Search criterion for lattice internal rearrangement modes: Correlation between lattice structural and magnetic structural transitions

Bernard R. Cooper

Department of Physics, West Virginia University,* Morgantown, West Virginia 26506

and Materials Science Division, Argonne National Laboratory,† Argonne, Illinois 60439

The occurrence of lattice internal rearrangements is of great interest because of the association through strong magnetoelastic interaction with first-order magnetic transitions, where the magnetic structure is likely to be unusual and highly anisotropic. We consider the physical basis for such modes occurring. The predictions for the NaCl and fluorite structures are quite restrictive on wave vector and polarization; and for the NaCl structure are highly evocative of a correlation between a lattice structural transition involving the predicted internal rearrangement mode and the magnetic transition to the IA magnetic structure.

There are a number of materials that undergo first-order magnetic transitions, yet show no evidence in conventional x-ray-diffraction experiments[1,2] for lattice distortion associated with this transition. This has presented a puzzle, since the behavior in these materials, such as CeBi, UAs, and UO_2, is characteristic[3-6] of very strong magnetoelastic interactions dominating the magnetic-ordering transition behavior. This puzzle leads to a desire to understand what correlation may exist between lattice structural and magnetic structural transitions. The key to understanding this correlation in these materials seems to lie in the concept of the lattice internal rearrangement mode. Internal rearrangement modes are modes where one ionic species remains at its site in the undistorted crystal structure, and the other species are displaced in a periodic sequence from their position in the undistorted structure.

Neutron-scattering experiments led to the recognition[7] in UO_2 of the lattice distortional transition, involving such a mode, occurring simultaneously with the first-order magnetic transition. In UO_2 the uranium ions occupy the fixed sites. The question then arises as to whether a similar mechanism might exist in the cerium and actinide monopnictides of NaCl structure (e.g., CeBi or UAs), and thereby explain the peculiar magnetic properties[5,8] of those materials. The desire to investigate this point, as well as the more general pertinence of lattice internal rearrangement modes to systems where interactions with the crystal lattice dominates the qualitative character of the magnetic behavior, provides incentive for finding a physically motivated way of recognizing what internal rear-

rangement modes are likely to occur in a specified lattice. A key point is to understand what causes the first-order transition from type-I to -IA magnetic structure in CeBi and UAs without evidence in conventional x-ray diffraction experiments[1,9] of distortion associated with the transition. (For these materials, moments within a given $\langle 001 \rangle$ plane are parallel and aligned along $\langle 001 \rangle$; at T_N the type-I structure occurs, i.e., an up-down-up-down sequence; at T_A there is a first-order transition to a IA structure, i.e., an up-up-down-down sequence).

The aim of the present note is to point out a physical basis for the occurrence of a lattice transition involving an internal rearrangement mode, and to show that this physical picture leads to a predictive criterion for the occurrence of specific internal rearrangement modes for a given crystal. This search criterion, in fact, predicts a particular internal rearrangement mode for the NaCl structure that is very evocative for the occurrence of the IA magnetic structure. The search criterion has the practical advantage of predicting modes with wave vectors both at high-symmetry points and at general points in the Brillouin zone, so that it expeditiously provides a way to survey *all* candidates for internal rearrangement modes in a given lattice structure.

To understand why an internal rearrangement distortion occurs in a crystal involves consideration of the overall energetics—elastic energy, crystal field, and exchange effects must all be considered. However, in these considerations, we can be guided by what actually happens in UO_2. In UO_2, it is clear from Allen's work[10] that Allen's suggested ordinary internal strain[11]

would provide a lower crystal-field energy for each U^{4+} ion as compared to the crystal-field energy for the internal rearrangement distortion that actually occurs. This then suggests the physical idea that the internal rearrangement occurs because it is the distortion least unfavorable with respect to raising the elastic energy.

