RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 13 1 MAY 1990

Isotope effect on displacive-type ferroelectric-phase-transition temperatures

A. Bussmann-Holder

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany
and Universität Bayreuth, D-8580 Bayreuth, Federal Republic of Germany*

H. Büttner

Universität Bayreuth, D-8580 Bayreuth, Federal Republic of Germany

(Received 20 February 1990)

The isotope effect on the ferroelectric transition temperature T_c is investigated within the polarizability model. The enhancement of any of the involved sublattice masses always yields an increase in T_c and its magnitude is a function of T_c. While the increase in the rigid-ion mass only induces a small enhancement of T_c, the replacement of the nonlinearly polarizable unit by its isotope shows large effects for small transition temperatures and is zero for high T_c's.

The isotope effect on the ferroelectric transition temperature T_c is experimentally well investigated and also the replacement of any of the involved sublattice masses by isovalent ions is well known to affect T_c.[1]

Theoretically the hydrogen-bonded ferroelectrics and especially the KH_2PO_4 (KDP) family have attracted much interest and tremendous efforts have been undertaken to explain the large effect of deuteration on T_c as well as on the Curie constant and the spontaneous polarization.[2] The first theoretical models for these compounds can be traced back to Slater[3] and Takagi,[4] who introduced a pseudo-spin-formalism for the order-disorder transition of the protons (deuterons) to explain the phase-transition mechanism. Within this model the isotope effect is found to be small and the model itself exhibits unphysical properties as long-range dipolar interactions and tunneling are not included. In a coupled proton lattice model[5] both terms are considered and quantum tunneling[6] between the hydrogen-bond double wells is taken into account. A variety of physical properties can be described using this concept, but still the isotope effect remains an open problem.

In this paper we do not only concentrate on KDP and its isomorphous compounds but investigate, in general, the isotope effect for displacive-type ferroelectric systems within the framework of the polarizability model.[7] The model,[8] its applications,[9,10] and nonlinear solutions[11,12] have been extensively discussed in a variety of recent papers, and it has also been shown that extensions of this model may well be suited to describe the dynamical and quantum-mechanical properties of superconducting oxides.[13,14] The polarizability model Hamiltonian reads

$$H=T+V+V_2\,, \tag{1}$$

$$T=\tfrac{1}{2}\sum_n(m_i\dot{u}_{in}^2+m_{ei}\dot{v}_{in}^2)\quad(i=1,2)\,, \tag{1a}$$

$$V=\tfrac{1}{2}\sum_n[f'(u_{1n+1}-u_{1n})^2+f(v_{1n}-u_{2n})^2+f(v_{1n+1}-u_{2n})^2]\,, \tag{1b}$$

$$V_2=\tfrac{1}{2}\sum_n[g_2(v_{1n}-u_{1n})^2+\tfrac{1}{2}g_4(v_{1n}-u_{1n})^4]\,, \tag{1c}$$

where m_i, m_{ei}, u_{in}, v_{in} $(i=1,2)$ are the ionic and electronic masses and their respective displacements in the n'th cell, f' and f are harmonic intersite phonon-phonon and electron-phonon couplings, respectively. V_2 represents an on-site double-well potential which combines harmonic attractive electron-phonon interaction g_2 with a stabilizing repulsive electron-two-phonon coupling term g_4. The microscopic reasoning for this potential is due to the local instability of the oxygen ion O^{2-} which leads to a volume-dependent nonlinear polarizability.[15,16]

