dipole–dipole interactions between adjacent Fe–O bonds.

In this context, the excess line broadening observed for the $BaFeO_4$ sample—as already noted—suggests a significant departure from T_d symmetry around the iron atom in this lattice. It is also to be noted that barium ferrate has the highest magnetic ordering temperature of any of the solids examined in the present study. However, the present data are not sufficiently extensive to correlate the two observations, especially in the light of the conclusions drawn by Shinjo et al.[13] concerning the fact that T_N in $SrFeO_4$ (with a cation size smaller than any of the other cations here discussed) is probably less than 2 K. Experiments to extend the low-temperature measurements on this compound to the 0.1 K range are currently underway.

While it has not been possible to prepare analytically pure solid samples of Na_2FeO_4 (thus there are no data pertaining to the lattice dynamics of this material), the ^{57}Fe Mössbauer spectra of the FeO_4^{2-} anion in a strongly basic frozen solution matrix of NaOH at 4.2 K have been discussed in detail by Oosterhuis and Barros.[28] These authors have observed no internal magnetic hyperfine field for their samples, even at liquid helium temperature. On the application of a modest (2–3 kOe) external field, however, a six-line hyperfine spectrum was observed, with a saturation value of ~175 kOe. These data have been interpreted as the superposition of three spectra, one from each member of a spin triplet, and the relaxation rate between these electronic states which is much less than the Larmor precession rate of the ^{57}Fe nucleus. Clearly it would be very desirable to extend the present study to an examination of neat solid samples of Na_2FeO_4, as well as to ferrate salts of other (large) cations. Such an extension will have to await the successful solution of the synthetic problems associated with obtaining materials free of lower oxidation state iron impurities in the lattice of the resulting solids.

Acknowledgment. The authors are very much indebted to Professor G. Hoy and Dr. M. R. Corson of Boston University for carrying out the low-temperature Mössbauer studies on K_2FeO_4. The detailed analyses of these data are to be published. This research was supported in part by the National Science Foundation under Grant No. DMR 78-08615 as well as by a grant from the Center for Computer and Information Services, Rutgers University, for data reduction. This support is herewith gratefully acknowledged. D.J. expresses his gratitude to the FMC Corp. for their support of a summer undergraduate student research grant in solid-state science.

Registry No. K_2FeO_4, 13718-66-6; Rb_2FeO_4, 38207-28-2; Cs_2FeO_4, 38207-29-3; $SrFeO_4$, 13773-22-3; $BaFeO_4$, 13773-23-4.

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Contribution from the Lash Miller Chemical Laboratories,
University of Toronto, Toronto, Ontario M5S 1A1, Canada

Potential Energy Interactions in Solid Dichlorine

STANLEY C. NYBURG* and WINNIE WONG-NG

Received March 29, 1979

Hsu and Williams have proposed a model to explain the observed centric space group and cell dimensions of crystalline dichlorine. Although this model satisfies the "force-free" criterion, it requires the dichlorine molecules to be dipolar. We believe that it is physically unrealistic to assign a permanent dipole to a homopolar diatomic molecule in a centric lattice. Moreover, the model invokes partial intermolecular bonding between nearest atomic neighbors. If there is no restriction on the number of such neighbors, it can be shown that there are several crystalline structures available to dichlorine which would be more stable than that observed. The observed crystal structure can be explained in terms of anisotropic dispersion–repulsion forces and quadrupole–quadrupole interactions.

Introduction

In a recent article,[1] Hsu and Williams (H & W) postulate atom–atom interaction parameters to account for the observed cell dimensions, atomic coordinates, and space group (orthorhombic *Cmca*) of crystalline dichlorine.[2] The interactions they propose meet two of the criteria normally accepted to be necessary, namely, (i) obtaining a good match with the experimental lattice energy and (ii) obtaining satisfactorily small changes in cell dimensions and/or atomic coordinates on relaxation (force-free model). Criterion i is not demanding since all empirical atom–atom parameters have adjustable multipliers. Criterion ii is much more demanding. A third criterion is that, with the assumed atom–atom interaction parameters, it should not be possible to pack the molecules in an alternative (hypothetical) way to yield a more stable structure (with a more negative lattice energy) than that found experimentally. As we indicate below, we have doubts whether the H & W parameters satisfy this criterion but, in any case, we believe their choice of parameters to be physically unrealistic.

The molecules in the crystal are said to be dipolar, the atoms carrying charges of opposite sign of magnitude $0.0914|e|$. Support for this is said to come from fundamental infrared absorption frequencies which have been observed in solid specimens of Br_2 and I_2[3] but not in solid Cl_2.[4] (The crystals are isostructural.) In the absence of a permanent molecular dipole there should be no absorption at these frequencies. H & W refer to the high absorption background which might have prevented the band being observed for Cl_2, and they use this interpretation to support their view that dihalogen molecules have permanent dipoles in the crystal. We believe, on purely symmetry grounds, that this cannot be so. To us, the most likely explanation of the infrared bands observed with solid Br_2 and I_2 is that the specimens were not homogeneously crystalline but had extensive polycrystalline and amorphous regions. This could cause a significant proportion of the molecules to have weak dipoles, induced by the quadrupoles of noncentrosymmetrically arranged neighboring molecules. To us, the fact that the band is not observed with Cl_2 indicates a more homogeneously crystalline specimen in this case.

In addition, but somewhat less importantly, H & W did not include molecular quadrupole–quadrupole, Θ–Θ, interactions because criterion ii above was then better satisfied. Dichlorine is accepted to have a positive quadrupole moment (estimated as[5] $+3.38 \times 10^{-26}$ esu cm^2) and thus Θ–Θ interactions must be included in any crystal potential-energy calculations. It should, in any case, be stressed that point-charge interactions considered by H & W are a poor approximation to Θ–Θ interactions for neighboring molecules. Such interactions should be calculated by suitable integration using the molecular difference charge density.[6] A third feature of the H & W model concerns the use of a Morse potential to represent intermolecular ("partial") valence bonding between nearest-neighbor atoms. The case against this is harder to argue, but we point out that the interatomic distances used to justify intermolecular bonding are not unusually short. Comparisons are being made with inappropriate van der Waals radii.[7] The question of partial bonding is taken up again below. H & W allocate charges to the atoms so that the molecular dipoles all have their z components in the same direction (Figure 1a). They state that the allocation of charges they propose assigns the crystal to the monoclinic space group *Cc*.[8] It seems to us, however, from their diagram, and our calculations confirm, that the space group of their structure is orthorhombic $Cmc2_1$.[10,11]

Results

We have used a locally modified version of WMIN[12] and parameters given by H & W to carry out calculations to a limiting radius of 13.5 Å on various crystal structures. The results are set out in Table I. The only results not calculated by us are those of H & W in the first line of Table I. It will be noted that, on the second line, where we have repeated the H & W calculation with our program, there are slight differences in final cell parameters and energy contributions. This could be due to the following possible causes: our use of steepest descent plus interpolation for refinement rather than least squares; possible different treatment (i.e., exclusion vs. inclusion) of molecules intersected by the limiting sphere; the use of integration rather than accelerated convergence for dispersion interactions outside the summation sphere (magnitude $0.015253A/V$ kJ mol^{-1}, where V is the unit cell volume in Å^3). Despite these programming differences, the total energies are identical for three significant figures. We noted, in passing, that the assumed polarity of the molecules can be reversed in successive yz layers (allocating the crystal to *Pmca*,