In particular, we make the ansatz that the internal rearrangement mode is least unfavorable with respect to raising the elastic energy through maintaining elastic equilibrium for the undistorted sites, i.e., we assume that the net elastic force on the undistorted sites vanishes in the internal rearrangement just as it does in the undistorted crystal. Note that this is a sufficient, but not a necessary condition at equilibrium, since the undistorted sites could have a decrease in crystal-field or exchange energy that balanced an increase in elastic energy (i.e., if the undistorted sites are magnetic ions); and for that matter, it is the overall energy of the system that must be minimized, that of the ions at both the distorted and undistorted sites. Nevertheless, once we adopt this point of view, we are led to a search criterion as described below, and that search criterion does predict the mode found in UO_2. Also the prediction for the NaCl structure is very striking in relationship to the IA and longer period linear magnetic structures found in CeBi, UAs, CeSb, and other materials; and the predictions for zirconia (fluorite structure) agree with experiment.[12]

Together with our ansatz of maintaining elastic equilibrium at the undistorted sites, we need a model for the elastic forces in order to arrive at a search criterion for selecting the likely internal rearrangement modes for a given crystal structure. To do this we adopt a short-range elastic force model,[13] with the simplification of only radial forces. Such a model does provide a good description for the phonon behavior[14,15] in the uranium compounds of interest; and, as shown below, this force model incorporated into our ansatz, without further assumptions provides a search criterion for lattice internal rearrangement modes yielding a result for the NaCl structure highly indicative of the anticipated correlation between the lattice and magnetic structural transitions.

Thus our search criterion for lattice internal rearrangement modes consists of doing the following. We consider all lattice distortions where one species (or subspecies, if two or more inequivalent sites are occupied by the same species) remains at undistorted positions, while the other species are allowed to have any displacements consistent with lattice translational symmetry. We then put on the requirement, dictated by our ansatz of elastic equilibrium for the undistorted sites, that the net elastic force due to these displacements vanishes at each undistorted site. This constraint of zero force at the undistorted site is very restrictive, and only a small number of modes can satisfy this constraint. I now discuss the situation for the NaCl and fluorite structures.

NaCl structure. Let u_{lmnx}^A and u_{lmnx}^C denote the component of displacement from equilibrium along $\langle 100 \rangle$ for the anions and cations, respectively, with corresponding expressions for the y and z components; and let $2\gamma_{AC}$ denote the nearest-neighbor cation-anion Hook's-law coupling constant. We seek solutions of the equations of force acting on the cation sites (we could equally well choose the anion sites) with vanishing force and displacement for the cations (vanishing displacement because we are seeking internal rearrangement modes, vanishing force because of our ansatz constraint that elastic force vanishes at the undisplaced sites).

So we consider anion displacements given by

$$u_{lmnx}^A = u_{qx}^A e^{i(\vec{q}\cdot\vec{r}+\delta)} \ , \tag{1}$$

with the corresponding expressions for the y and z components; and obtain the vanishing-force equations

$$0 = -4\gamma_{AC}\cos(\tfrac{1}{2}q_{x,y,z}a)u_{qx,y,z}^A \ . \tag{2}$$

We have included the possibility of an overall phase shift, i.e., shifting phase of displacement wave relative to the lattice planes. The phase factor cancels from the NaCl structure internal rearrangement mode force equations. Thus we must remember that for the NaCl structure results obtained below, we have an arbitrary phase of the predicted internal rearrangement modes relative to the lattice planes.

For $\vec{q} \| \langle 100 \rangle$, the only solution of the set of equations (2) is $u_{qy}^A = u_{qz}^A = 0$. This means that the mode is *required to be longitudinal.* Furthermore, since $\cos(\tfrac{1}{2}qa) = 0$, $q = \pi/a$, i.e., halfway to the Brillouin-zone boundary in the $\langle 100 \rangle$ direction, so that the mode has a four-layer period. *Thus the only solution for $\vec{q} \| \langle 100 \rangle$ is a longitudinal displacement wave with a period of four layers.* The phase relative to the lattice planes is undetermined by these considerations. If the phase is such that the lattice planes fall halfway between extrema and modes, we have the $++--$ mode shown in Fig. 1. This is the structural analogue to the IA magnetic structure found in CeBi and UAs; and this result is quite suggestive that the IA magnetic structural transition follows as a result of strong magnetoelastic effects, through exchange striction, for a lattice transition to an internal rearrangement of the type shown in Fig. 1. If the phase is shifted by $\tfrac{1}{4}\pi$ relative to this, we have the $+$null$-$null mode shown in Fig. 2. If we associate null displacement planes with paramagnetic planes, then this mode, together with that of Fig. 1, could explain the complex magnetic structural behavior of[16,17] CeSb.