In the following, we concentrate on V_2 which will be treated in the self-consistent phonon approximation (SPA). With the definition $v_{1n}-u_{1n}=w_{1n}$ the SPA yields for the equations of motion $g_2w_{1n}+g_4w_{1n}^3=(g_2+3g_4\langle w_{1n}^2\rangle_T)w_{1n}=gw_{1n}$, where g now represents an effective harmonic but temperature-dependent quantity. The phase-transition temperature is defined by $g=0$, i.e., $\langle w_{1n}^2\rangle_{T_c}=-g_2/3g_4$. Thus, by evaluating self-consistently $\langle w_{1n}^2\rangle_T$ for fixed parameters, the influence of increasing any of the involved masses on T_c can be investigated. The mean value $\langle w_{1n}^2\rangle_T$ is given by

$$\langle w_{1n}^2\rangle_T=\frac{1}{N}\sum_{q,j}\frac{\hbar}{\omega(q,j)}w_1^2(q,j)\coth\frac{\hbar\omega(q,j)}{2kT}\,, \tag{2}$$

with $w_1^2(q,j)$ being the eigenvector squared

$$w_1^2(q,j)=\frac{[m_1\omega^2(q,j)-4f'\sin^2qa]^2[m_2\omega^2(q,j)-2f]^2}{m_1g^2[m_2\omega^2(q,j)-2f]^2+4m_2\cos^2qa[m_1\omega^2(q,j)-g-4f'\sin^2qa]^2}\,. \tag{3}$$

Here the $\omega(q,j)$ refer to the q-dependent dispersions of the jth mode. The one-dimensional dispersions are extended in an isotropic Debye approximation to account for the three-dimensional lattice. Thus, the summation in (2) refers to the three-dimensional Brillouin zone. Here it has to be pointed out that quantitative agreement between a full three-dimensional calculation[17] and our treatment for $\langle w_{1n}^2 \rangle_T$ has been obtained[18] which justifies this simplified model and simultaneously demonstrates that the ferroelectric properties are highly anisotropic.

In the high-temperature approximation, i.e., $\hbar\omega(q,j) < 2kT$, an analytical expression for T_c can be derived from Eq. (2) as

$$kT_c = \frac{|g_2|}{9_{g_4}} \frac{3}{V_c} \int q^2 dq \frac{8f'f \sin^2 qa}{2f + 4f' \cos^2 qa} . \tag{4}$$

Obviously, any mass dependence in T_c vanishes.

In a numerical investigation the parameters of f, f' were taken from $SrTiO_3$ and g_2, g_4 were determined self-consistently from the experimental inelastic neutron-scattering data[19] of the temperature dependence of the soft mode squared (Table I).

A variation in T_c was achieved by changing the depth of the double-well potential given by g_2. Yet, it is obvious from Eqs. (2) and (3) that the variation could also be carried through by changing g_4 as well as f, f', respectively. The dependence of T_c on g_2 is linear and illustrated in Fig. 1. Thus, with fixed parameters for each g_2 the equivalent transition temperature T_c was determined self-consistently. Hereafter, m_1, m_2 were increased and again the SPA was used to find the new transition points.

TABLE I. Parameters used in the numerical calculation.

$m_1 = 1.549$	$(10^{-22}$ g)
$m_2 = 1.461$	$(10^{-22}$ g)
$f = 14.410$	$(10^4$ gs$^{-2})$
$f' = 1.270$	$(10^4$ gs$^{-2})$
$g_4 = 0.904$	$(10^{22}$ gs^{-2}cm$^{-2})$

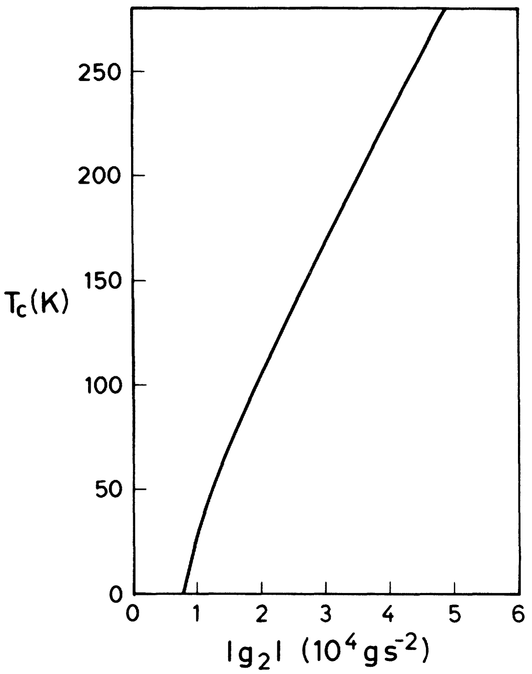

FIG. 1. The dependence of T_c on $|g_2|$.