For $\vec{q} \| \langle 110 \rangle$, both longitudinal and transverse modes are allowed with a $\vec{q}$ $\tfrac{2}{3}$ of the way to the zone boundary. For $\vec{q} \| \langle 111 \rangle$, both longitudinal and transverse modes are allowed with a $\vec{q}$ at the L point at the Brillouin-zone boundary. The mode suggested
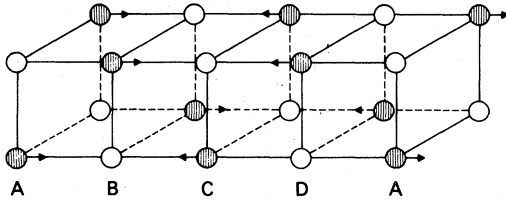
FIG. 1. $++ +--$ internal rearrangement mode for the NaCl structure. Displacements of anions are as indicated with cations fixed, or vice versa.

by Stevens and Pytte,[18] on the basis of quite different considerations, to explain the HoP "flopside" magnetic structure is a mixed longitudinal-transverse mode of this type.

Fluorite-structure. Again we consider the force equation for cation sites fixed. Now there are two kinds of anion sites, denoted A and B; and the force equations are more complicated, and involve the Hooke's-law constants γ_{AC} and γ_{BC}. From physical considerations we expect that $\gamma_{AC} = \gamma_{BC} \equiv \gamma$.

Then, for $\bar{q} \parallel \langle 100 \rangle$, the consideration of zero elastic force at the cation sites gives

$$0 = -\frac{8}{3}\gamma\cos(\tfrac{1}{4}qa)u_{qx}^{A} - \frac{8}{3}\gamma\cos(\tfrac{1}{4}qa)u_{qx}^{B} , \quad (3a)$$

$$0 = -\frac{8}{3}\gamma\cos(\tfrac{1}{4}qa)u_{qy}^{A} - \frac{8}{3}\gamma i\sin(\tfrac{1}{4}qa)u_{qz}^{A}$$
$$-\frac{8}{3}\gamma\cos(\tfrac{1}{4}qa)u_{qy}^{B} + \frac{8}{3}\gamma i\sin(\tfrac{1}{4}qa)u_{qz}^{B} , \quad (3b)$$

$$0 = -\frac{8}{3}\gamma i\sin(\tfrac{1}{4}qa)u_{qy}^{A} - \frac{8}{3}\gamma\cos(\tfrac{1}{4}qa)u_{qz}^{A}$$
$$+\frac{8}{3}\gamma i\sin(\tfrac{1}{4}qa)u_{qy}^{B} - \frac{8}{3}\gamma\cos(\tfrac{1}{4}qa)u_{qz}^{B} . \quad (3c)$$

There are two types of solutions: either (I) $\bar{q} = (2\pi/a, 0, 0)$, $u_{qz}^{A} = u_{qz}^{B}$, and $u_{qy}^{A} = u_{qy}^{B}$; or (II) $u_{qx}^{A} = -u_{qx}^{B}$ and $u_{qy}^{A} = u_{qy}^{B} = u_{qz}^{A} = u_{qz}^{B} = 0$.

For the first type of solution, i.e., (I), $\bar{q}$ is completely determined to be $(2\pi/a, 0, 0)$; and we can consider both longitudinal and transverse modes. For $u_{qx}^{A} = u_{qx}^{B}$ the longitudinal mode is shown in the center of Fig. 3; while the corresponding transverse mode, i.e., with $\bar{q} = (0, 2\pi/a, 0)$, is shown on the left-hand side in Fig. 3. In fact, these are just the modes that were arrived at[7]
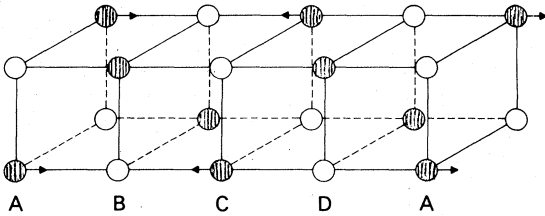

FIG. 2. $+$null$-$null internal rearrangement mode for the NaCl structure. Displacements of anions are as indicated with cations fixed, or vice versa.

on an empirical trial and error basis for UO_2, and the transverse mode is the one that occurs experimentally. For $\bar{q} = (2\pi/a, 0, 0)$, the longitudinal mode with $u_{qx}^{A} = -u_{qx}^{B}$ (this solution is the one that satisfies conditions for both type I and type II) is shown on the right in Fig. 3. This mode has been identified as occurring[12] in calcium stabilized zirconia.

It is interesting to note that for $\bar{q} \parallel \langle 110 \rangle$, the zero-cation force equations can only be satisfied for $q = 0$ and $u_{qz}^{A} = -u_{qz}^{B}$. This is the ordinary internal strain[11] predicted by Allen[10] to occur in UO_2, but which in fact does not occur experimentally[7] as already noted above.

Summary and discusion. As illustrated for the NaCl and fluorite structures our search criteria leads to quite restricted predictions as to the wave vector and polarization of lattice internal rearrangement modes that will occur in these structures. To also determine the amplitude and phase (relative to the crystal layers) involves developing a phenomenological model including crystal-field interaction, short-range elastic forces, and linear exchange striction.

The strongest prediction from the search criterion is of the occurrence of the lattice internal rearrangement mode shown in Fig. 1, presumably in coincidence with the occurrence of the IA magnetic structure, in the NaCl structure. This prediction is susceptible to direct experimental verification in the intermetallic compounds CeBi, CeSb, and UAs. Experimentally, in looking for such inhomogeneous distortion effects, there may be some skin effect before achieving the periodic internal rearrangement mode in the bulk. Therefore, experimentally there may be a difference between the results of x-ray experiments, basically sampling the surface regions and neutron experiments, which penetrate the bulk of the material. So far, the internal rearrangement in UO_2 has only been seen[7] with neutrons, i.e., the type of x-ray experiment suitable for observing the internal rearrangement mode has not been done. As noted above, the search criterion predicts the possible occurrence of internal rearrangement modes both with $\bar{q}$ at high-symmetry points (such as X, L, W) in the Brillouin zone *and* at

LATTICE INTERNAL REARRANGEMENT MODES

FLUORITE LATTICE

transverse   longitudinal   longitudinal
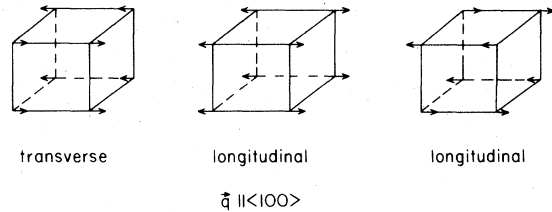
$\bar{q} \parallel \langle 100 \rangle$

FIG. 3. Internal rearrangement modes with $\bar{q} \parallel \langle 100 \rangle$ for the cubic fluorite structure. Fixed cation is at center of cube of anions, the displacements of which are indicated.

general points in the Brillouin zone [e.g., $\bar{q} = (2\pi/a)(\frac{1}{2}, 0, 0)$ in the NaCl structure lattice], so that it expeditiously provides a way to survey *all* candidate internal rearrangement modes for occurrence in a given lattice structure. Those with $\bar{q}$ at high-symmetry points will, in general, be symmetry determined (i.e., the $\bar{q}$ value will remain at the high-symmetry point independent of the particular force model). Those with $\bar{q}$ at general points, such as $(2\pi/a)(0.5, 0, 0)$, will have $\bar{q}$'s that shift with the force model (slightly if the nearest-neighbor-force model is reasonably good.) For example, as we introduce more-distant neighbor cation-anion interactions for the NaCl structure, $\bar{q} = (2\pi/a)(0.5, 0, 0)$ remains a solution for second-neighbor interactions, but ceases to be a solution for third-neighbor interactions. So that for complete force models, the $\bar{q}$ for a solution may shift away from $\bar{q} = (2\pi/a)(0.5, 0, 0)$ along the $\bar{q} = (2\pi/a)(\xi, 0, 0)$ axis, say typically to ξ between 0.55 and 0.70. However, we expect the interactions, other than elastic, present to favor $\bar{q} = (2\pi/a)(0.5, 0, 0)$ because of its relatively higher symmetry, giving a simple periodic structure, and thus to cause the structure to "lock in" at $\bar{q} = (2\pi/a)(0.5, 0, 0)$.

It is interesting to consider the possible association of a "soft" phonon with the predicted internal lattice-displacement transitions. In doing this, it is particularly interesting to consider the anticipated difference in behavior for $\bar{q}$ at a high-symmetry point (say X, L, or W) compared to that at a general point such as $(2\pi/a)(\frac{1}{2}, 0, 0)$. For the high-symmetry point, if a phonon has detectable softening, we would expect the minimum to remain at the $\bar{q}$ as it softens. On the other hand, for the general point, we would expect the phonon minimum to shift toward a point of relatively higher symmetry with decreasing temperature, say along the $(2\pi/a)(\xi, 0, 0)$ axis from $\xi = 0.55-0.70$ toward $\xi = \frac{1}{2}$ with decreasing temperature.