The results for enhancing m_1 are depicted in Fig. 2 and for m_2 in Fig. 3, where in both cases the relative change in T_c is shown as a function of the relative change in masses. Here ΔT_c corresponds to T_c (isotope)-T_c (original) and $\Delta m_i = m_i$ (isotope)-m_i (original) ($i = 1,2$). Obviously the relative change in T_c is a function of T_c itself and in both cases T_c increases with increasing masses. Yet it is also clear from Figs. 2 and 3 that the relative increase in transition temperature for large $\Delta T_c/T_c$, which corresponds to small T_c's, is much larger for an isotopic mass replacement in m_1 than in m_2. This effect disappears the smaller the relative difference in T_c. Defining in analogy to superconductors, a critical exponent γ like $k_B T_c \approx m_i^{\gamma_i}$ ($i = 1,2$), in ferroelectrics γ_i is always positive, strongly dependent on T_c, and also dependent on m_i. For large enough $k_B T_c$ γ_i tends to zero. From the above numerical analysis the dependence of γ on $k_B T_c$ results in $\gamma_1 \cong 56 T_c^{-1.43}$ and $\gamma_2 \cong 9.53 T_c^{-1.15}$ (see Fig. 4). The above findings are confirmed experimentally. The effect of deuteration on T_c in KH_2PO_4 corresponds to a coupled double-well problem where the protonic double well has to be treated in the quantum limit, while the (PO_4) related double-well potential requires a classical treatment.[20] Our result for very small masses corresponds to $\gamma = 2$ and this is in agreement with experimental findings. In the class of IV-VI-type ferroelectrics the substitution of Se by Te in SnX (X = Se,Te) drives T_c from less than zero to about 90 K.[21] For high-transition temperatures this effect is less spectacular. For instance, replacement of P by As in $PbHPO_4$ shifts T_c from 310 K (Ref. 22) to 313 K.[23] A

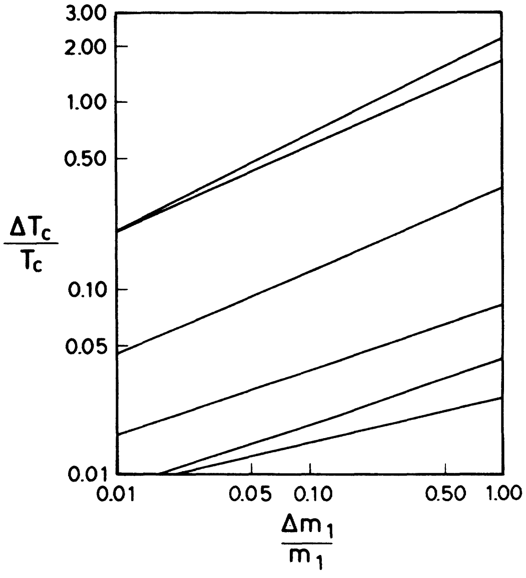

FIG. 2. Double logarithmic plot of $\Delta T_c/T_c$ as a function of $\Delta m_1/m_1$ for various values of $|g_2|$.

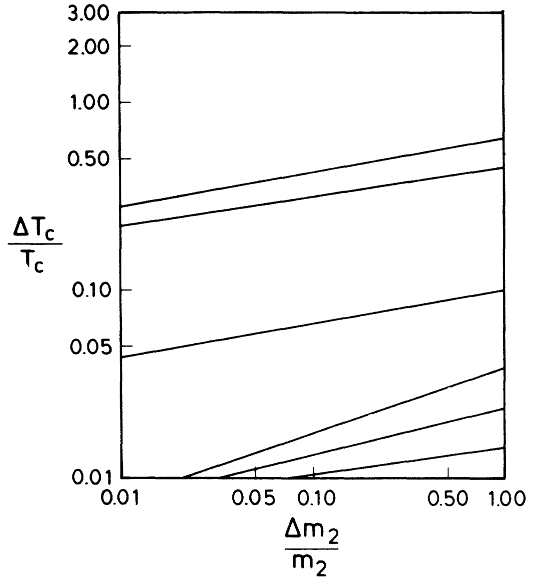

FIG. 3. Double logarithmic plot of $\Delta T_c/T_c$ as a function of $\Delta m_2/m_2$ for various values of $|g_2|$.

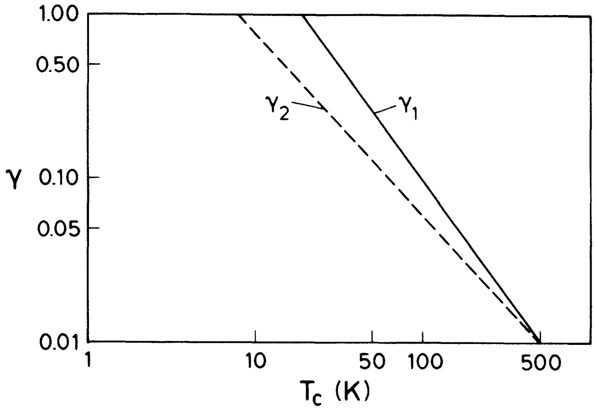

FIG. 4. Double logarithmic plot of the critical exponents γ_1, γ_2 (as explained in the text) as functions of T_c.

similar effect is observed in $SbNbO_4$ with $T_c = 673$ K (Ref. 24) which increases to $T_c = 676$ K (Ref. 25) in the isostructural compound $SbTaO_4$.

The examples above, which are qualitatively in agreement with the numerical results, represent only a small fraction of a variety of ferroelectrics with equivalent substitutional behavior. Yet, it should be pointed out here that the substitution of any of the sublattice masses may also show up in a variation of the involved force constants which again influence T_c. Thus, only experiments including isotopic mass replacements could confirm the model predictions.

In conclusion, it has been shown that the isotope effect on the ferroelectric phase transition is always positive independent of the respective sublattice mass. Furthermore, γ is strongly dependent on T_c and becomes zero for high-transition temperatures. It should be noted here that this is in strong contrast to perovskite-type oxide superconductors. A similar model calculation for these compounds[26] shows that the transition temperature to a paired electron (hole) state always decreases with increasing mass and that the critical exponent is small and shows no systematic trends with increasing transition point.

We are very much indepted to the late H. Bilz who initiated the research in this field. A.B.-H. received full support from the Deutsche Forschungsgemeinschaft.

---

[1] See, e.g., M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).

[2] W. Bantle, Helv. Phys. Acta **15**, 373 (1942); G. A. Samara, Ferroelectrics **5**, 25 (1973).

[3] J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

[4] Y. Takagi, J. Phys. Soc. Jpn. **3**, 271 (1948).

[5] J. Villain and S. Stamencovic, Phys. Status Solidi **15**, 585 (1966); K. K. Kobayashi, J. Phys. Soc. Jpn. **24**, 487 (1968).

[6] R. Blinc, J. Phys. Chem. Soc. **13**, 204 (1960); V. G. Vaks and V. J. Zinenko, Zh. Eksp. Teor. Fiz. **64**, 650 (1973) [Sov. Phys. JETP **37**, 330 (1973)]; R. Blinc and B. Zeks, J. Phys. C **15**, 4661 (1982); Y. Takagi, J. Phys. Soc. Jpn. **3**, 271 (1984).