When we consider the possible connection with phonon behavior, the solutions of Eq. (2) with $u_{qy}^A = u_{qz}^A = 0$ have an interesting property. As already noted, q_x is required to have the value π/a, but q_y and q_z are not determined. Now *if we consider possible correspondence to phonons with polarization along* $\langle 100 \rangle$, the only solution satisfying that polarization condition for $\bar{q}$ inside the Brillouin zone is that for $q = (2\pi/a)(\frac{1}{2}, 0, 0)$, i.e., the mode already discussed as shown in Figs. 1 and 2. However, the mode with $\bar{q}$ at the zone-boundary position $W[\bar{q} = (2\pi/a)(\frac{1}{2}, 0, 1)]$ also satisfies the force equation [Eq. (2)], while corresponding to a phonon polarized along the $\langle 100 \rangle$ direction (i.e., polarization along this direction occurs because of the W point's special properties at the zone boundary). Note, however, that the mode with $\bar{q}$ at W looks different from that with $\bar{q}$ at $(2\pi/a)(\frac{1}{2}, 0, 0)$ and does not give a displacement analogue to the IA magnetic structure.

ACKNOWLEDGMENTS

*Permanent address: Supported in part by the NSF Grant No. DMR 77-06721.

†Supported by the U.S. ERDA.

[1]G. H. Lander and M. H. Mueller, Phys. Rev. B **10**, 1994 (1974).

[2]B. C. Frazer, G. Shirane, D. E. Cox, and C. E. Olsen, Phys. Rev. **140**, A1448 (1965).

[3]O. G. Brandt and C. T. Walker, Phys. Rev. **170**, 528 (1968).

[4]G. Dolling and R. A. Cowley, Phys. Rev. Lett. **16**, 683 (1966).

[5]B. R. Cooper, in *Magnetism in Metals and Metallic Compounds,* edited by J. T. Lopuszanski, A. Pekalski, and J. Przystawa (Plenum, New York, 1976), pp. 225–263.

[6]B. R. Cooper, *Proceedings of the Second International Conference on the Electronic Structure of the Actinides, Wroclaw, Poland, September, 1976,* edited by J. Mulak, W. Suski, and R. Troc (Zaklad Narodwy, Ossolinskich, Wroclaw, Poland, 1976), pp. 369–380.
Lett. **35**, 1770 (1975).

[8]G. H. Lander, M. H. Mueller, and J. F. Reddy, Phys. Rev. B **6**, 1880 (1972).

[9]F. Hulliger, M. Landolt, H. R. Ott, and R. Schmelczer, J.

Low Temp. Phys. **20**, 269 (1975).

[10]S. J. Allen, Jr. Phys. Rev. **166**, 530 (1968).

[11]M. Born and K. Huang, in *Dynamical Theory of Crystal Lattices,* (Oxford U. P., Oxford, 1954), p. 134.

[12]J. Faber, Jr., and M. H. Mueller, and B. R. Cooper (unpublished).

[13]J. Delaunay, *Solid State Physics,* edited by F. Seitz and D. Turnbull, (Academic Press, New York, 1956), Vol. 2, pp. 219–303.

[14]F. A. Wedgwood, J. Phys. C **7**, 3203 (1974).

[15]G. Dolling, R. A. Cowley, and A. D. B. Woods, Can. J. Phys. **43**, 1397 (1965).

[16]J. Rossat Mignod, P. Burlet, H. Bartholin; J. Villain, D. Florence, and O. Vogt, Physica (Utr.) **86-88B**, 129 (1977); J. Rossat-Mignod, P. Burlet, J. Villain, H. Bartholin, W. Tcheng-Si, D. Florence, and O. Vogt, Phys. Rev. B **16**, 440 (1977).

[17]P. Fischer, G. Meier, and O. Vogt, Neutronen Streuung Progress Report, E. I. R., Wurenlingen, Switzerland, AF-SSP-98, January, 1977 (unpublished), pp. 8–10.

[18]K. W. H. Stevens and E. Pytte, Solid State Commun. **13**, 101 (1973).