[7] R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. **37**, 1155 (1976); H. Bilz, A. Bussmann, G. Benedek, H. Büttner, and D. Strauch, Ferroelectrics **25**, 339 (1980).

[8] H. Bilz, G. Benedek, and A. Bussmann-Holder, Phys. Rev. B **35**, 4840 (1987); C. H. Perry, R. Currat, H. Buhay, R. M. Migoni, W. G. Stirling, and J. D. Axe, *ibid.* **39**, 8666 (1986).

[9] A. Bussmann-Holder, H. Bilz, and P. Vogl, in *Electronic and Dynamical Properties of IV-VI Compounds*, Springer Tracts in Modern Physics Vol. 99, edited by B. Höhler (Springer-Verlag, Berlin, 1983); A. Bussmann-Holder, H. Bilz, and G. Benedek, Phys. Rev. B **39**, 9214 (1983).

[10] A. Bussmann-Holder, Phys. Rev. B **40**, 11639 (1989).

[11] H. Büttner and H. Bilz, in *Recent Developments in Condensed Matter Physics*, edited by J. T. Devreese (Plenum, New York, 1981), Vol. I, p. 49; H. Bilz, H. Büttner, A. Bussmann-Holder, W. Kress, and U. Schröder, Phys. Rev. Lett. **48**, 264 (1982).

[12] G. Benedek, A. Bussmann-Holder, and H. Bilz, Phys. Rev. B **36**, 630 (1987).

[13] A. Bussmann-Holder, H. Büttner, and A. Simon, Phys. Rev. B **39**, 207 (1989); Ferroelectrics (to be published).

[14] A. Bussmann-Holder, H. Büttner, and A. Simon, in *Proceeding of the International Conference on Materials and Mechanisms of Superconductivity High-Temperature Superconductors II*, edited by R. N. Shelton, W. A. Harrison, and N. E. Phillips (North-Holland, Amsterdam, 1989), p. 779.

[15] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[16] A. Bussmann-Holder, H. Bilz, R. Roenspiess, and K. Schwarz, Ferroelectrics **25**, 343 (1980).

[17] R. Migoni, Ph.D. thesis, University of Stuttgart, 1977 (unpublished).

[18] R. Migoni, H. Bilz, A. Bussmann-Holder, and W. Kress, in *Proceedings of the Second International Conference on Phonon Physics, Budapest, 1985*, edited by J. Kollar *et al.*

(World Scientific, Singapore, 1985), p. 272.

[19] P. A. Fleury and J. M. Worlock, Phys. Rev. **174**, 613 (1968); Y. Yamada and G. Shirane, J. Phys. Soc. Jpn. **26**, 366 (1969).

[20] A. Bussmann-Holder and H. Büttner, Ferroelectrics **79**, 3 (1988).

[21] T. Chattopadhyay, A. Werner, and H. G. v. Schnering, Rev. Phys. Appl. **19**, 807 (1984); H. Kawamura, in *Physics of Narrow-Gap Semiconductors,* edited by G. Rautuszkiewicz, M. Gorka, and E. Kaamarek (North-Holland, Amsterdam, 1977).

[22] T. J. Negram, A. M. Glass, C. S. Brickenkamp, R. D. Rosenstein, R. K. Osterheld, and R. Susott, Ferroelectrics **6**, 179 (1974).

[23] B. Brezina, F. Smutny, and J. Fousek, Czech. J. Phys. B **25**, 1411 (1975).

[24] A. N. Lobachev, V. F. Peskin, V. J. Popolitov, L. N. Syrkin, and N. N. Feoktistova, Fiz. Tverd. Tela (Leningrad) **14**, 604 (1972) [Sov. Phys. Solid State **14**, 509 (1972)].

[25] W. Jeitschko and A. W. Sleight, Acta Crystallogr. B **30**, 2088 (1974).

[26] A. Bussmann-Holder, H. Büttner, and A. Simon, Ferroelectrics (to be published).